

Synthesis and properties of polyester-based polymeric surfactants from diterpenic rosin



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ABSTRACT

A series of polymeric surfactants, poly acrylic acid rosin polyethylene glycol esters (P-AAR-PEG), have been synthesized from natural diterpenic rosin. Their structures were characterized by Fourier Transform Infrared Spectrometer (FTIR) and their molecular weights were characterized by Gel Permeation Chromatography (GPC). Their critical micelle concentration (CMC), surface tension (γ_{CMC}), foaming property (FP), and hydrophile-lipophile balance (HLB) value were evaluated. Their thermal properties were measured by Thermal Gravimetric Analyzer (TGA) and fluid behaviors were studied by Rotational Rheometer. The influence of concentration on the properties of oil-in-water emulsions was examined and contrasted the stability of emulsion by the mean droplet size between day1 and day7. The weight-average molecular weight of P-AAR-PEG ranged from 1770 to 5071. CMC values of P-AAR-PEG were ranged from 0.33 to 0.87 g/L and the corresponding γ_{CMC} values were ranged from 37.8 to 39.1 mN/m respectively. Their CMC and γ_{CMC} values decreased and then increased with the increment of molecular weight of hydrophile group. Rheological measurements indicated that the P-AAR-PEG solutions changed from pseudoplastic property to Newtonian with increasing shear rate. P-AAR-PEG1000 had good emulsion ability to turpentine in water. When the concentration of P-AAR-PEG1000 was 8 wt%, the emulsion remained stable for more than 7 days.

1. Introduction

Polymeric surfactants provide many significant benefits to industrial lattices, such as low foaming, good chemical and mechanical stability, rheology modification and improved quality of coatings (Chang et al., 2000). Therefore, polymeric surfactants have drawn increasing attention in the past decades, particularly for their applications in several fields including emulsion polymerization, coatings and enhanced oil recovery (Huang et al., 2016).

With the increasing concern for the need to save energy and protect the environment, renewable resource is a crucial area in the search for alternatives to fossil-based raw material (Rao, 2012). Rosin is composed of a series of tricyclic diterpene resin acid that occurs naturally in the oleoresin of pine trees and its derivatives are accepted as being eco-friendly, biodegradable and biocompatible (Sahu et al., 1999) (Satturwar et al., 2003). The structure of rosin has a latent conjugated double bonds and a carboxylic acid group which can be used for further modification to convert to a monomer or various suitable intermediates to be used for the synthesis of polymers (Atta et al., 2009). As its tricyclic backbone of rosin has excellent hydrophobicity, it can be used as

raw material to prepare surfactants by introducing hydrophilic group to the basic skeleton. Compared with those from long chain fatty acids, the surfactants from rosin have better emulsification ability to those compounds with ring structure thanks to the rigid structure of rosin. Besides, the thermo stabilization, chemical and mechanical stability of surfactants can be enhanced by introducing the rigid structure of rosin.

In previous work, many types of low molecular surfactants from rosin have been synthesized and their applications were investigated such as rosin-based cationic surfactants (Tadros, 2005), anionic surfactants (Cai et al., 2010), zwitterionic surfactants (Cui et al., 2007), nonionic surfactants (Sun et al., 2003). Besides, some new types of surfactants from rosin also were reported such as gemini surfactants (Jia et al., 2009).

In practical application, polymer is also needed to adjust the rheological property and improve the stability of emulsion. However, few surfactants from rosin with high molecular weight have been reported. Therefore, in this work, we synthesized nonionic polymeric surfactants from rosin and investigated their properties.

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2. Materials and methods

2.1. Materials

Rosin was obtained from Richeng forest product chemical co. LTD (Guangxi province, China). Other chemical reagents were purchased from Aladdin Industrial Corporation (China), such as acrylic acid, polyethylene glycol (PEG) with different molecular weight (400, 600, 1000, 2000 or 4000), zinc oxide, absolute ethyl alcohol, benzene, (1,4) – dioxine. All reagents were analytical grade and were used without further purification.

2.2. Synthetic methods

Acrylic acid rosin was synthesized by previously reported routes (Zhao et al., 2008). A certain amount of rosin and 0.5 wt% hydroquinone, which was designated as inhibitor were put into a three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer. They were stirred at 100 °C until the rosin melt completely and then heated to 180 °C in nitrogen atmosphere. Then, acrylic acid was added drop by drop within 30 min (the mass ratio of rosin and acrylic acid was 4.5:1). The mixtures were reacted at 180 °C for 1 h, and followed by 200 °C for 2 h and then heated to 230 °C to remove unreacted acrylic acid. Finally, acrylic acid rosin were obtained (AAR, acid value of AAR was 220 mg/g KOH).

