

RESEARCH ARTICLE

Synthesis and characterization of castor oil-based polymeric surfactants

Xujuan HUANG^{1,2}, He LIU (✉)¹, Shibin SHANG (✉)¹, Zhaosheng CAI², Jie SONG³, Zhanqian SONG¹

¹ Institute of Chemical Industry of Forestry Products, Chinese Academy of Forestry, Key Laboratory of Biomass Energy and Material, National Engineering Laboratory for Biomass Chemical Utilization, Key and Laboratory on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, China

² School of Chemical and Biological Engineering, Yancheng Institute of Technology, Yancheng 224051, China

³ Department of Chemistry and Biochemistry, University of Michigan-Flint, Flint, MI 48502, US

Abstract Dehydrated castor oil was epoxidized using phosphoric acid as a catalyst and acetic acid peroxide as an oxidant to produce epoxidized castor oil (ECO). Ring-opening polymerization with stannic chloride was used to produce polymerized ECO (PECO), and sodium hydroxide used to give hydrolyzed PECO (HPECO). The HPECO was characterized by Fourier transform infrared, ¹H and ¹³C nuclear magnetic resonance spectroscopies, gel permeation chromatography, and differential scanning calorimetry. The weight-average molecular weight of soluble PECO and HPECO were 5026 and 2274 g·mol⁻¹, respectively. PECO and HPECO exhibited glass transition. Through neutralizing the carboxylic acid of HPECO with different counterions, castor oil-based polymeric surfactants (HPECO-M, where M = Na⁺, K⁺ or triethanolamine ion) exhibited high efficiency to reduce the surface tension of water. The critical micelle concentration (CMC) values of HPECO-M ranged from 0.042 to 0.098 g·L⁻¹ and the minimum equilibrium surface tensions at CMC (γ_{cmc}) of HPECO-M ranged from 25.6 to 30.0 mN·m⁻¹. The water-hexadecane interfacial energy was calculated from measured surface tension using harmonic and geometric mean methods. Measured values of water-hexadecane interfacial tension agreed well with those calculated using the harmonic and geometric mean methods.

Keywords epoxidized vegetable oil, ring-opening polymerization, interfacial tension, polymeric surfactant

1 Introduction

At a time of depleting fossil oil reserves and an increasing emission of greenhouse gases, the utilization of renewable resources in energy and material applications is receiving increased attention in both industrial and academic settings, due to concerns about environmental sustainability^[1]. This situation has raised interest in the use of biodegradable polymers from inexpensive renewable resources and the utilization of renewable raw materials meets the principles of green chemistry. Furthermore, Polymeric surfactants have drawn much attention in the last decades because they offer many novel performances attributes such as low cost, associative properties in water, and surface-active properties that can control foaming or emulsion stability. Vegetable oils are renewable, biodegradable, low-cost, eco-friendly, and low-toxicity natural resources. They consist of triglycerides and exhibit high diversity related to the length of the fatty acid chain and degree of saturation^[2]. The functional groups, such as the hydroxyl groups, and double bonds in fatty acid chains can provide additional natural chemical functionality for modifications, cross-linking and polymerization.

Soybean oil is one of the most abundant renewable edible oils in the world, and is not only consumed as food for humans, but is also a raw material for industrial processing^[3,4]. However, edible oils are in short supply for human food, so non-edible oils are an attractive alternative for industrial processing. Castor oil is a major candidate to replace edible oils in industrial production, due to its inherent advantages and potential applications^[5,6]. The major content of the triglyceride fatty acid residue of castor oil is ricinoleic acid (89%). Other fatty acids present are linoleic (4.2%), oleic (3.0%), stearic (1.0%), palmitic (1.0%), dihydroxystearic acid (0.7%), linolenic acid

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Correspondences: liuheicifp@hotmail.com, shangsb@hotmail.com

(0.3%), and eicosanoic acid (0.3%)^[7]. Castor oil consists mainly of esters of 12-hydroxy-9-octadecenoic acid (ricinoleic acid), thus the presence of hydroxyl groups and the carbon-carbon double bonds make it valuable for many chemical reactions and modifications. Being a polyhydroxy compound, the hydroxyl groups of castor oil can be removed through dehydration. As the name implies, dehydration involves the removal of water molecule from the fatty acid portion of the polyhydroxy oil^[8,9]. The hydroxyl group and an adjacent hydrogen atom from the C-11 or C-13 position of the ricinoleic acid portion are removed as a water molecule. Dehydrated castor oil (DCO) results from the formation of new double bonds in the fatty acid chains and leads to a similar structure to soybean oil.

