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. 1

8 References API American Petroleum Institute apparent viscosity AV American Society for Testing and Materials ASTM β-naphthalene sulfonic acid formaldehyde condensate BNS chemical hazard assessment and risk management CHARM CL-CLS chrome lignite-chrome lignosulfonate calcium silicate hydrate C-S-H DS degree of substitution ESEM environmental scanning electron microscope high temperature/high pressure HT/HP methyl cellulose MC melamine formaldehyde sulfite resin MFS MS molar degree of substitution polycarboxylate PC perchlorated phenol PCP ΡV plastic viscosity self-compacting concrete SCC self-leveling underlayment SLU TVOC total volatile organic compound VOC volatile organic compound ΥP yield point

1

Introduction

The construction industry has become a major field of use for biopolymers. In 2000, an estimated \$1-1.5 bn in sales was made at the manufacturer's level, and this growth is expected to continue. Applications of biopolymers in construction are widespread and diverse. In some cases, biopolymers offer distinct advantages in performance and/or cost over synthetic polymers, while in other areas biopolymers may be the only product available that can provide certain properties for building materials. Biopolymers also bear the image of being environmentally more acceptable than synthetic polymers produced in a chemical plant, and although this point can be argued it does influence the choice of materials used, especially for interior home building.

This review begins with a brief description of the construction industry and its usage of chemicals, in order to introduce the market. The technology of building materials using biopolymers is then presented to enable the reader to understand the functionality and benefits of biopolymers, after which the main applications of biopolymers in various segments of the construction industry are described. Because of limited space, only biopolymers with a significant usage volume are discussed here. Although many more biopolymers are in current use, their volume is often very limited, and so they were omitted from this discussion. Rather, an attempt was made to present details of the major biopolymers, to highlight their advantages over synthetic materials, and to identify their overall contribution to modern construction technology. Finally, an overview

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of selected biopolymers which are used in industries other than construction is presented. The aim of this chapter is to stimulate ideas among readers for new applications in building products, and in this respect the article concludes with a discussion of trends and perspectives for biopolymers in construction. For those readers interested in studying the subject in greater detail, selected references are provided throughout each section.

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Historical Outline

The urbanization of mankind was made possible only because of the development of advanced construction engineering techniques and building materials. Under the Romans, construction technology flourished and significant discoveries were made, one of these being the manufacture of a cementitious material called "opus caementitium". This was used, for example, in the foundations of the Roman Coliseum. Marcus Vitruvius Pollio (84–10 вс) described the astounding knowledge of his time about construction and materials in his famous encyclopedia, *De architectura libri decem*. This proves that the Romans had already recognized the role of admixtures to improve their building materials; for example, dried blood was used as an air-entraining agent, while biopolymers such as proteins served as set retarders for gypsum.

Most of the Roman construction knowhow was lost when their empire perished, but in the 19th century Aspdin and Bleibtreu reinvented cement and developed industrial methods for its production. The 20th century became the age of admixtures, the history of which started in the 1920s with the introduction of lignosulfonate, a biopolymer, for concrete plastification. This was the first functional polymer in construction to be used on a large scale, though later on the use of lignite, cellulosics, and microbial biopolymers also became popular.

An overview of major milestones in the development of biopolymeric and synthetic admixtures is provided in Table 1. Biodegradable polymers are the most recent trend in the ongoing quest for improved functional materials in construction.

 Tab. 1
 Major milestones in chemical admixture technology for construction

| Year of Introduction | Admixture chemistry | Function | Type of admixture |
|-------------------------|-----------------------------------|---------------------------------------|----------------------|
| 1920s | Lignosulfonate | Concrete plasticizer | Biopolymer |
| 1940s | Lignite | Bentonite thinner | Biopolymer |
| 1960s | Xanthan gum | Viscosifier | Biopolymer |
| 1962 | Melamine, naphthalene condensates | Concrete super plasticizer | Synthetic polymer |
| 1970s | Cellulose ethers | Water-retention agent | Biopolymer |
| 1980s | Vinylsulfonate Copolymers | Water-retention agents | Synthetic polymer |
| 1980s | Polycarboxylate Copolymers | Concrete super plasticizer | Synthetic polymer |
| 1990s | Polyaspartic acid | Biodegradable dispersant, retarder | Biopolymer |

3 The Construction Industry

Construction – one of the earliest industries – was developed to provide safe shelters for mankind. Today, while the industry provides basic housing and functional buildings, the breath-taking architecture of high-rise buildings and bridges also serves as an expression of our culture and civilization. It is only to be expected that, because of its importance and size, the construction industry still plays a significant role in our economy.

