

混凝土外加剂应用技术专业委员会2017年会

# 聚羧酸系高性能减水剂及其 应用技术新进展—2017

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



Recent Advances in Polycarboxylate  
Superplasticizer and Application Technology — 2017

 **北京理工大学出版社**  
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# 前 言

聚羧酸系高性能减水剂已成为我国外加剂主流产品。近 20 年的工程实践表明，聚羧酸系高性能减水剂的优异性能对提高混凝土工程质量发挥了十分重要的作用。随着我国混凝土技术的迅速发展，聚羧酸系高性能减水剂制备与应用技术也不断提高。特别是在“一带一路”进程中，海外工程量的增多、国内装配式混凝土的大力推广、国家重点大型工程项目如“港珠澳大桥”“北京第二国际机场”和“中国尊”的建设等，聚羧酸系高性能减水剂在优化混凝土性能方面起到了至关重要的作用。

为了更好地总结聚羧酸系高性能减水剂的国内外研究成果及其工程应用经验，促进聚羧酸系高性能减水剂研究的技术创新和技术发展，进一步推动聚羧酸系高性能减水剂及其应用技术的可持续性发展，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于 2017 年 5 月 23—25 日在北京举办了“第六届聚羧酸系高性能减水剂及其应用技术交流会”暨“混凝土外加剂应用技术专业委员会 2017 年会”。

本次会议征集到学术论文 70 余篇，经会议学术委员会专家审核，择录了 59 篇论文，其中 53 篇为中文，6 篇为英文，经编辑后，正式出版名为《聚羧酸系高性能减水剂及其应用技术新进展—2017》的论文集。本论文集内容涉及聚羧酸系高性能减水剂国内外研究进展与发展趋势；聚羧酸系高性能减水剂理论研究；聚羧酸系高性能减水剂在各类混凝土制品与工程中应用技术新进展及其案例分析；聚羧酸系高性能减水剂最新制备技术；聚羧酸系高性能减水剂相关检测、标准；其他混凝土外加剂等。论文集内容较丰富、涉及面较广、研究水平较高，具有一定的学术参考价值，为从事混凝土外加剂及混凝土研究、生产、设计、检测和施工的专家、学者、研究生及广大技术人员提供了大量的技术资料。

由于时间与水平有限，论文集中难免有不妥之处，谨请读者予以指正。

混凝土外加剂应用技术专业委员会  
2017 年 5 月

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# 综述与基础理论

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# The Contribution of PCE Superplasticizers to Present and Future Concrete Technology

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(Chair for Construction Chemistry, Technische Universität München, Garching, Germany)

## 1 Introduction

Chemical admixtures constitute indispensable ingredients for the production of modern advanced concrete. In developed countries, at least 80% of the concrete produced contains one or several admixtures. They include plasticizers, superplasticizers, retarders, accelerators, stabilizers, defoamers, foamers, shrinkage reducers, to name the most important classes. With their help it is possible to optimize the properties of fresh and hardened concrete in such way as to adapt better to local climate and processing conditions and to enhance the mechanical properties and durability. Furthermore, highly sophisticated products such as ultra-high strength concrete (UHPC) or self-levelling and self-compacting concrete (SCC) became possible only with the invention of specific high performance admixtures.

In this article, an overview of current PCE technology and the state-of-art is provided. The main technologies will be described and gaps existing in each field will be identified. Finally, an outlook on potential developments in the future will be provided.

## 2 Current PCE technology

PCE-based admixtures have taken an unprecedented rise since their invention in 1981. It is estimated that in 2014, the global volume of PCE produced exceeded 3 mio tons, based on 30% liquid concentration. Meanwhile, the term “PCE” includes a huge variety of chemically often substantially different polymers, with significant variances in performance characteristics. In the following, the main classes of PCE products on the market are described and their general chemical composition is exhibited in Figure 1.

