Minerals Engineering 95 (2016) 29–39

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Using acrylamide/propylene oxide copolymers to dewater and densify mature fine tailings

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ARTICLE INFO

Article history:
Received 16 December 2015
Revised 16 May 2016
Accepted 9 June 2016
Available online 15 June 2016

Keywords:
Amphiphilic polymers
Polyacrylamide flocculants
Tailings dewatering
Tailings flocculation
Mature fine tailings

ABSTRACT

Adding hydrophobic groups to polyacrylamide (PAM) flocculants improves flocculation and dewatering (settling, turbidity, capillary suction time and solids content after centrifugation) of mature fine tailings (MFT). In this study, we copolymerized different amounts of polypropylene oxide macromonomers (PPO) with acrylamide to produce PAM-PPO graft copolymers with different hydrophobicities and molecular weights. According to CST, turbidity and centrifugation results, the PAM-PPO copolymers dewatered and densified MFT more efficiently than a reference commercial anionic PAM supposedly because the PPO hydrophobic groups reduced the amount of water trapped inside the polymer floccules. Besides densifying and dewatering tailings more efficiently, the PAM-PPO copolymers had molecular weights ten times smaller than the reference anionic PAM flocculant, which reduced their viscosities and shear-sensitivities. As a result, it is easier to mix these copolymers with tailings under a wider window of operating conditions. We also observed that *aged* MFT (stored for approximately 10 months) were more easily dewatered, especially at high solids content (20 wt%). This behavior might be attributed to the evaporation of water, hydrocarbons, or other low molecular weight organic compounds. However, further studies are required to understand what and how chemical compositional changes alter the stability of MFT. The information generated in these studies could be used to design polymers that could target the MFT components responsible for its high stability and slow consolidation.

1. Introduction

Dewatering and consolidation of oil sands tailings are technical and environmental challenges for the oil sands industry. Current dewatering technologies, especially paste technology, use polyacrylamide (PAM) flocculants. Polymers are extensively used in oil production from well drilling to environmental applications (Wang et al., 2014; Stocks and Parker, 2006; Masliyah et al., 2011). Polyacrylamides produce gel-like networks through hydrogen bonding that retain large volumes of water, leading to poor sediment consolidation. Because of these limitations, it is not possible to produce sediments with solids content higher than 65 wt%, even with the assistance of mechanical dewatering methods such as filtration and centrifugation (Masliyah et al., 2011). Unfortunately, we need to densify tailings to about 75 wt% to properly reclaim the land where tailing ponds are currently located (Masliyah et al., 2011; Wang et al., 2014).

New alternatives to PAM flocculants have been proposed to improve the dewatering and consolidation of oil sands tailings. Yang et al. (2004) prepared an inorganic-organic hybrid polymer based on $Al(OH)_3$ and PAM (Al-PAM). The hybrid Al-PAM flocculated kaolinite suspensions more efficiently than commercial PAM because the positively-charged $Al(OH)_3$ groups neutralized the negative charges in kaolinite. Unfortunately, Al-PAM flocculants did not flocculate mature fine tailings (MFT) effectively (Masliyah et al., 2011; Vedoy and Soares, 2015).

Temperature-sensitive polymers, notably poly(N-isopropylacrylamide) (PNIPAM), have also been used to treat oil sands tailings. The solubility of these polymers in water changes with temperature, making them either hydrophilic or hydrophobic. When they become hydrophobic at higher temperatures, these polymers form sediments that are more compact than those flocculated with PAM. Despite the positive results achieved with fresh tailings, PNIPAM has been used only once to dewater MFT (Li et al., 2015), in part because of the cost involved in heating up large volumes of tailings to achieve the hydrophilic-hydrophobic transition. In addition, the transition temperature significantly increases

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http://dx.doi.org/10.1016/j.mineng.2016.06.005
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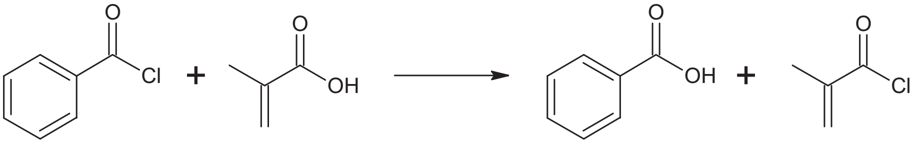


Scheme 1. Synthesis of methacryloyl chloride.

when ionic PNIPAM is used instead of non-ionic PNIPAM (Li et al., 2015; Long et al., 2011; Li et al., 2007, 2009; O'Shea et al., 2010; Sakohara et al., 2013).