Furthermore, the carbon-carbon double bonds in the fatty acid chains of the vegetable oils can undergo various reactions including addition^[10], oxidation^[11] and polymerization^[12,13] reactions, which increase their reactivity. A useful reaction for the modification of vegetable oils is the epoxidation of double bonds. Epoxidized soybean oil (ESO) provided commercially at reasonable cost has been used as a raw material for synthesis of new polymers^[14–19]. According to the literature, ring-opening reaction of ESO with different alcohols was achieved using dry Amberlyst 15 as a catalyst^[20]. Several vegetable oil-based polyols have been prepared by ring-opening of epoxidized soybean oil, in which the hydroxyl groups of reactants acted as initiators^[21,22]. Ring-opening polymerization catalyzed by boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) in liquid carbon dioxide and methylene chloride can be used to produce polymerized ESO (PESO)^[23]. Therefore, the double bonds in DCO can be epoxidized and the epoxidized DCO (ECO) with a high degree of epoxidation can be used to produce PECO.

In this paper, DCO was first prepared from castor oil by dehydration, and ECO was synthesized using phosphoric acid as catalyst and acetic acid peroxide as the oxidant by subsequent epoxidation of DCO. The ring-opening polymerization of ECO was carried out using stannic chloride (SnCl_4) as catalyst, in which the hydroxyl groups in ECO acted as initiators. Hydrolysis of PECO was performed with NaOH (Fig. 1). HPECO was characterized by Fourier transform infrared (FT-IR), ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The surface properties and interfacial properties of the polymeric surfactants (HPECO-M, where $\text{M} = \text{Na}^+$, K^+ or TEA^+) were investigated.

2 Materials and methods

2.1 Materials

Castor oil, stannic chloride (SnCl_4), 46%–50% peracetic

acid, HPLC grade tetrahydrofuran (HPLC grade THF), Wijs' reagent ($0.1 \text{ mol} \cdot \text{L}^{-1}$), potassium iodide and tert-butylhydroquinone (TBHQ) were purchased from Shanghai Aladdin Industrial Co., Ltd. (Shanghai, China). Phosphoric acid, sodium thiosulfate and sodium hydrogen sulfate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Nanjing, China). Sodium hydroxide, potassium hydroxide, triethanolamine (TEA), acetone, hydrochloric acid, acetic acid, cyclohexane and ethyl acetate were obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Deionized water was purified to a conductivity of $18.3 \text{ M}\Omega \cdot \text{cm}$ on a Hitech-Sciencetool Master-Q laboratory water purification system (Shanghai Hetai Reagent Co., Ltd., Shanghai, China). All chemicals were analytical reagents and used without further purification.

2.2 Preparation

2.2.1 Preparation of ECO

ECO was prepared as previously described^[24]. DCO was prepared using castor oil, sodium hydrogen sulfate and TBHQ with mass ratio of 1 : 0.005 : 0.002. The dehydration process was carried out at 230°C under vacuum for 80 min. The product (DCO) was separated by filtration when the solution temperature had cooled to 100°C . DCO (10 g) was then added to a three-necked round-bottomed flask with phosphoric acid (0.05 g) as catalyst. Peracetic acid (10.32 g) was added dropwise into this mixture for 30 min and the reaction was maintained at 30°C for 3 h. The mixture was then neutralized with $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH at room temperature. The product was extracted by ethyl acetate and the organic phase was washed three times with hot distilled water. Finally, ECO was purified by reduced pressure distillation and 9.8 g (98% yield) of ECO product was obtained.

2.2.2 Ring-open polymerization of ECO

Twenty gram ECO was added to a three-necked round-bottomed flask with 20 mL ethyl acetate and the mixture stirred by mechanical agitation at room temperature. A mixture of 0.1 mL SnCl_4 and 5 mL ethyl acetate was then added dropwise into the reactor at room temperature and the reaction was maintained for 15 min. The resulting product (PECO) was washed sequentially with 5% aqueous sodium bicarbonate and deionized water. PECO was dried in the vacuum at 60°C . Finally, about 19 g (95% yield) of solid PECO was obtained.

2.2.3 Hydrolysis of PESO

Five gram PECO was added into a flask with 100 mL of $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution. The reactor was heated to

100°C with agitation for 12 h under condensing conditions. The solution was then separated by filtration and the aqueous solution was removed by reduced pressure distillation. The solid product was washed three times with ethyl acetate to remove glycerin. The solid product was then re-dispersed in deionized water and the solution became turbid when the pH was adjusted to between 6 and 7. The solution was extracted by ethyl acetate and the organic phase was washed three times with hot distilled water. Finally, 4.1 g (82% yield) of HPECO product was obtained by reduced pressure distillation.

2.2.4 Preparation of HPECO-M with different counterions

HPECO with different counterions (HPECO-M, where M = Na⁺, K⁺ or TEA⁺) were prepared using NaOH, KOH and triethanolamine as neutralizing agents. Stock solutions of 0.2% aqueous HPECO-M were prepared according to the following procedure^[25]: 0.5 g of HPECO was weighed into a 50 mL beaker and the required amount of NaOH or KOH solution (to neutralize all carboxylic acid groups) was added into the beaker. Then, the resulting solution was transferred to a 250 mL volumetric flask. The beaker was rinsed three times with deionized water that was added to the volumetric flask before adjusting the volume to 250 mL. The aqueous stock solution of 0.2% HPECO-TEA⁺ was prepared by using a 2 : 1 molar ratio of TEA to carboxylic acid group in HPECO.