**MPEG-type PCEs:** They constitute the first type of PCE which was invented in Japan. MPEG PCEs can be synthesized either via aqueous free radical copolymerization of methacrylic acid with

an  $\omega$ -methoxy poly (ethylene glycol) methacrylate ester macromonomer (this route is predominantly used by the industry) or by esterification (“grafting”) of short chain poly (meth) acrylic acid with  $\omega$ -methoxy poly (ethylene glycol). Note that both synthesis routes can lead to substantially different products, even when exactly the same molar ratios of monomers are used. Via esterification, a PCE polymer exhibiting a regular (statistical) repartition of side chains along the main chain is achieved while from the copolymerization process, gradient polymers exhibiting a decreasing side chain density along the backbone chain are formed as a result of the higher reactivity of the ester macromonomer versus methacrylic acid. Performance tests have revealed that in many cases, gradient polymers perform better, because their blocks of polymethacrylic acid allow higher adsorption on cement. One major disadvantage of MPEG-PCEs is their limited stability (especially when acrylate instead of methacrylate ester macromonomers are used) which derives from hydrolysis of the ester linkage between the main and the side chain. Furthermore, the diol or diester content present in the raw materials must be kept below 1% to avoid undesirable crosslinking.

**APEG-type PCEs:** This kind is prepared via free radical copolymerization from  $\alpha$ -allyl- $\omega$ -methoxy or  $\omega$ -hydroxy poly (ethylene glycol) ether and maleic anhydride or acrylic acid as key monomers, either in bulk or in aqueous solution. APEG-PCEs always possess a strictly alternating monomer sequence (ABAB), because the allyl ether macromonomer does not homopolymerize as a consequence of mesomeric stabilization of the allyl radical. This stabilization makes allyl ethers to react rather slowly and can lead to low conversion rates for the macromonomer. Polymerization in bulk works well for side chain lengths of up to 34 EO units while polymerization in water typically yields copolymers possessing very short trunk chains (“star polymers”) made of  $\sim 10$  repeating units only which however were found to exhibit superior dispersing performance. The disadvantages of aqueous copolymerization are longer reaction times, lower conversion rates and lower concentration of the finished PCE solution.

Initially, APEG-PCEs suffered from a reputation of causing delayed plastification (i.e. the slump of concrete first increased over  $\sim 30$  min to reach a maximum, and then dropped). Meanwhile, this problem has been solved, for example by incorporation of specific comonomers as spacer molecules such as styrene or allyl maleate which can modulate 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 copolymerization of e.g. 4-hydroxy butyl poly (ethylene glycol) vinyl ether and maleic anhydride or acrylic acid. Their polymerization must be conducted at temperatures  $< 30$  °C to avoid vinyl ether monomer degradation. As a result, a specific low temperature initiator such as Vazo 50<sup>®</sup> (2, 2'-Azobis (2-methyl propionamide) dihydrochloride) is required. The advantage of the vinyl over the allyl ether technology is the much higher reactivity of vinyl ethers.

**HPEG-type PCEs:** Here,  $\alpha$ -methallyl- $\omega$ -methoxy or  $\omega$ -hydroxy poly (ethylene glycol) are used as macromonomers in copolymerization with e.g. acrylic acid. This kind of PCE which is easy to manufacture in large industrial scale emerged a few years ago, especially in China. There, even a

process has been developed where copolymerization is performed at room temperature and is applied in many factories. Most HPEG-PCEs can outperform the MPEG-or APEG-PCEs with respect to their dispersing ability.

**IPEG-type PCEs:** This type of PCE (sometimes also referred to as TPEG-PCE) is synthesized from isoprenyl oxy poly (ethylene glycol) ether as macromonomer by copolymerization with e.g. acrylic acid. In recent years, this PCE has become quite popular, especially in Japan and China, because of its excellent performance which often exceeds that of any other type of PCE, and its simple preparation utilizing free radical copolymerization. A disadvantage of IPEG-PCEs is their potential to decompose into isoprene, water and glycol. To prevent this undesired process, the IPEG macromonomer and the IPEG-PCE should not be handled in bulk, but always kept in aqueous solution.

