The Categories and Application of PCE Superplasticizers in Concrete

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Abstract. Polycarboxylate ether superplasticizers (PCEs) are water reducers in the concrete mix that play a significant function in aspects of reducing the water-to-cement ratio, improving impermeability, increasing compressing strength, and meditating the shrinkage. This paper introduces the characteristics of PCEs, discusses the application, advantages, and disadvantages of concrete, and puts forward some measures. The mechanism of PCEs is the dispersion function of the molecular structure and the neutralization. Currently, PCEs are updated from one generation to another, conventional PCEs mainly include methacrylate ester, isoprenol ethe, and methallyl ether-PCEs. Another two major types of PECs are vinyl ether-based and calcium silicate hydrates PCEs, respectively. The application of PCEs revolutes novel types of concrete, such as ultra-high performance concrete and self-compacting concrete. When applying PCEs, retardation has to be considered. Meanwhile, another drawback of PCEs is that they can hardly work with other admixtures. A novel type that is considered clay properties can be another research field.

Keywords: UHPC; SCC; Shrinkage; Concrete; PCE categories.

1. Introduction

Among various construction materials, concrete is one of the most commonly used ones, with significant sustainability. However, its application still has some problems in the real world. For instance, in order to further improve the strength, workability, and other performance indices, engineers invent and apply admixture. Air admixtures can be categorized into five, accelerating, retarding, water-reducing/plasticizing, air-entraining, and waterproofers. Accelerating admixture shortens the setting time of concrete, and retarding admixture, on the other hand, longer placing time. Air-entraining admixture introduces air into the concrete, forming bubbles inside, thus developing a lighter concrete. The waterproofers prevent concrete from absorbing moisture in the air, affecting its properties. Water reducer, a type of admixture, has been applied to reduce the amount of water, leading to a lower water-to-cement ratio. From the reduction of water, concrete gains a more significant compressing strength. In certain circumstances, it paves the way to high-strength concrete or even ultra-high-strength concrete. Compared with ordinary concrete, they possess an extremely high quality that breaks away from steel bars and can be used themselves when constructing, especially with exotic shapes of curves and uncommon connections.

Prevalent water reducers that combine concrete are polycarboxylate ether superplasticizers (PCEs). Prior to PCE, this series of chemicals had several generations: poly naphthalene sulfonate (PNS), poly melamine sulfonate (PMS), and acetone formaldehyde sulfite (AFS) superplasticizers [1]. The effectiveness of this type of superplasticizer with little dosage but generating a large dispersion prompts the application of PCEs to increase over the years. Meanwhile, since the components and structure of organic molecules are unlimited, the molecule structure of PCEs is numerous. Therefore, paying more attention to molecule structures has become a more popular and hot topic. From the existing results, scientists have invented many new PCE-family superplasticizers, and every substitution could be a revolutionary invention that generates a better performance.

This paper introduces the characteristics of PCE, discusses the application, advantages, and disadvantages of concrete, and puts forward some measures. With the use of superplasticizers, from an environmental perspective, water resources are conserved by using less water, and less concrete is needed by substituting less amount but higher compressing strength concrete.

2. PCEs background

PCEs are primarily used in the construction industry for regulating the properties of concrete to meet the requirements of different circumstances, such as temperature and humidity. The mechanism embedded within PCEs is to disperse cement particles with their outward-extending molecular chain, called steric hindrance. The structure of this kind of chemical involves a main chain, mainly methoxy-polyethylene glycol copolymers, and side chains. In theory, side chains have a wide range of options. By introducing specific grafters, the performance of different PCE superplasticizers is distinct along their functional grafters, which is also one of the most valuable intrinsic characteristics of being flexible to various conditions. This characteristic contributes to its physical characteristics, such as molar mass and density, which are not settled and could have a large span. Side chains are grafted on the molecules of the functional side chain groups, providing steric hindrance. Since the structure of PCEs molecules can be extensive, which keeps cement particles apart and supports a space where they are still isolated.

In terms of the question about the relationship between side chains and dispersion of PCEs, there have been distinct opinions. One is that the length of side chains positively affects their dispersing function. On the contrary, another is that side chains negatively change the dispersion. Even some reached out that there is no obvious connection between the two [2].

Additionally, due to electrostatic force, cement particles hydrate when adding water to the dry mix and flocculate with a positive charge on the surface. Negative electrons are hidden inside these plate-shaped flocculates. PCEs normally are negatively charged because their backbone always consists of water molecules. In applying superplasticizers, flocculation is neutralized and separated. Therefore, the fluidity of concrete increases even more, and less proportion of water is needed as a secondary mechanism.

3. Effect of PCEs on Concrete Properties

PECs have four major functions in concrete application.

(1) The major function is the reduction of water proportion. Superplasticizers such as PCEs increase the fluidity of the cement, allowing the mixture to be fully stirred while using less water. Voids that were originally filled with water can, therefore, be replaced by finer aggregates such as metakaolin and silica fume, which greatly reduces the porosity and increases the strength of the concrete [3].