2.3 Characterization

2.3.1 Iodine value

The degree of saturation of vegetable oils is expressed as its iodine value. DCO (0.12–0.15 g) was weighed and dissolved in a measured mixture of cyclohexane and acetic acid. A measured amount of Wijs' reagent was added. The solution was allowed to stand in the dark for 1 h. Then, the excess Wijs' reagent was converted to I₂ by addition of KI. The concentration of I₂ was determined by titration with 0.1 mol·L⁻¹ sodium thiosulfate^[26]. A blank experiment was performed at the same time. The iodine value of the DCO sample was tested three times and averaged. The iodine value was calculated by the following equation:

$$W_1 = \frac{12.69 \times (V_1 - V_2)c}{m} \quad (1)$$

where, W_1 (0.01 g·g⁻¹) is the iodine value defined as the number of grams of iodine absorbed by 100 g of vegetable oil, m (g) is the dry weight of the sample, c (mol·L⁻¹) is the exact concentration of standardized sodium thiosulfate solution, V_1 and V_2 (mL) are the volumes of standardized sodium thiosulfate consumed by blank sample and test sample, respectively.

2.3.2 Epoxy value

The epoxy value of ECO was tested by the following procedure^[27]: ECO (about 0.5 g) was weighed into a flask and 20 mL of hydrochloric acid-acetone solution added and swirled until the ECO sample was dissolved. Then, the solution was allowed to stand in the dark for 30 min and titrated with 0.1 mol·L⁻¹ aqueous NaOH solution, using methanolic methyl red as an indicator. The epoxy value of the ECO sample was determined three times and averaged. The epoxy value was calculated by the following equation:

$$X_1 = \frac{(V_1 - V_2)N \times 0.016}{W} \times 100 \quad (2)$$

where, X_1 (%) is the epoxy value of vegetable oils, W (g) is the dry weight of the sample, N (mol·L⁻¹) is the exact concentration of standardized NaOH solution, V_1 and V_2 (mL) are the volumes of standardized NaOH solution consumed by blank sample and test sample, respectively.

2.3.3 Structure characterization

FT-IR spectra which can identify the structure of HPECO were obtained on a spectrometer (Thermo Scientific Nicolet IS10, Waltham, Massachusetts) by the attenuated total reflectance method. The spectra were recorded over the range 4000–650 cm⁻¹ at 4 cm⁻¹ resolution and averaged over 16 scans per sample. ¹H NMR and ¹³C NMR spectra were recorded at 25°C on a spectrometer (Bruker AV400, Rheinstetten, Germany) operating at a frequency of 400.13 and 100.61 MHz, respectively. Deuterated chloroform (CD₃Cl) was used as the solvent.

2.3.4 DSC analysis of PECO and HPECO

DSC measurements of PECO and HPECO were performed by differential scanning calorimetry (Diamond DSC, PerkinElmer Instruments, Shanghai, China) employing 40 mL·min⁻¹ flow of dry nitrogen as a purge gas. Typically about 4 mg of HPECO was accurately weighed in an aluminum pan and sealed with pin-perforated lids. The sample was cooled to -60°C at a rate of 10°C·min⁻¹ and a refrigerated cooling system was used to equilibrate the sample at -60°C for 5 min. Data were recorded while the oven temperature was raised from -60 to 60°C at a rate of 10°C·min⁻¹.

2.3.5 Determination of the molecular weight of PECO and HPECO

GPC was used to measure relative molecular weight and molecular weight distribution of soluble PECO (soluble PECO section in HPLC grade THF) and HPECO. GPC was performed at room temperature using a Malvern Viscotek 3580 System equipped with Viscotek GPC2502

RI detector and a GPC1007 pump (Malvern, England). The columns were T6000M, general mixed org 300 mm \times 7.8 mm (CLM3009). The eluent was HPLC grade THF and the flow rate was 1 mL \cdot min $^{-1}$. Monodispersed polystyrene was used as the standard to generate the calibration curve. Samples were filtered over microfilters with a pore size of 0.2 μ m (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, America).

2.3.6 Surface tension

The surface tension of HPECO-M was measured at 25 $^{\circ}$ C using the Wilhelmy plate T107 (19.44 mm wide, 0.1 mm thick, 65 mm high and 39.08 mm circumference) on the Sigma 701 Automatic Surface Tensiometer (Goteborg, Sweden). The instrument was calibrated against pure water before measurements were made. The concentration of surfactant was increased gradually by dispersing stock solution into the measurement cell. The software automatically determined the surface tension as a function of the bulk concentration. The surface tension data were plotted against the HPECO-M concentration in water in the concentration range from 0.0003 to 2.0 g \cdot L $^{-1}$. Each concentration of aqueous HPECO-M solution was performed automatically by the instrument and tested three times. Before each measurement, the plate was flushed

with water and then heated over an alcohol blast burner for a few seconds to remove contamination. The critical micelle concentration (CMC) and minimum surface tension (γ_{cmc}) of HPECO-M were derived from the inflection point of the curve. All data were obtained using OneAttention software (Biolin Scientific).