**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 further on the surface are believed to present more effective PCEs. Following this concept, slightly crosslinked PCE molecules utilizing diesters (e.g. synthesized from PEG and methacrylic acid or maleic anhydride) were shown to provide enhanced dispersion. Moreover, hyperbranched and dendrimeric PCE polymers which present an interesting new approach were suggested using polycarboxylated polyglycerols.

**PAAM-type PCEs:** These zwitterionic PCEs possess mixed side chains composed of polyamidoamine (PAAM) and PEO segments. This structural motif 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.

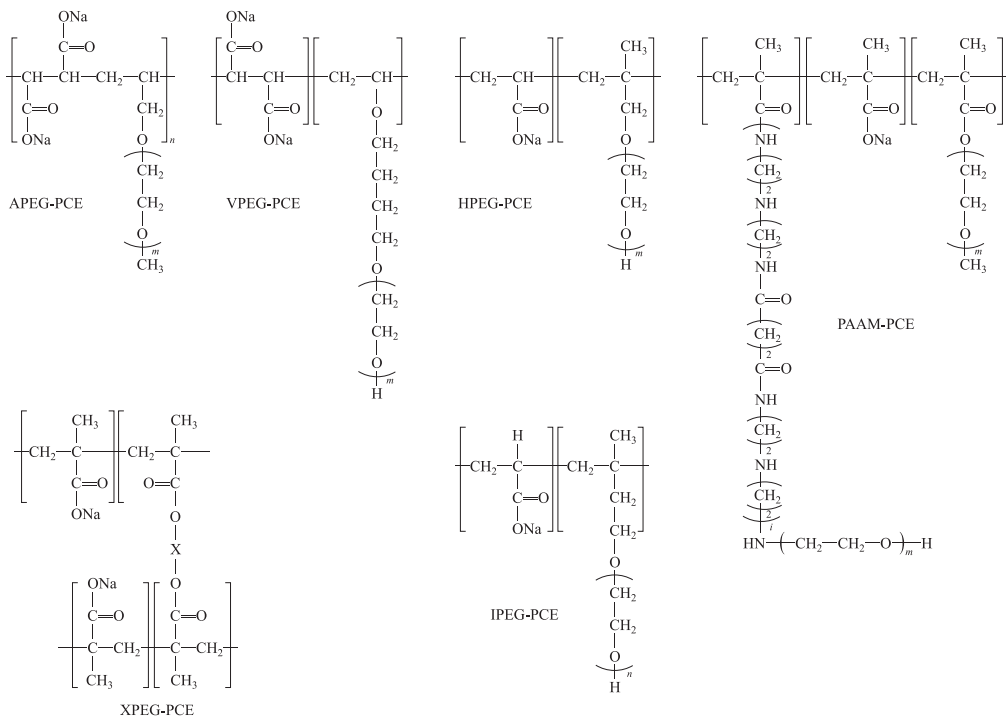


Fig. 1 Chemical structures of the different classes of PCE products currently produced by the industry

### 3 New PCE products

Industrial and academic researchers continue to develop and introduce new and improved polymers, in spite of the great diversity of already existing PCE products. Those include:

**Organo-silane (OSi) modified PCEs:** They can be prepared by incorporating either 3-trimethoxysilyl propyl methacrylate (MAPTMS) or N-maleic  $\gamma$ -amidopropyl triethoxy silane (MAPS) as a new comonomer into a conventional PCE, e.g. the MPEG-type (Figure 2). The consideration behind this concept was to achieve a chemical bond between C-S-H 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 on the surface of hydrating cement and prevent its desorption e.g. by sulfate ions or anionic retarders resulting from competitive adsorption.

**Phosphated (PHOS) PCEs:** Superplasticizers generally achieve their dispersing power through adsorption on the surface of cement, especially on ettringite. Such adsorption is facilitated through anionic anchoring groups which typically include carboxylate or dicarboxylate groups. Some years ago it has been shown that phosphonate presents a more powerful anchoring group than carboxylate. Very recently, novel superplasticizers have been presented which incorporate phosphate as an anchoring group. Phosphatation can be accomplished by esterification of e.g. hydroxyethyl methacrylate with phosphoric acid, leading to the PCE copolymer shown in Figure 2. The phosphated PCEs are said to adsorb on cement almost instantaneously which presents a major advantage in specific concrete and dry-mix mortar applications. Furthermore, they appear to be more sulfate-tolerant, compared to conventional PCE superplasticizers, and often require lower dosages.