Inspired by the positive effect observed for the hydrophilic-hydrophobic transition in PNIPAM, we introduced hydrophobic groups into PAM chains to permanently reduce their hydrophilicity. Our novel copolymers have two main segments: a polar PAM backbone and non-polar, or weakly polar, PPO grafts. The PAM-PPO copolymers are less hydrophilic than commercial PAM (Sadicoff et al., 2000, 2001), and are more likely to expel water from the flocculated MFT, reducing, if not completely eliminating, the water retained inside the flocs formed during MFT treatment. Furthermore, we can change the frequency and molecular weight of the PPO chains grafted to the PAM backbones to optimize polymer hydrophobicity and flocculation behavior, enhancing dewatering performance while maintaining the ability of the polymer to be dissolved in water. We can also design the molecular weight and ionic charge of the PAM backbone to get optimum performance. Better dewatering and densification of MFT with this novel polymer chemistry are the main benefits of PAM-PPO copolymers compared to the typical commercial PAM. To the best of our knowledge, the use of PAM-PPO copolymers for dewatering and consolidation of MFT has never been reported in the literature.

2. Experimental methodology

2.1. Copolymer synthesis

A series of PAM-PPO copolymers were made by polymerizing acrylamide and macromonomers of PPO functionalized with methacrylate (PPO-MA). To make the PPO-MA macromonomers, methacryloyl chloride needs to be made first, as described in the section below.

2.1.1. Synthesis of methacryloyl chloride

Methacryloyl chloride is the product of the reaction between benzoyl chloride and methacrylic acid in a molar proportion of 1.4:1 in the presence of 10% (wt/v) of hydroquinone (Scheme 1). The final product was distilled from the reactive mixture in a temperature range of 80–110 °C. The methacryloyl chloride was then redistilled at 98 °C (Lucas and Oliveira, 1990).

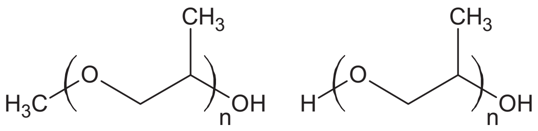


Fig. 1. Monofunctional (left) and difunctional (right) PPO polymers.

2.1.2. Synthesis of PPO-MA

PPO-MA was made by reacting methacryloyl chloride and PPO in the presence of pyridine, which acts as a sequestration agent for chloridric acid formed in the reaction. Two commercial PPO polymers were used: Dowfroth 250 (monofunctional, M_n = 300 g/mol, PPO-300) and Polyglicol Fluent-Mat 612 (difunctional, M_n = 1000 g/mol. PPO-1000). Dow Brasil supplied both samples (Fig. 1) (Sadicoff et al., 2001).

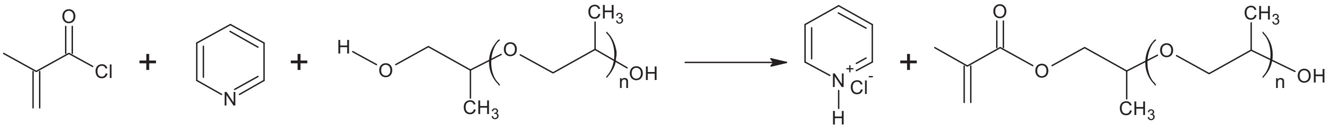
The molar proportions of methacryloyl chloride to PPO varied slightly depending on the PPO type. We used a ratio 1:1 to modify the monofunctional PPO-300, and a ratio 0.5:1 to modify the difunctional PPO-1000. Both reactions (Schemes 2 and 3) were carried out under stirring in dry toluene inside an ice bath until pyridine hydrochloride precipitated from solution. We then filtered the pyridine hydrochloride from the PPO-MA solution, and removed the toluene from the PPO-MA using a rotary evaporator at 65 ± 5 °C (Lucas and Oliveira, 1990; Lucas et al., 1997).

2.1.3. Synthesis of PAM-PPO

Polyacrylamide-g-poly(propylene oxide) (PAM-PPO) copolymers was synthesized by micellar polymerization, using acrylamide, potassium persulfate as the initiator (0.3 and 0.4% m/m in relation to acrylamide), and sodium dodecyl sulfate (SDS) as surfactant agent (3% m/v). All polymerization were done at 65 °C in distilled and deionized water under nitrogen atmosphere (Sadicoff et al., 2001; Lucas et al., 1997), varying the PPO content from 5 to 40 wt% in relation to the total PAM concentrations to make copolymers with different molecular weights and PPO grafting frequency. The copolymers were purified by successive dissolutions and precipitations in deionized water and methanol, respectively (Pires et al., 2011). Schemes 4 and 5 illustrate these polymerizations.

2.2. Copolymer characterization

The composition of the copolymers was determined by carbon-13 nuclear magnetic resonance (^{13}C NMR) using a Varian Mercury VX300 spectrometer operated at the following conditions: frequency = 75 MHz, delay time = 1 s, acquisition time = 1.3 s, probe volume = 5 ml, analysis temperature = 50 °C, pulse width = 90°, spectral width = 18,000 Hz, and number of scans = 118,000. PAM-PPO samples were diluted to 50 mg/mL prior analysis in deuterated water (99.8%, Cambridge Isotope Laboratories Inc). The standard solvent TMSP (Sodium-3-TrimethylSilylPropionate, DLM-48-1, 98%) was used as calibration reference. The following peaks were used in the calculations: (1) 72–82 ppm for CH and



Scheme 2. Functionalization of difunctional PPO-1000 with methacrylate.