2.3.7 Interfacial tension

The interfacial tension of HPECO-M was measured at 25 $^{\circ}$ C using the standard ring ($R = 9.58$ mm and $r = 0.185$ mm) on the Sigma 701 Automatic Surface Tensiometer. Before each measurement, the standard ring was flushed with water and then heated over an alcohol blast burner for a few seconds to remove contamination. The instrument was calibrated with water and then checked by measuring the water-hexadecane interfacial tension with different concentration of HPECO-M in water. Measurements of interfacial tension at each concentration of aqueous HPECO-M in water-hexadecane were performed in triplicate.

3 Results and discussion

Figure 1 outlines a simplified process for the entire

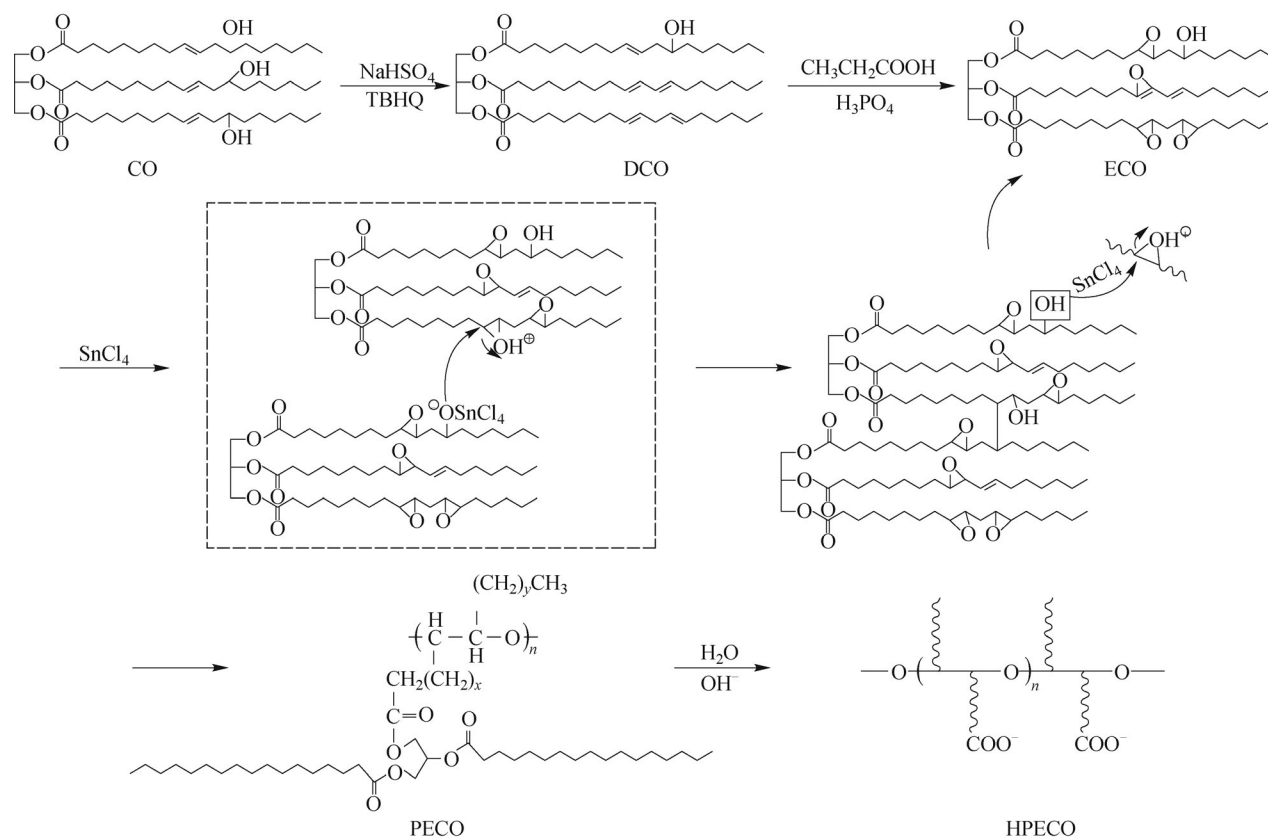


Fig. 1 The synthesis scheme for HPECO

reaction. The iodine value of DCO increased to 140 g per 100 g from 86 g per 100 g for castor oil. The epoxy value of ECO was 5.30%. PECO was prepared via ring-opening polymerization by the SnCl_4 catalyst with the hydroxyl groups in ECO acting as initiators. In addition, the ring-opening polymerization generated new hydroxyl groups that also acted as initiators. The most important factor that determines whether a cyclic monomer can be converted to a polymer is the thermodynamics. Ring-opening polymerization of a 3-membered ring is favored thermodynamically^[23] and temperature is not a significant factor in this reaction. Consequently, the ring-open polymerization reaction was performed at room temperature with short reaction time. Finally, hydrolysis of PECO was performed with a base.