**PCEs from macroradicals:** Current PCE technology relies on the availability of macromonomers for the copolymerization process or of specific short-chain poly (meth) acrylic acid as backbone for the grafting (esterification) reaction. This limitation can be overcome by a new preparation method involving macroradicals which presents a much simplified synthesis method compared to conventional PCE preparation.

In a typical example, common  $\omega$ -methoxy poly (ethylene glycol) is reacted with maleic anhydride in the presence of benzoyl peroxide (BPO) as initiator whereby an MPEG macroradical is formed which then can polymerize with maleic anhydride to form a PCE structure. In this polymer, MPEG provides the backbone as well as the side chain while maleic anhydride delivers the carboxylate anchoring group and the linkage to the side chain (Figure 2).

**Brown coal-based superplasticizer:** Recently it has been presented that even alkaline extracts from ordinary brown coal (so-called “caustic lignite”) can be used to synthesize effective concrete superplasticizers. There, e.g. (meth) acrylic acid or a combination of (meth) acrylic acid and 2-acrylamido-2-tert-butyl sulfonic acid (ATBS) are grafted onto a lignite backbone yielding a comb polymer whereby the homo- or copolymerized monomers constitute the side chain while lignite

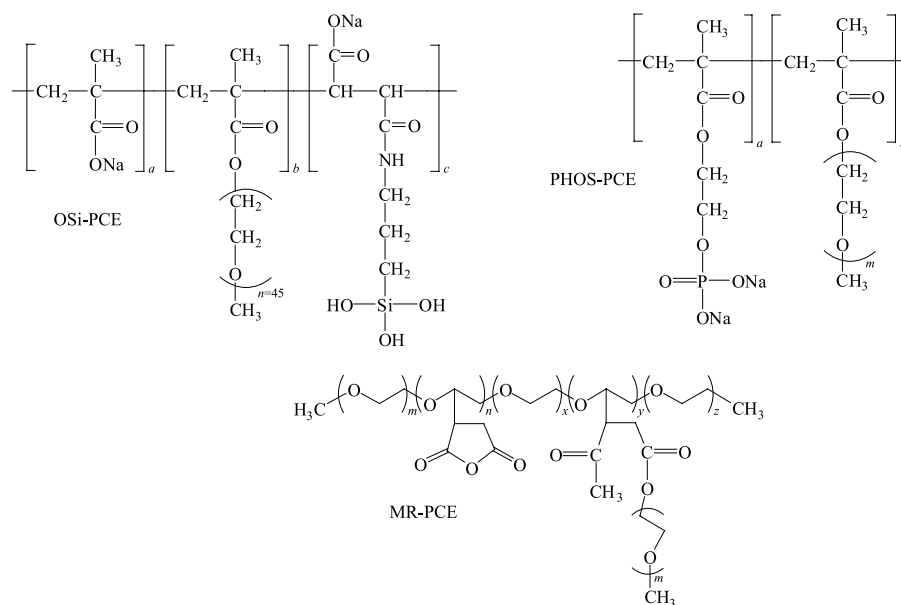


Fig. 2 Examples of organo-silane modified (OSi-PCEs), phosphate- (PHOS-PCEs) and macroradical-based MR-PCEs

presents the backbone (Figure 3). These superplasticizers are simple to produce from inexpensive and abundant raw materials, and can match the performance of polycondensate-based superplasticizers such as BNS or MFS, but not that of PCE polymers.