3.1 Size of the Industry

The construction industry is clearly one of the largest industries. In 2000, an estimated \$3 trillion were spent worldwide on the construction of homes, industrial buildings and infrastructure such as roads, bridges, railway tracks, and water supply lines. In Europe, the total turnover of the construction industry in 2000 reached 835 bn Euros. A detailed break-down of European construction expenditure is given in Figure 1 (Becker, 2002). According to this source, home construction accounted for almost half of the construction expense, and industrial construction for about one-third. The remainder was spent on civil engineering projects. Of all expenses, 57% went into new construction and 43% into repair and renovation.

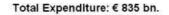
3.2

Building Materials

Common building materials include:

- inorganic, non-metallic materials (85% of total material consumption), e.g., binders, clay, ceramics
- metallic materials (10% of total consumption), e.g., iron, steel, aluminum, copper
- organic materials (5% of total consumption), e.g., lumber, plastics, polymers, textiles

Clay is still by far the most widely used inorganic building material, followed (albeit at long distance) by cement. Many types of cement that differ in composition, grinding size, etc., are available commercially, and in Germany alone over 600 different cements



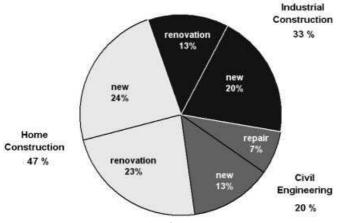


Fig. 1 European construction expenditure in 2000.

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have been registered for construction use. Overall, in 2000, an estimated total of 1.5 billion tons of cement was produced for construction.

Gypsum and its dehydrated forms, hemihydrate and anhydrite, form another important group of building materials. Approx. 150 million tons of $CaSO_4$ products are used in construction, with the bulk (~60%) being added to cement to control cement setting time. Other major uses of gypsum products include wall plaster, anhydrite-based floor screeds and plasterboards. A comprehensive description of gypsum and its use in construction is provided by Kuntze (1984).

3.3

Chemicals Used in Construction

Modern construction often relies on the use of chemical admixtures to achieve the desired property of a building product. For example, the addition of lignin-based plasticizers to concrete enhances its flowability and workability, and permits the amount of mixing water in concrete to be reduced. The result is a gain in compressive strength of the concrete, and a better building product.

Other uses of chemicals in construction include higher labor efficiency, improved economics, and less environmental impact. Some products have helped to reduce heavy labor to a more acceptable level. For example, a self-leveling floor screed which contains a superplasticizer requires minimal labor to be spread and to achieve an even surface, whereas traditional floor screeds are a thick paste and are hard work to lay in place.

A wide variety of chemicals are used for different purposes and applications (Figure 2) (Becker 2002), and of the \$50 bn spent on chemicals for construction, 48% were used in coatings such as interior and exterior paints.

Building materials based on inorganic binders and coatings constitute the segment of the construction industry where biopolymers find their greatest application. Here, they are used as chemical admixtures for a variety of purposes, including:

Global sales of chemicals in construction: \$ 50 bn.

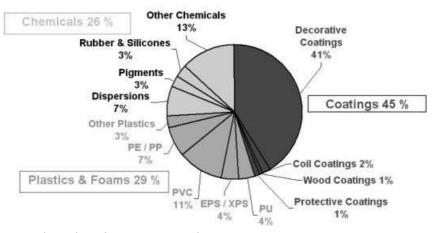


Fig. 2 Chemicals used in construction applications.

- dispersing/thinning effects
- viscosity enhancement
- water retention
- set acceleration and retardation
- air-entrainment
- defoaming
- hydrophobing
- adhesion and film forming

Biopolymers clearly dominate the fields of rheology control (dispersing/thinning or thickening) and water-retention. In the latter application, the market relies almost entirely on biopolymers. With the exception of oil well construction, very few synthetics are used in conventional construction for water-retention.

4 Main Duildi

Major Building Materials

Biopolymers are used in a great diversity of construction applications which will be unfamiliar to most readers. Therefore, the fundamentals of building systems using biopolymers are introduced first, the aim being to provide a better understanding of product requirements and an appreciation of the benefits accrued from the use of biopolymers.

4.1 Concrete

Concrete is the most widely used of all manmade building materials, and in 2000 approx. 5 bn m^3 of concrete were produced.

4.1.1

Fundamentals of Concrete Technology

Concrete is made from cement, aggregates, chemical and mineral admixtures, and water. The active constituent of concrete is cement paste, the nature of which largely determines the performance of the concrete produced.

Cement is made by heating calcareous materials such as limestone or chalk and a source of silica and aluminum oxide such as shale, clay or slate in a rotary kiln to a temperature of about $1300-1450^{\circ}$ C. The resultant clinker is cooled and ground with about 2-5% gypsum and/or anhydrite to a specified degree of fineness. The surface area of cement typically ranges between 2500 and 6000 cm² g⁻¹.