3.1 FT-IR

The infrared spectra of ECO, PECO and HPECO are shown in Fig. 2. The comparison showed that the characteristic oxirane absorption at 946.61 cm^{-1} in ECO was not present in PECO as a result of ring-opening polymerization. The characteristic ester carbonyl absorption, at 1738 and 1736 cm^{-1} respectively, were clearly observed in spectra of ECO and PECO. The spectra of HPECO showed a shift in the ester carbonyl band from 1735.91 to 1707.61 cm^{-1} relative to PECO. This is attributed to strong H-bonding between carboxylic acids forming dimers, which weakened the absorption of $\text{C}=\text{O}$ bond, resulting in an absorption shift to a lower frequency.

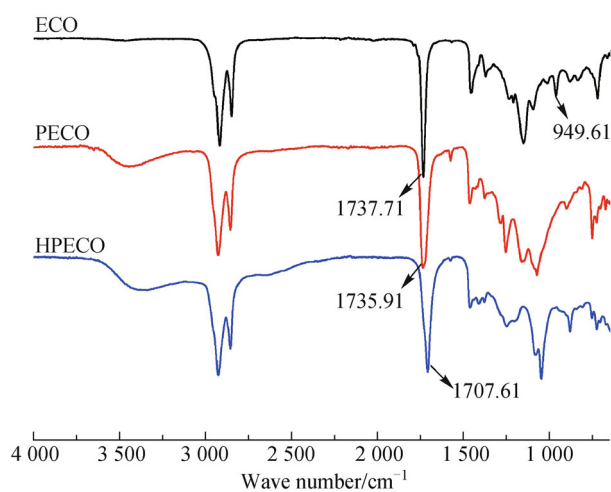


Fig. 2 Comparison of FT-IR spectra

3.2 ^1H NMR and ^{13}C NMR

Figure 3a shows the ^1H NMR spectra of ECO and HPECO. The signals at 5.1–5.4 ppm represented the methine proton ($-\text{CH}_2-\text{CH}-\text{CH}_2-$) of the glycerin backbone and the signals at 4.0–4.4 ppm were from the methylene protons

($-\text{CH}_2-\text{CH}-\text{CH}_2-$) of the glycerin backbone. The oxirane protons of ECO were observed in the 3.0–3.2 ppm region. As evident in Fig. 3a, the peaks at 5.1–5.4 ppm, 4.0–4.4 ppm, and 3.0–3.2 ppm in the ^1H NMR spectra of HPECO disappeared completely. In addition, the signals at 2.2–2.4 ppm corresponded to the methylene protons located beside carboxylic carbon were greatly enhanced because of the ring-open polymerization. Furthermore, the signal at 2.0 ppm of ECO, which was attributed to the methylene protons located beside epoxy groups, was absent in HPECO due to the disappearance of epoxy groups.

Figure 3b shows the ^{13}C NMR spectra of ECO and HPECO. The ^{13}C NMR spectra confirmed that the ring-opening polymerization of ECO and hydrolysis of HPECO had occurred. The peaks at 50–62 ppm in the ^{13}C NMR spectrum of ECO were due to epoxy carbons and had disappeared in the spectrum of HPECO. In addition, the signals at 170–173 ppm in the spectrum of ECO assigned to the ester carbonyl carbon had also disappeared in the spectrum of HPECO. Furthermore, the appearance of the characteristic absorption of carboxylic carbon at 180 ppm, obtained by hydrolysis that converted the ester group into a carboxylic acid, clearly demonstrated that hydrolysis of PECO had been successful. The ^1H NMR and ^{13}C NMR spectroscopy also clearly demonstrated the structure of HPECO and ECO.

3.3 GPC analysis

PECO was partially soluble in HPLC grade THF because of the high cross-linked network structures generated from ring-opening polymerization. The molecular weight of soluble PECO and HPECO were determined by GPC. As shown in Fig. 4, the molecular weight of soluble PECO had a broad distribution compared with HPECO. The number-average (M_n) and weight-average (M_w) molecular weight of soluble PECO and HPECO are given in Table 1. The data show that the insoluble segment of PECO has a higher molecular weight than the soluble PECO. Ring-opening polymerization, both intramolecular and intermolecular, can occur at oxirane groups of ECO. Hydrolysis of PECO led to the cleavage of ester bond, which in turn resulted in the reduction of molecule weight. The polydispersity indices of soluble PECO and HPECO were 2.30 and 1.17, respectively. It indicated that the molecular weight of HPECO had a narrow distribution compared to that of soluble PECO.

