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ORIGINAL PAPER

Polycarboxylate superplasticizers of acrylic acid–isobutylene polyethylene glycol copolymers: monomer reactivity ratios, copolymerization behavior and performance

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Abstract Acrylic acid–isobutylene polyethylene glycol (AA-TPEG) copolymers are typical of polycarboxylate superplasticizers (PCEs). AA-TPEG copolymers are prepared via free-radical polymerization with potassium persulfate as the initiator. The obtained copolymers were characterized by gel permeation chromatography (GPC) and infrared spectra (FTIR). The GPC method can break through the former limitations of the instruments and receive instantaneous unreacted and instantaneous monomer concentrations and not the initial monomer feeds. Since TPEG monomer is highly bulky, the common calculation methods for determining monomer reactivity ratios in copolymerization based on terminal copolymerization equation are not suitable. However, this study created non-linear least squares curve fitting of terminal copolymerization equation (NLLSQ-T) and penultimate copolymerization equation (NLLSQ-P) methods, which used Python's NumPy, SciPy, and SymPy libraries to generate code and did numerical computations, bringing greater accuracy of monomer reactivity ratios. The monomer reactivity ratios were calculated with Fineman–Ross, Kelen–Tüdös, YBR, NLLSQ-T, and NLLSQ-P methods and found to be $r_{AA} = 10.888$, $r'_{AA} = 1.131$, $r_{TPEG} = 0.012$, and $r'_{TPEG} = 0.042$ for AA-TPEG copolymers. Moreover, this study also explored specific copolymerization behavior of similar structure of copolymers with steric hindrance under penultimate copolymerization equation, such as dependence of the mole fractions in the copolymer on the mole fractions of unreacted monomers in solution, variation of copolymer compositions with conversion and sequence length distribution. The fluidity and flow loss of pastes containing PCEs were investigated, and the appropriate PCEs dosages resulted in a better workability of cement pastes.

Keywords Polycarboxylate superplasticizer · Acrylic acid · Isobutylene polyethylene glycol · Reactivity ratios · Penultimate copolymerization equation

Introduction

In the 1980s, a new generation of polycarboxylate superplasticizers (PCEs) was developed in Japan [1]. They are not linear ionic polymers but have a comb-like structure. They consist of a so-called backbone polymer to which side chains are connected in a more or less regular manner. Because there are many tunable structural parameters of PCE molecules which are easy to adjust, PCEs can accommodate many different purposes, such as providing long slump retention, high speed of flow, and effectiveness at ultralow water-to-cement ratios. However, all of them are based on the same principle: PCEs are composed of lateral polyethylene oxide (PEO) side chains grafted onto an anionic polymer backbone. The PEO side chains instigate a steric hindrance effect between the cement particles suspended in water [2, 3]. Consequently, a great diversity of chemically different PCEs is on the market today, and the common AA-TPEG-type PCEs are made from isobutylene polyethylene glycol macromonomers by copolymerization with acrylic acid (Fig. 1).

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