A novel kind of concrete superplasticizer based on lignite graft copolymers

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ABSTRACT

A novel superplasticizer was synthesized by grafting 2-acrylamido-2-tert.butyl sulfonic acid (ATBS) and acrylic acid (AA) monomers onto a lignite backbone using free radical copolymerization technique. Different molar ratios of ATBS:acrylic acid were tested to investigate the influence of the acrylic acid content on the dispersing performance of the graft copolymer. The synthesized polymers were characterized relative to their molecular properties and their dispersing performance in cement. It was found that especially the graft copolymer with an ATBS:acrylic acid molar ratio of 1:0.15 exhibits high dispersing force, long slump retention, high sulfate tolerance and only minor cement retardation. The polymer is more effective than industrial grade BNS. Successful grafting of the monomers was confirmed by size exclusion chromatography and measurement of the adsorbed layer thicknesses.

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1. Introduction

Concrete presents the most common man-made building material at present. It constitutes the fundamental element of our modern architecture and infrastructure [1,2]. A key factor for its widespread use is its unprecedented versatility. For example, it can be utilized for the construction of skyscrapers and bridges, in the manufacturing of prefabricated concrete elements, as shotcrete in tunneling or as drymix concrete [3]. Other important advantages include the ubiquitous availability of the raw materials (cement, sand, gravel and water), its simple fabrication, its stability and durability as well as its relatively low price. The variability of concrete properties also results from the application of chemical admixtures such as, e.g., superplasticizers [4]. These chemical admixtures are added in small amounts to the cement to enhance its workability (increased flowability and pumpability) and to improve the material properties of the hardened concrete (higher compressive and bending tensile strength) [5]. Superplasticizers facilitate the reduction of the water-to-cement ratio, thus enabling the production of concrete with higher strength and durability.

Since the invention of superplasticizers in the 1960s, this group of chemical admixtures experienced a rapid growth. Nowadays, different kinds of superplasticizers can be identified: polycondensates, polycarboxylates, small molecules and biopolymers [6]. Although the present kinds of polycondensates and polycarboxylates represent highly effective superplasticizers, still new structures and concepts are targeted by scientific and industrial researchers [7]. A new approach for the synthesis of superplasticizers is the utilization of natural polymers as a starting material [8]. They can offer novel structural motifs and often possess a high density of functional groups. Therefore, they can present perfect substrates for chemical modifications, including graft copolymerization reactions. Some examples have already been reported in the literature, where novel superplasticizers have been synthesized through functionalization (i.e., *via* sulfonation or carboxymethylation) of natural polymers [9–11]. Lignite, a synonym used in the scientific literature for ordinary brown coal, presents an outstanding starting material for such preparations because of its global abundance, low cost and its high structural diversity.

Lignite is a sedimentary type of coal often occurring near the surface of earth that formed million years ago through coalification [12,13]. This process was initiated in flooded areas such as swamps whereby plant residues (i.e., roots, leaves and spores) were submerged in water, thus preventing the aerobic degradation of the plant material. The high bioproduction rates prevailing under the primeval subtropical climate conditions ensured that more plant residues were deposed than degraded [13]. As a result, plant material was accumulated and partially decomposed to peat. Burial of these humic substances over millions of years by sediments and geological changes (e.g., tectonic movements) caused an increased pressure leading to drainage and the release of gases like methane or carbon dioxide [14]. This process caused the plant residues to successively metamorphose into lignite. Depending on the degree of coalification, four different coal types are distinguished: lignite, sub-bituminous coal, bituminous coal and anthracite. According

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to this classification, lignite presents a coal of low quality possessing the highest water and the lowest carbon content.

Chemically, lignite constitutes a complex, inhomogeneous mixture containing a variety of organic and inorganic compounds. The organic components include bitumen (wax, resins), humic substances and incompletely charred lignin and cellulose residues. The humic substances can be divided according to their solubility in aqueous solution in humin, fulvic and humic acids [15]. The organic constituents that are insoluble over the entire pH range are designated as humin, while the fulvic acid fraction includes the substances that are soluble under all pH conditions. Contrary, humic acids are only soluble in alkaline media, but insoluble in strongly acidic environments (pH <1). Humic and fulvic acid represent the main part of the organic constituents (up to 80 wt.%). They can be extracted by treating lignite with alkali hydroxide solution [16,17]. The alkali-soluble components of lignite are commercially available as "caustic lignite," which for example is used in millions of tons as fertilizer in agriculture [15,18] or as drilling fluid additive by the oil industry [19]. However, up to date, no lignite-based superplasticizer has been developed.

In recent work, we already have described the synthesis of a graft copolymer from ordinary brown coal mined in Germany [20]. Due to its high amount of insoluble components, an alkaline extraction was first performed to remove all non-reactive components (e.g., humin, ashes, minerals, etc.) and to isolate the fraction which contains the humic and fulvic acids because only they can be utilized as starting material for the grafting process. In contrast, the lignite sample studied here had been purified already and was selected for a high content of humic acids, which is particularly advantageous for the grafting reaction. Therefore, one purpose of the paper here was to prove the applicability of our process to commercial purified lignite samples.