3.4 DSC analysis of PECO and HPECO

The glass transition temperatures (T_g) for PECO and HPECO were measured by DSC. As the crosslinking density, which can influence T_g , decreases, the free volume of a material increases, and T_g decreases correspondingly^[12]. Figure 5 showed the DSC curves for PECO and HPECO. The T_g values determined by the temperature at

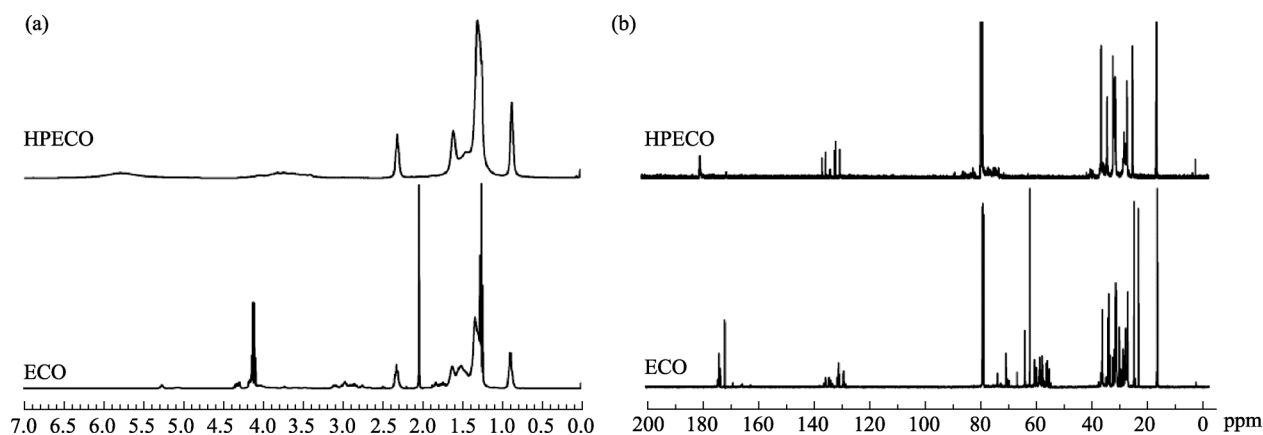


Fig. 3 ^1H NMR (a) and ^{13}C NMR (b) of ECO and HPECO

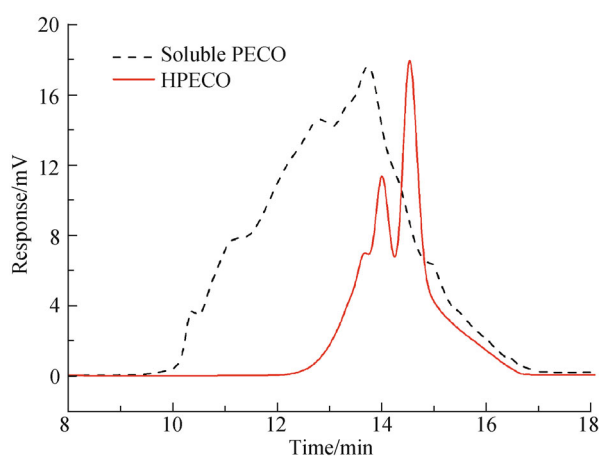


Fig. 4 GPC trace for soluble PECO and HPECO

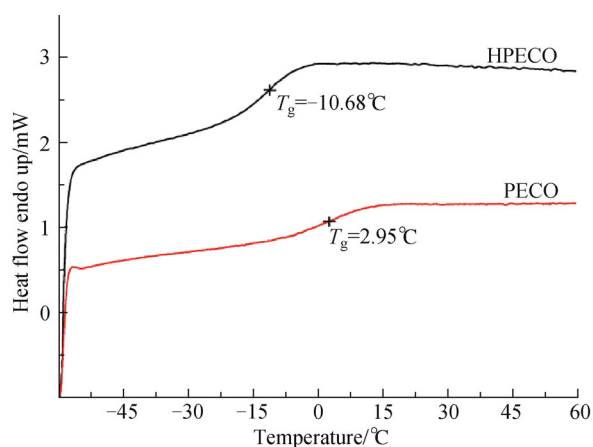


Fig. 5 DSC curves for PECO and HPECO

Table 1 GPC of soluble PECO and HPECO

Samples	$M_n \times 10^5 / (\text{g} \cdot \text{mol}^{-1})$	$M_w \times 10^5 / (\text{g} \cdot \text{mol}^{-1})$	PDI (M_w/M_n)
Soluble PECO	2189	5026	2.30
HPECO	1949	2274	1.17

the inflection point of the curve were 2.95 and -10.68°C for PECO and HPECO, respectively. The lower cross-linking density of HPECO was associated with the lower molecular weight and T_g . According to the GPC analysis, the molecular weight of HPECO was less than PECO, so consequently the T_g of HPECO was also lower.

3.5 Equilibrium surface tension of HPECO-M

It is well known that amphiphilic polymers (such as soaps, polysoaps and surfactants) with a suitable hydrophilic-hydrophobic balance can form amicelle structure when expose to a selective solvent^[28]. The equilibrium surface tension of amphiphilic polymers in water decreases significantly at low concentration. When the concentration is higher, the equilibrium surface tension is reduced slightly. Also, the equilibrium surface tension is almost constant when its concentration is sufficient. Accordingly, the concentration corresponding to the break point in the curve is regarded as the critical micelle concentration (CMC)^[29]. At CMC, amphiphilic molecules spontaneously aggregate and form organized structures such as micelles. The lower the CMC of the amphiphilic polymers, the more effective the amphiphilic polymers are at lowering surface tension of water.