The major constituents of Portland cement are the four clinker phases:

- tricalcium silicate (3 CaO · SiO₂), C₃S
- dicalcium silicate (2 CaO · SiO₂), C₂S
- tricalcium aluminate (3 CaO·Al₂O₃), C₃A
- tetracalcium aluminate ferrite (4 CaO·Al₂O₃·Fe₂O₃), C₄AF

Upon contact with water, the phases hydrate in an exothermic reaction, and a hardened cementitious matrix mainly consisting of calcium silicate hydrate (C-S-H), is formed. C-S-H forms tiny needles which are 600 nm to 2 μ m in length and 5–10 nm thick (Figure 3). The needles intertwine as in a zip fastener, and this gives hardened cement its considerable compressive strength. A comprehensive presentation of cement chemistry and technology has been provided by Taylor (1988).

Aggregates consist of fine or coarse silica sand and gravel. A mix of cement, water and aggregates of particle size < 4 mm is called a mortar. Concrete also contains coarse aggregates with particle sizes up to 32 mm.

Mineral admixtures such as ground or granulated blast-furnace slag, fly ash, silica fume and others are incorporated into concrete to improve its quality.

Chemical admixtures confer beneficial effects such as flowability, water reduction, retardation or acceleration, air-entrainment and anti-settling properties.

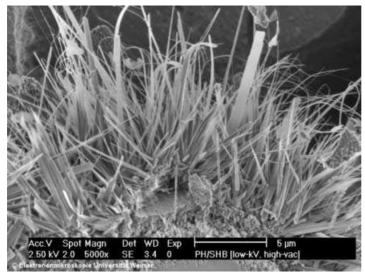


Fig. 3 Environmental scanning electron micrograph of calcium silicate hydrate (C-S-H) in hardened cement.

The performance of concrete depends on the quality of the ingredients, their proportions, placement, and exposure conditions. For example, the hydraulic activity of the clinker, the fineness and particle size distribution of the cement and the amount of mixing water influence the physico-chemical behavior of the hardened cement paste. As a general rule, a fine cement and a low water-to-cement (w/c) ratio result in high compressive strength. Typical w/c ratios in concrete range from 0.30 to 0.70. A w/c ratio below 0.30 does not provide enough water for the cement to hydrate completely, and therefore is undesirable. A concise description of cement chemistry and concrete properties is given by Lea (1970), while general aspects of concrete technology are described by Neville (1981) and a valuable review of material science aspects of concrete has been provided in a recent article (Moranville-Regourd, 1997). These articles contain valuable information for those wishing to learn more about cement hydration, structures of hydrates, the colloidal chemistry of cement setting and hardening, the microstructure of concrete, concrete durability, high-performance concrete and organo-cement composites.

4.1.2

Ready-mix Concrete

Today, about 50% of the concrete produced is made in so-called ready-mix concrete plants. These units store cement in huge silos, with different grades of aggregates in covered compartments, and liquid chemical admixtures in dosage tanks (Figure 4). Ready-mix concrete is prepared by dosing the ingredients according to a recipe through automatic dosage units into a large concrete blender. Ready-mix trucks deliver the concrete to the construction site while the mixing drum is slowly rotated to ensure homogeneity upon delivery. The main advantages of ready-mix plants are better quality control of the concrete ingredients and improved quality consistency of the



Fig. 4 A ready-mix concrete plant.

concrete batches. Many of these plants are equipped to recycle waste concrete and concrete wash water rather than attend to their disposal.

4.1.3

Precast Concrete

Large concrete elements such as beams, pillars, floors or walls are often produced at so-called precast concrete plants. There, concrete is poured into molds to produce large numbers of elements of the same shape and size (Figure 5). Steam curing is applied to accelerate the development of early strength of the concrete, thereby improving the economics of the expensive molds. In comparison with ready-mix plants, precast plants typically produce concrete with a higher compressive strength. This is achieved by reducing the amount of mixing water, thus lowering the

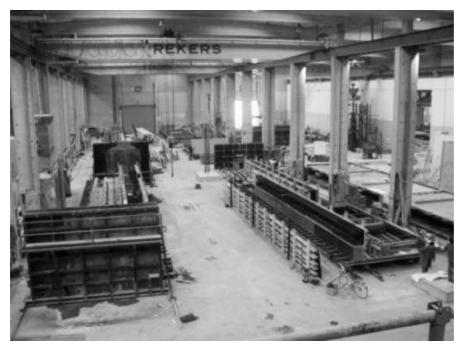


Fig. 5 A precast concrete plant.