(2) A second performance of concrete is to improve durability. The durability is influenced by the impermeability of water, penetration from sulfate and chloride ions, and carbonation. By restructuring the concrete from a micro aspect, the structure is less under damage from the three factors above, thus strengthening the durability and longing the life circle. For the permeability, Huang et al. conducted an experiment by pressuring water into six concrete cylinder samples that were mixed with different superplasticizers and measuring the permeated water depth after cutting the samples into halves. By comparison, the depths of concrete samples with PCEs are significantly reduced [4]. When exposed to seawater and other source of water that contains bountiful of sulfate and chloride irons, the penetrated irons are likely to interreact with concrete particles forming additional substances that interferes innerstress. From the same set of experiments by soaking sliced and vacuumed samples in water, the same conclusion is reached that PCE has excellent resistance to the penetration of chloride irons. Meanwhile, air contains a certain amount of carbon dioxide. The result showed that compared to polynaphthalene sulfonate, a type of superplasticizer, PCEs defend approximately half of the carbonation invasion [4]. The application of superplasticizer compensates for the shortcomings of concrete by intervening in its microstructure of a minor porose.

(3) PCEs' third function is to reduce the shrinkage of concrete, which is a phenomenon that accompanies concrete in the whole stage from placing to curing. Shrinkage can be ascribed to fout risons. The evaporation of moisture inside the concrete; the different evaporation rates between the inner part of the concrete and its surface; water absorbed by cement particles; and carbonation

reaction to atmospheric carbon generating unexpected substances and changing its particle arrangement [5]. Sulakshna Sanjay and other researchers devised an experiment with four groups of concrete mixes. The usage of PCE as shrinkage-reducing admixtures is from 0%, 0.25%, 0.5%, and 0.75% taken by weights of binding materials. During the experiment, scientists recorded the shrinkage of each individual experimental sample at 90min, 120 min, and 150 min after mixing. The outcome indicates that without adding any PCEs, the shrinkage is 58.03 *10-3 mm. However, the shrinkage reduces to 28.2 *10-3 mm with 0.5% of PCEs and drops to 4 *10-3 mm with 0.75% of PCEs. [6] From the data, the function of PCE is significant, that could be put into use as a shrinkage-reducing admixture.

4. Types of PCEs

Since the development of iterative research in the 1980s, various types of PCEs have been invented. The conventional three products are methacrylate ester (MPEG-PCE), isoprenol ether (IPEG-PCE), and methallyl ether (HPEG-PCE). As the first PCE was published in the market around the world, its dispersion was not as good as other later published PCEs, such as IPEG-PCE and HPEG-PCE. However, the lower hydrophilic–lipophilic balance (HLB) value contributes to less bleeding and segregation of concrete [7]. The adaption of HPEG-PCE has become mainstream compared with other PCEs due to its high dosage effectiveness and easy preparation. With a less attainable raw material of preparation, isoprenol, the price of IPEG-PCE is higher than others. Its dispersing ability is weaker than HPEG-PCE. Conversely, its slump retaining is more effective.

Another family of PCEs is vinyl ether-based PCEs (VPEG-PCEs). Under a temperature beneath 25 degrees Celsius, this type of PCEs can reach out a more bountiful compositions. Therefore, this type of superplasticizer can exert a more powerful effect than simple water-reducing in winter, such as slump-retaining. Based on VPEG-PCEs, two advanced branches are ethyl glycol vinyl ether polyoxyethylene ether (EPEG-PCEs) and GPEG-PCEs. EPEG-PCE possesses better reactivity, producing more products easily. However, this process involves a toxic substance. GPEG-PCE is still under observation of its performance [7].

A third categorise that has been studied by scientists is calcium silicate hydrates PCEs (C-S-H-PCEs). Unlike the previous PCEs, this is considered an accelerator and super filler. The mechanism embedded is the ability to decrease activation energy and CaCO3 crystallization, individually. With the accelerating ability, C-S-H-PCEs enable a higher early strength, which convenients the construction [7]. For another, the process of crystallization fills minor cracks and porous within concrete and reduces the permeability.

5. Application of PCEs

5.1. PCE-based Concrete Products

5.1.1. Ultra-high Performance Concrete

PECs create a higher strength of concrete products. In its application, ultra-high performance concrete (UHPC) is a striking branch that leads to a new revolution of concrete. As an emerging type of concrete, has a compression reaching up above 150 PMa, with a water-to-cement ratio of around 0.2; whereas the ordinary one has approximately 35 PMa compression, with a water-to-cement ratio from 0.4 to 0.6 [8]. With the possibility of slandering concrete members such as columns, less concrete is needed for a structure. Moreover, concrete has a high carbon dioxide emission, accounting for 40% of a concrete-steel structure.

5.1.2. Self-compacting concrete

Self-compacting concrete (SCC) is another product with the application of admixtures. The characteristic of this type of concrete is that it does not need to be compacted. Compared to ordinary concrete, SCC is able to flow into construction mold and fill the place by gravity. Its construction costs of moulding and vibration are reduced, thus cutting the budget [9]. However, shrinkage is sacrificed to trade the self-compacting ability. Compared with normal concrete, SCC has a striking shrinkage, which is likely to cause cracks on and within the concrete body. PCEs cut the initial water content within the water, thus effectively reducing the shrinkage of SCC. Therefore, the application of SCC is expanded from this, which can be widely used in other situations that are complex and inconvenient for vibrating.