This phenomenon is illustrated in Fig. 6, in which the surface tensions of the HPECO-M were plotted as a function of concentration. As can be seen (Fig. 6), the equilibrium surface tension of each HPECO-M decreased with increasing concentration and then plateaued to an effectively constant level at high concentrations. As shown in Table 2, the minimum equilibrium surface tensions of the aqueous HPESO-M were in a narrow range of 26.5–30.0 $\text{mN} \cdot \text{m}^{-1}$. HPECO-M displayed efficient surface properties compared to hydrolyzed ECO which could decrease the surface tension of water to 35 $\text{mN} \cdot \text{m}^{-1}$. HPECO- Na^+ and HPECO- K^+ displayed similar minimum equilibrium surface tensions of 26.5 and 25.6 $\text{mN} \cdot \text{m}^{-1}$, respectively. The higher minimum equilibrium surface

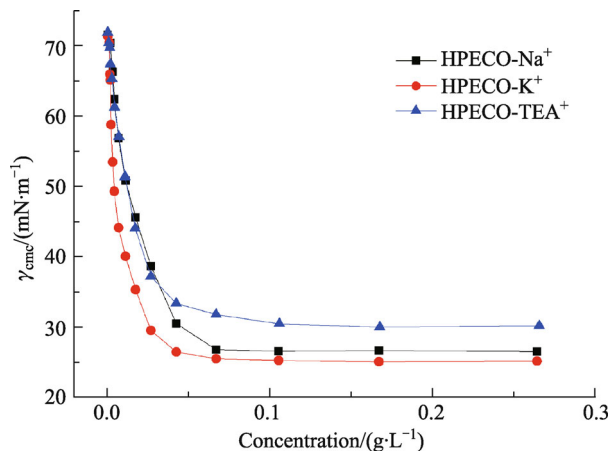


Fig. 6 Effect of HPECO-M concentration on the surface tension of water

Table 2 CMC and γ_{cmc} of HPECO-M

HPECO-M	CMC/(g·L ⁻¹)	γ_{cmc} /(mN·m ⁻¹)
HPECO-Na ⁺	0.066	26.5±0.8
HPECO-K ⁺	0.042	25.6±0.7
HPECO-TEA ⁺	0.098	30.0±1.0

tension of HPECO-TEA⁺ implied that a more polar interface occurred when fully covered by HPECO-TEA⁺ rather than HPECO-Na⁺ or HPECO-K⁺. This might be due to the presence of TEA molecules at the surface, because excess TEA (2 : 1 molar ratio of TEA to carboxylic acid) was used to solubilize HPECO in water^[30].

Comparison of CMC values showed that HPECO-K⁺ provided the greatest surfactant efficiency among the three counterions. The CMC value of HPECO-K⁺ was less than that of HPECO-Na⁺, even though these two counterions displayed similar minimum equilibrium surface tensions. The effectiveness of K⁺ counterion compared with Na⁺ counterion might be a consequence of the sizes of these two ions. The larger K⁺ counterion can reach full surface coverage with fewer molecules than the Na⁺ counterion^[30]. The data in Fig. 6 and Table 2 indicate that both CMC and minimum equilibrium surface tension were affected by the nature of the counterion of the HPECO-M.

3.6 Effect of HPECO-M on water-hexadecane interfacial tension

Equilibrium interfacial tension values were dependent on the concentration of the HPECO-M in the water. The higher the concentration of the HPECO-M in water below CMC, the higher its equilibrium concentration at the water-hexadecane interface and the lower the water-hexadecane interfacial tension obtained. The equilibrium interfacial tension values were obtained by averaging the interfacial tension data from three determinations at each concentration.

The equilibrium interfacial tension values were dependent on the counterion (Fig. 7). As can be seen in Fig. 7, the equilibrium interfacial tension of water-hexadecane decreased with increasing concentration of HPECO-M in water and then plateaued to an effectively constant level at higher concentrations. As shown in Table 3, similar minimum equilibrium interfacial tensions (IT_{min}) were obtained for HPECO-K⁺ and HPECO-Na⁺, 11.2 and 10.4 mN·m⁻¹, respectively. HPECO-K⁺ and HPECO-Na⁺ were more effective in reducing the water-hexadecane equilibrium interfacial tension than HPECO-TEA⁺. This may be due to the effect of counterions on surfactant orientation and adsorption at the liquid-liquid interface. The orientation that favors the association of the surfactant molecules at the interface will result in higher equilibrium concentration at the interface and the particularity of TEA⁺