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w/c ratios; consequently, precast plants use a significant volume of water-reducing polymers, referred to as plasticizers or super-plasticizers.

Approximately 25% of all concrete is produced in precast plants, 50% as readymix, and 25% in small mixers, or by hand.

4.1.4

Self-compacting Concrete

In 1983, Okamura and Ouchi in Japan began to develop a concrete with such exceptional fluidity that it later became known as selfcompacting concrete (SCC). This concrete is so fluid that it requires little if any vibration to densify and release air after placement. In fact, it has almost self-leveling properties (Okamura and Ouchi, 1999).

The flowability of concrete is commonly measured by the slump test, as described by ASTM C 143. The test uses a frustum of cone 30 mm (12 inches) high. The test procedure is illustrated in Figure 6. Concrete is filled into the cone, which is lifted slowly. Concrete flowability is determined by measuring the decrease in height of the center of the slumped concrete, with the greater the decrease, the better the flowability. For structural concrete, a slump of 75-100 mm (3-4 inches) is sufficient for placement in forms. Highly workable, so-called flowing concrete shows a slump of about 150-200 mm (6-8 inches).

Other methods are also used to determine concrete flowability, and the German flow table method has recently become accepted as the European norm and is now included in the DIN EN 12 350 standard.

Powerful superplasticizers based on polycarboxylate chemistry are used to obtain SCC with a slump of 270-300 mm. It is easy to imagine that, because of its fluidity, such concrete has a tendency to segregate, but this is only apparent if bleeding water occurs on the concrete surface or if heavy aggregates settle at the bottom.

Two approaches have been taken to stabilize SCC. One method is to add larger amounts of fine aggregates or filler (particle size < 0.1 mm), particularly fine sand or limestone. The fine aggregates, by virtue of their large surface area, tie up large amounts of water and prevent bleeding. They also impart some viscosity into the cement paste

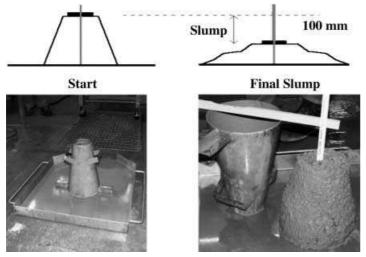


Fig. 6 Slump test for measuring concrete flowability.

and reduce the settling of large aggregates. This type of SCC loaded with fine aggregates is referred to as "powder-type" SCC.

An alternate method of stabilizing SCC is to add a polymeric viscosifier that prevents bleed and sag. As will be discussed later, biopolymers have proven extremely effective for this purpose.

4.1.5

Chemicals Used in Concrete

Concrete uses almost exclusively liquid chemical admixtures, the main reason being ease of dosing and mixing. Major chemical admixtures for concrete include: dispersants based on lignosulfonates, βnaphthalenesulfonate resins (BNS), melamine formaldehyde sulfite resins (MFS), or polycarboxylates [PC; e.g., methacrylic acidpoly(ethyleneglycol)methacrylate ester copolymers]; retarders based on sodium gluconate or sugar-rich lignosulfonate; accelerators based on calcium nitrate or calcium formate; air-entraining agents based on root resin extracts, alkylsulfates of phenol ethoxylates; foamers based on protein hydrolysates; anti-segregation admixtures based on welan gum or starch; anti-washout admixtures based on hydroxypropyl cellulose; shotcrete accelerators based on sodium aluminate or fine, amorphous aluminum oxide; and shrinkage-reducing admixtures based on neopentyl glycol. Comprehensive overviews on chemical admixtures used in concrete have been produced by Ramachandran (1995) and Rixom and Mailvaganam (1999).

Clearly, the concrete industry uses a great diversity of admixtures, some important members of which belong to the group of biopolymers.

4.2

Grouts and Mortars

In contrast to concrete, grouts consist of fine and not coarse aggregates, a binder (cement or gypsum), and water. Most grouts contain aggregates with particle sizes < 1 mm. Grouts with coarse aggregates up to 4 mm are called a mortar, and include floor screeds, self-leveling underlayments (SLUs), tile adhesives, joint fillers and compounds, and injection grouts.

4.2.1

Floor Screeds

Floor screeds are placed on concrete or wooden panels of floors to provide a firm, planar basis for laying floor carpets or parquet in homes and buildings. The most common are the "non-slump" cement-based floor screeds which are thick and require heavy labor to be placed and smoothed (Figure 7). Anhydrite-based floor screeds using a superplasticizer for high fluidity



Fig. 7 Placing of "non-slump" cement-based floor screed (left) and flowing anhydrite-based floor screed (right).