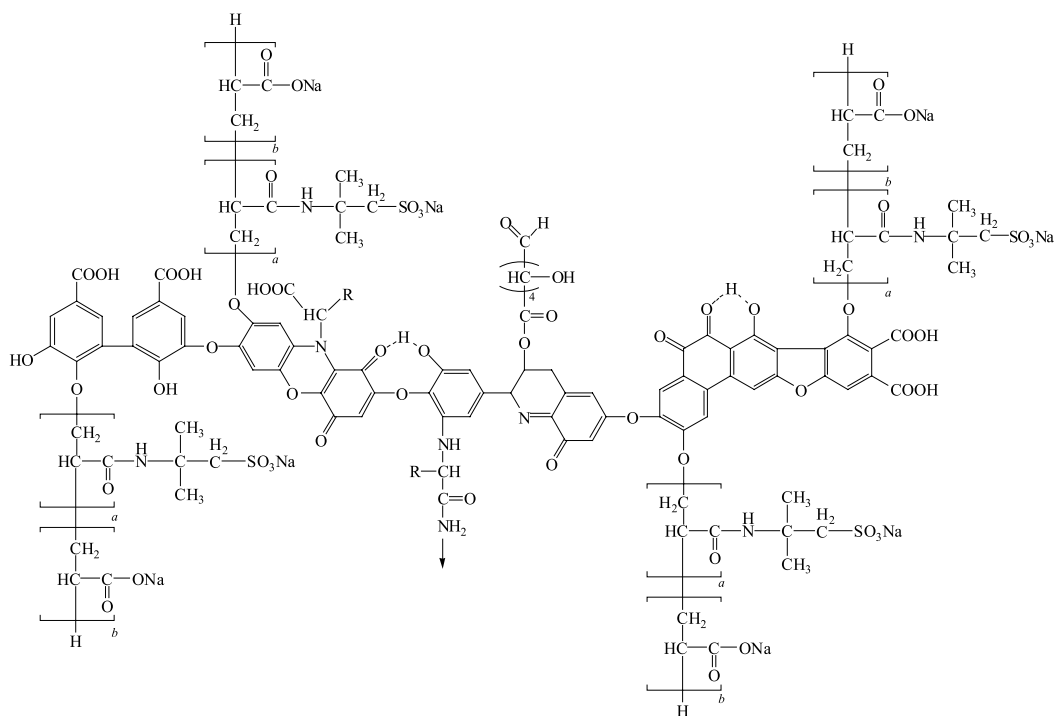


Fig. 3 Chemical structure of a lignite-based superplasticizer holding side chains of acrylic acid-co-ATBS

## 4 Tailoring PCEs to Specific Applications

Recently, substantial progress has been made in the optimization of current PCE products for difficult applications. Those include concretes of particularly low W/C ratios ( $<0.30$ ), the compatibility of PCEs with specific cements which are hard to fluidify, and the compatibility of PCEs with clay contaminants occurring in aggregates.

### 4.1 Stickiness of concrete at low W/C ratio

The problem of stickiness and slow flow of concrete prepared at low W/C ratio is well-known and was solved as follows: It was found that the hydrophilic-lipophilic balance (HLB) value of a PCE molecule determines whether the concrete admixed with this polymer exhibits slow or fast flow. According to this study, PCE molecules should be as hydrophilic as possible and their HLB value should be  $>18.5$ . Such PCEs (preferably of IPEG-and APEG-type) produce cement pastes with particularly low plastic viscosity and exhibit fast flow without any stickiness. Such rheologically optimized concrete is easier to pump, spread and compact and presents a huge step forward in improving the workability of high-strength concretes of low w/c ratios.