The PEG, AAR and 0.2 wt% zinc oxide were put into a three-necked flask equipped with a mechanical stirrer, a reflux condenser and a thermometer (the molar ratio of carboxyl and hydroxyl was 1:1). The mixture was stirred at 270 °C for 6–8 h until the acid value was under 10 mg/g KOH and the target products were obtained. PEG with different molecular weight (PEG400, PEG600, PEG1000, PEG2000, PEG4000) was used to react with AAR, respectively, formed five poly acrylic acid rosin polyethylene glycol esters (P-AAR-PEG). For example, poly acrylic acid rosin polyethylene glycol 400 ester (P-AAR-PEG400) was synthesized by esterification of AAR and PEG400. The naming method was the same to other products. Synthesis routes of P-AAR-PEG were shown in Scheme 1.

GC spectrometry of AAR determined by methyl-esterified method was shown in Fig. 1. The result of GC–MS showed that the peak at 42–48 min, whose molecular ion peak was 316, was monobasic acid by methyl-esterified and the peak at 56–62 min, whose molecular ion peak was 402, was dibasic acid by methyl-esterified. The detailed analysis of GC–MS spectrometry was shown in Fig.S1–S7 in attached supporting information. The substances at peak of 57.302 and 60.472 in GC spectrometry were two isomers. One was the product of syn-addition and the other was the product of tras-addition after D-A addition between acrylic acid and rosin. Their structures were shown in Fig.S8. The

proportion of dibasic acid was about 60% and monobasic acid was about 30% as shown in Fig. 1. Rosin is a mixture of the isomers composed of tricyclic diterpene resin acids. Its main component is abietic resin acid, in which there is a conjugated double bond. Dibasic acid was prepared by Diels-Alder addition of abietic resin acid reacted with acrylic acid. The main components of monobasic acid were dehydroabietic, pimaric and isopimaric which cannot take place Diels-Alder addition with acrylic acid but they also can react with PEG. When occurs to esterification reaction between debased acid and PEG, it is very complex in the actual situation (Qi, 2015). The structure of main product was as shown in Scheme 1.

2.3. Characterization and performance

2.3.1. GC

Gas chromatography (GC) spectra were used to analyze contents of different components in AAR. Its spectra were obtained on a GC-950 by using hydrogen flame detector. Chromatographic column was DB-5, whose column length was 30 m and diameter was 0.25 mm. The temperature program was as follows: holding at 150 °C for 2 min, and then increasing to 260 °C at rate of 3 °C/min, and finally holding at 260 °C for 10 min.

2.3.2. FTIR

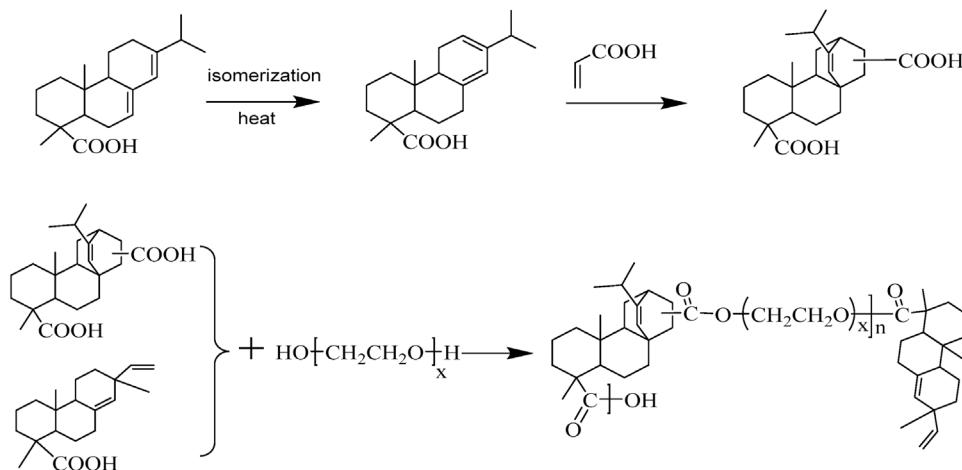
Fourier transform infrared (FT-IR) spectra were used to compare the structure of rosin, AAR and P-AAR-PEG. The spectra were obtained on a Thermo Scientific Nicolet IS10 IR spectrophotometer by KBr pellets method and were recorded over the range 4000–500 cm^{-1} at 4 cm^{-1} resolution and averaged over 16 scans per sample.

2.3.3. GPC (Yu et al., 2014)

Molecular weight distribution curves and relative values of number-average (Mn) and weight-average (Mw) molecular weight of P-AAR-PEG were determined by GPC (Gel permeation chromatography). GPC was performed at room temperature using a Malvern Viscotek 3580 System equipped with Viscotek GPC2502 RI detector and a GPC1007 pump. The columns were Styrag HR1 and HR2 (300 mm \times 7.8 mm, two columns in series connection), General Mixed Org 300 \times 7.8 mm (CLM3009). The eluent was HPLC grade THF, and the flow rate was 1 mL/min

2.3.4. Thermal properties

TGA analysis was performed by using NETZSCH STA 409 PC ranging from 20 to 800 °C at a rate of 10 °C/min under nitrogen gas at a flow rate of 100 mL/min.



Scheme 1. Synthesis routes of P-AAR-PEG.

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