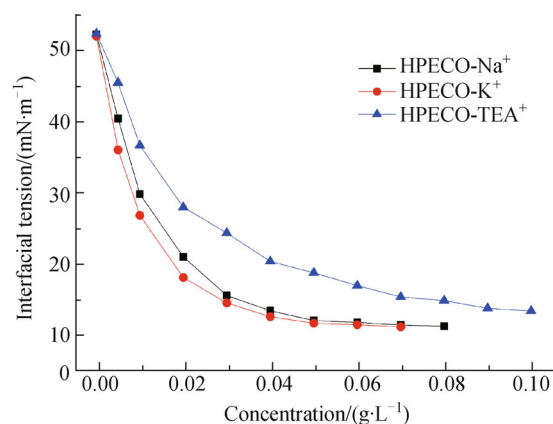


Fig. 7 Effect of HPECO-M concentration on the water-hexadecane interfacial tension

Table 3 Calculated versus measured interfacial tension between HPECO-M surfactant and hexadecane

HPECO-M	γ_{cmc} /(mN·m ⁻¹)	IT_{min} /(mN·m ⁻¹)	Calculated interfacial tension/(mN·m ⁻¹)		
			χ_s^d	GM method	HM method
HPECO-Na ⁺	26.5	11.2±0.5	0.55	15.64	13.83
HPECO-K ⁺	25.6	10.4±0.7	0.55	15.58	13.60
HPECO-TEA ⁺	30.0	13.8±0.6	0.55	16.03	14.79

counterion gives HPECO-TEA⁺ higher interfacial tension. Thus, it appears that more favorable orientations are obtained with K⁺ and Na⁺ counterions than with TEA⁺.

3.7 Surface and interfacial energy

The surface energy of a surfactant, γ_S is the sum of polar (γ_S^p) and dispersive (γ_S^d) components. The simplest method for relating the interfacial tension between two substances by their respective surface energies is the Antonoff method: $\gamma_{SH} = |\gamma_S - \gamma_H|$ ^[31]. This method does not require knowledge of the polar and dispersive surface energy components of materials. The geometric mean (GM) and harmonic mean (HM) methods, which require knowledge of polar and dispersive components, are as follows:

$$\gamma_{SH} = \gamma_S + \gamma_H - \frac{4\gamma_S^d\gamma_H^d}{\gamma_S^d + \gamma_H^d} - \frac{4\gamma_S^p\gamma_H^p}{\gamma_S^p + \gamma_H^p} \quad (3)$$

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(\gamma_H^d\gamma_S^d)^{0.5} - 2(\gamma_H^p\gamma_S^p)^{0.5} \quad (4)$$

where γ_{SH} is the interfacial energy between the two surfaces (surfactant and hexadecane in this paper), γ_S and γ_H are the surface energies of the surfactant and hexadecane, respectively.

Since the surface tension of hexadecane does not comprise a polar component^[32], γ_H^p in Eq. 3 and Eq. 4 is zero. Further simplification of Eq. 3 and Eq. 4 is achieved by replacing γ_H^d with γ_H , and defining γ_S^d as follows: $\gamma_S^d = \chi_S^d\gamma_S$. The χ_S^d value of water-saturated hydrocarbon system is approximately 0.55^[33]. Hence, the simplified GM and HM equations for the surfactant-hexadecane system are as follows:

$$\gamma_{SH} = \gamma_S + \gamma_H - \frac{4\chi_S^d\gamma_S\gamma_H}{\chi_S^d\gamma_S + \gamma_H} \quad (5)$$

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(\chi_S^d\gamma_H\gamma_S)^{0.5} \quad (6)$$

Equations 5 and 6 were used to calculate the hexadecane-water interfacial tension and the calculated values were then compared with the measured values (IT_{\min}). The reported surface tension of hexadecane is about 27.0 mN·m⁻¹^[34]. The γ_{cmc} values given in Table 2 correspond to the surface energies of the HPECO-M surfactants. Table 3 presents a summary of the water-hexadecane interfacial tension calculated using GM and HM methods. The results show that the HM methods predicted slightly higher interfacial energy than the GM method and are close to the IT_{\min} .

4 Conclusions

In summary, ECO was synthesized using castor oil as raw

material through dehydration and epoxidation. Ring-opening polymerization of ECO was performed with SnCl₄ as catalyst and the hydroxyl groups in ECO acting as initiators. Hydrolysis of PECO was performed with NaOH. HPECO-M with different counterions was prepared using NaOH, KOH and TEA. The DSC results indicated that PECO and HPECO could undergo glass transition at T_g . M_w of soluble PECO and HPECO were 5026 and 2274 g·mol⁻¹, respectively. The CMC and γ_{cmc} of HPECO-M were dependent on the counterion and increased in the order, K⁺, Na⁺ and TEA⁺. Water-hexadecane interfacial energy was also calculated using Antonoff, HM and GM methods. IT_{\min} of water-hexadecane interfacial tension were consistent with calculated values using the HM and GM.

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Compliance with ethics guidelines Xujuan Huang, He Liu, Shibin Shang, Zhaosheng Cai, Jie Song, and Zhanqian Song declare that they have no conflict of interest or financial conflicts to disclose.

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