### 4.2 Cement compatibility of PCEs

Applicators of PCEs are familiar with the fact that some cements seem to be “incompatible” with PCEs, i.e. even at high dosages ( $>1\%$ ) no reasonable fluidity of the concrete is achieved. Analysis of this problem led to the conclusion that most PCEs act as morphological catalyst for ettringite, meaning that they can modulate its crystal growth in such way that significantly smaller, nano-sized crystals are formed in the presence of PCEs. For example, it was observed that especially MPEG-PCEs reduce the length of early ettringite crystals to 600–900 nm, versus  $\sim 2\ \mu\text{m}$  for the ettringite grown in the absence of PCE. The smaller crystals however provide a much higher surface area which needs to be occupied by adsorbed PCE molecules to achieve high fluidity. Consequently, in such case a much increased PCE dosage of 2% or even more is required which makes applicators to think that an incompatibility between those cements and PCEs exists. The study also suggests that such “incompatibility” can only occur for cements which contain  $>5\%$   $\text{C}_3\text{A}$  and thus produce an enormous amount of ettringite. It can be avoided by admixing PCE polymers which do not impact much on the crystal growth of ettringite such as e.g. APEG-PCEs. The main lesson learnt from this investigation is that a better knowledge of the factors impacting the crystal growth of early ettringite will greatly improve our understanding of cement — admixture interaction. For this reason, recently ettringite crystallization has been studied under zero gravity conditions on parabolic flights. There, because of the absence of convection, generally smaller, but a larger number of crystals which exhibit fewer defects are formed.

### 4.3 Enhanced clay tolerance

Over the last years, applicators have observed that PCE superplasticizers — unlike polycondensates — exhibit a pronounced sensitivity to clay and silt contaminants. As a result, their performances are greatly reduced or the PCEs become entirely ineffective. Montmorillonite, a 2:1 smectite clay, has been found to be more harmful than other clay minerals such as kaolinites or muscovites. Generally, the capacity of clays to sorb water, hydrate and swell leads to more viscous cement pastes. This effect results in a loss in workability or a higher water demand, independent of whether a superplasticizer is present or not.

Previous research has established that in cement pore solution, the surfaces of bentonite clay particles become positively charged as a result of  $\text{Ca}^{2+}$  adsorption onto the negative aluminosilicate layers. Onto these surfaces, polyanionic superplasticizers such as polycondensates or polycarboxylates adsorb, thus resulting in a partial depletion of superplasticizer from the pore solution. This way, clay competes with cement for superplasticizer molecules. Moreover, PCE polymers can intercalate chemically into the interlayer space between the individual aluminosilicate layers of specific clay minerals, especially montmorillonite (bentonite), resulting in an organo-mineral phase whereby their poly (ethylene glycol) side chains occupy the interlayer space, as is shown in Figure 4. This reaction with clay is specific for PCEs and is a consequence of their PEO side chains, as was evidenced by XRD measurements. Consequently, PCEs can be used up by clay by both surface adsorption and chemical sorption whereas polycondensates such as BNS are consumed only by surface interaction. This explains why PCEs are significantly more affected by clay than polycondensates.

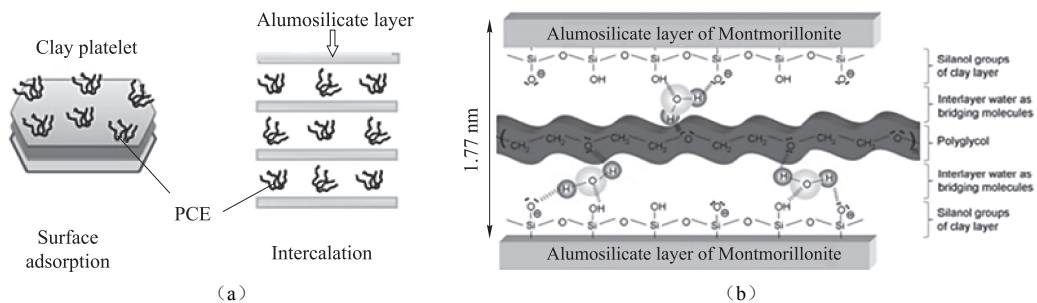


Fig. 4 Fundamental types of interaction between PCE and montmorillonite clay (a) and chemical sorption (intercalation) of a poly (ethylene glycol) side chain in between aluminosilicate layers (b)

The industry has developed several strategies to mitigate the negative effects of clay on PCEs. The first concept includes the use of sacrificial agents.