5.2. Problems of application in PCEs

5.2.1. Limitations of PCEs application

An evitable side effect of PCEs is retardation. The longer the concrete takes to set, the less strength it gains at an early age [10]. Under some circumstances of construction, engineers focus on slowing down the setting time of concrete, because concrete is easy to be solidified halfway through transporting and pumping. Especially in winter, a longer setting time helps to get better concrete performance under a low temperature. However, the retarding effect could be a disadvantage, as too much time will be wasted, and the process will be delayed. Research held by Zhang and others found the result that a longer setting time undercuts the strength of the concrete in the early stage. As the technology revolution of functional groups that have been tested as side chains of PCEs, various lengths of these groups were put to the test. Shorter and less dense side chains have more impave on the retardation. Furthermore, another feature of PCEs is that disregarding the various molecule structure, the absorption of PCEs is the driving factor that causes the retardation. Compared with Ca^{2+}, a greater dosage of PCEs provides a greater abspobtion, accordingly, which greatly affects the fcps and increases its fluidity.

The moleculer structures of PCEs are unstable. As different side chains are introduced to PCEs, the cost of this type of superplasticizer has evolutionally increased compared to previous versions such as PNS, PMS, and AMS. Thus, the price of a new and better product is a significant factor to be considered. Especially for PCE products, if people want to achieve the ideal purpose, only a large amount of dosages will exert its corresponding effect, with insufficient dosages of PCEs that can be neglected from the hydration reaction. In actual construction, people do not use a single additive, they will be mixed with a variety of admixtures, such as air-entraining or accelerating admixtures. Because scientists tend to combine so many different things with PCEs, there are some products that are not very molecular stable, and even function well with other admixtures. Therefore, systematic experiments are more important, and a large number of practices and experiments are needed to prove the stability of the product.

5.2.2. Future development

Even though PCEs hardly work along with other admixtures, they are able to retard the concrete paste and introduce air into the concrete body. Therefore it is possible for PCEs to develop a multifunctional admixture or enable this type of admixture to have better accommodation with other admixtures.

Another problem is that the excellent results of PCEs leave space for some people to replace normal pure aggregates with cheaper aggregates that contain clay. As the effect of PCE on dry mixtures with high clay content is not proliferating, certain research could be carried out in the future to improve the suitability of PCEs for sediments [10]. At the same time, the continuous consumption of natural resources in the concrete industry, such as pure sand, these reserves are being depleted. With the considerations above, we would conclude that the later refinement direction of PCE is to align with the environmental background. Additionally, the stability of PCEs structures that work with other admixtures is still weak. Therefore, by studying a more stable molecule, PCEs can be used as additional water reducers with other admixtures, such as retardation admixture for summer and warm areas, and anti-freezer for higher-latitude areas.

6. Conclusion

PCEs are a popular type of superplasticizer that has been used in concrete mixing. As water-reducing admixtures, they significantly reduce concrete water content. The mechanism embedded in this function is by separating the cement particles with large and extensive molecular structures and neutralizing the charges of cement agglomeration, releasing trapped water. With the reduction of water, there are several other benefits accompanying it. Durability is one of the concrete parameters that has been refined. As more porous that were filled by water now have been filled with finer aggregate, the concrete body obtains a more powerful resistance against the penetration of sulfate and chloride irons, and carbomization. Therefore, the inner microstructures are less likely to be interfered with by those unexpected reactions. A more stable concrete ensures a longer-lasting life cycle. And there is no need to replace concrete regularly. Another function is that PCEs are able to mitigate the shrinkage of concrete. With evaporation happening throughout the whole construction period, the shrinkage of the concrete becomes a critical factor controlling the quality of concrete. With a rapid rate of losing water, cracks appear on the concrete surface and in the deep body. The properties of concrete, such as strength and durability, are being hampered. However, by adding PCEs, water is less significant as a driving factor. Thus the shrinkage problem is alleviated from this.

Under these concepts, generations of PCEs are being studied and invented. The first product is MPEG-PCEs. Based on this, IPEG-PCEs and HPEG-PCEs are found. Another major family is VPEG-PCEs. This is a branch that is for winter or higher latitude areas. A third type is C-S-H-PCEs, this is recently popular among researchers. Two types of novel concrete are being published and welcomed by the market. One is ultra-high performance concrete. This kind of concrete possesses with an extremely high compressing strength, allowing the use of concrete drops at a remarkable level. Slenderer concrete columns with the same withstanding force conserve a substantial amount of concrete annually. Another application is self-compacting concrete. This concrete is more convenient for construction than others because it fills the mould automatically by gravity. A shortcoming is the shrinkage of SCC is above other concrete categories. PCSs compensate for this drawback and enlarge its market. However, at current, PCEs are not stable enough to be mixed with other admixtures, and the price is high. A multi-functional side chain and a more feasible preparation are needed.

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