In this study, we report on the synthesis of a novel superplasticizer prepared by grafting ATBS and acrylic acid onto the alkali-soluble constituents of lignite. The lignite sample differs in its chemical composition from the previously studied brown coal regarding its higher amount of humic acids.

The alkali-soluble constituents exhibit a high number of functional groups (i.e., aliphatic/aromatic carboxylate, amino, hydroxyl and phenolic groups) and thus represent an ideal substrate for graft copolymerization reactions [21]. Through the addition of an initiator, the different functionalities allow the formation of free radical sites. Vinyl monomers can be grafted onto these sites leading to a polymer with lateral graft chains and lignite as backbone. Different lignite{ATBS-co-AA} graft copolymers were synthesized and the molar ratio of the monomers ATBS and acrylic acid was varied from 1:0.15 to 1.50 to investigate the influence of the acrylic acid content on the dispersing power. To ascertain the contribution of the lignite backbone to the dispersing effect, an ATBS-acrylic acid copolymer was synthesized as comparative sample to the respective lignite{ATBS-co-AA} graft copolymer. Furthermore, the overall aim of this study was to evaluate new structural motifs and concepts for the synthesis of potent new superplasticizer molecules.

2. Materials and methods

2.1. Cement

An ordinary Portland cement CEM I 52.5N (Milke®classic from HeidelbergCement, Geseke plant, Germany) was used in this study. The phase composition of the cement as determined by Q-XRD and subsequent Rietveld refinement is illustrated in Table 1. Its specific surface area as obtained by the Blaine method was 3,583 cm^2/g. For the average particle size (d_{50} value; determined by laser granulometry using a CILAS 1064 instrument, Cilas, Marseille, France), a value of 11.5 μm was found, and the density of the cement was 3.15 g/cm^3 (Helium pycnometer from Toni Technik, Berlin, Germany).

Table 1
Phase composition of the CEM I 52.5N sample as determined by Q-XRD using Rietveld refinement.

Phase	wt.%
C$_3$S, m	54.14
C$_2$S, m	26.63
C$_3$A, c	3.28
C$_3$A, o	4.26
C$_4$AF, o	2.45
Free lime (Franke)	0.10
Periclase (MgO)	0.03
Anhydrite	2.64
Hemihydrate[a]	1.21
Dihydrate[a]	0.20
Calcite	3.61
Quartz	1.16
Arcanite (K$_2$SO$_4$)	0.46

[a] Determined by thermogravimetry.

2.2. Chemicals

2-Acrylamido-2-tert.butyl sulfonic acid (ATBS; AMPS® 2404 monomer; >99% purity) was received from Lubrizol (Rouen, France). AMPS® is a registered trademark of the Lubrizol Corporation (Wickliffe, Ohio). Acrylic acid (AA; >99%), sodium hydroxide (NaOH; >98%), sodium peroxodisulfate (Na$_2$S$_2$O$_8$; >99%) and sodium pyrosulfite (Na$_2$S$_2$O$_5$; >99%) were purchased from Merck (Darmstadt, Germany), while ethylenediamine tetraacetic acid (EDTA; purity >99.5%) came from Sigma-Aldrich (Munich, Germany). All chemicals were used without further purification.

Melcret® 500 F, a spray dried β-naphthalenesulfonate (BNS)-based superplasticizer powder received from BASF Construction Polymers GmbH (Trostberg, Germany), was used as an industrial reference sample.

2.3. Lignite sample

Superlignite, an untreated lignite supplied as a dark brown powder which exhibits a pH of 5.7 in 10 wt.% aqueous solution, was obtained from American Colloid Company (Hofmann Estates, Illinois, USA). This lignite sample is mined in North Dakota; it contains a high amount of humic acids and was used as is. The data obtained from the elemental analysis of the lignite sample are tabulated in Table 2. Superlignite exhibits a carbon content of only 42.30 wt.%, which confirms its low degree of coalification. The molecular weights of this lignite as determined by size exclusion chromatography where found at 36,000 g/mol (M_w) and 30,000 g/mol (M_n), respectively. The chemical composition of the sample was quantified according to an experimental procedure described in literature [16]. It was found that superlignite contains about 41 wt.% alkali-insoluble components (i.e., humin and inorganic matter), while the main part represents the alkali-soluble fraction (57 wt.% humic acid; 2 wt.% fulvic acid). Furthermore, anionic charge measurements revealed a slightly anionic character of the raw material in DI water (183 μEq/g), and a higher charge in 0.1 M NaOH (464 μEq/g).

2.4. Preparation of the lignite{ATBS-co-AA} graft copolymers

The lignite{ATBS-co-AA} graft copolymers were synthesized by aqueous free radical copolymerization using sodium peroxodisulfate

Table 2
Elemental analysis data of the lignite sample.

Element	C	H	N	S	Na	K	O[a]
[wt.%]	42.30	3.73	0.95	1.65	2.00	0.20	49.17

[a] O content calculated as difference to 100%.