Analysis of sorbed amounts of individual PCE constituents (backbone, represented by poly (methacrylic acid) and side chain, represented by poly (ethylene glycol)) revealed that the side chain sorbs in large amounts on clay ( $\sim 400$  mg MPEG/(g clay)) while the polymer trunk is consumed much less ( $\sim 30$  mg PMA/ (g clay)). This not only signifies that the PEO side chain present in PCE provides the main interaction with clay; it also offers a remedy for the problem



whereby pure PEG or MPEG are utilized as sacrificial agents to occupy the interlayer spaces while the PCE molecule which exhibits a lower tendency to intercalate as a result of its anionic charge is preserved and can thus interact with the cement to achieve dispersion. As another remedy, addition of cationic polymers which inhibit the swelling of clay entirely has been proposed. This method offers the advantages of zero water consumption because the clay will not hydrate at all. Additionally, the interlayer spacing will not be accessible for the PCEs.

Obviously, the best solution to the incompatibility problem of PCE and clay would be a novel PCE structure which does not contain PEO side chains. Recently, such polymers have been synthesized using either hydroxy alkyl esters of methacrylic acid or vinyl ethers as side chain bearing macromonomers. Utilizing XRD analysis, it was found that indeed these novel polycarboxylates do not undergo side chain intercalation with clay and adsorb in small quantity only ( $\sim 25$  mg polymer/ (g clay)). Consequently, they exhibit robust performance even in the presence of clay contaminants. This behavior perfectly confirms the concept of non-PEO side chains as a remedy for the intercalation problem of conventional PCEs into clay structures.

## 5 C-S-H-PCE for early strength enhancement

A very recent invention includes the application of C-S-H-PCE nanocomposites as seed crystals for the hydration of the silicate phases  $C_3S$  and  $C_2S$ . The nanocomposites can be prepared by combining aqueous solutions of e.g. sodium silicate and calcium formate with a PCE solution. The resulting instantaneous precipitate contains nanofoils of C-S-H with surface adsorbed and possibly intercalated PCE (Figure 5).

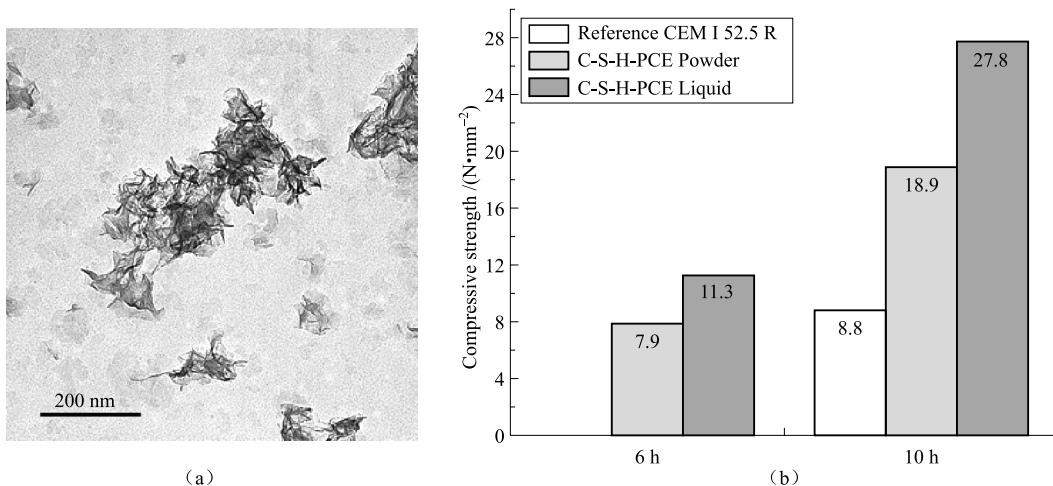


Fig. 5 TEM image of C-S-H-PCE nanocomposite foils (a) and their effectiveness as strength enhancing seeding material for CEM I 52.5 R (b)

The nanofoils greatly accelerate the silicate hydration by reducing the free activation energy  $\Delta G$  of the crystallization to zero. In cement hydration this barrier needs to be overcome to initiate