Preparation and Properties of Dimeric Fatty Acid/Polyethylene Glycol Polyester Terminated with Rosin Acid

FENG Guang-zhu

FENG Guang-zhu[1,3], CUI Ying-de[2*], LU Kui[3,1], QU Hai[3], LI He-ping[3]

(1. School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China; 2. Zhongkai University of Agriculture and Technology, Guangzhou 510225, China; 3. School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, China)

Abstract: A new kind of non-ionic polymeric surfactant, the dimeric fatty acid (DFA)/polyethylene glycol (PEG) polyester terminated with rosin acid, was prepared with rosin acid and a polyester which was synthesized from DFA and PEG 400, and its surface activities were studied. The optimum reaction conditions of esterification were as follows: molar ratio of DFA /PEG 400 1 : 1.20, stannous chloride as the preferable catalyst at amount 0.30 % of DFA, reaction temperature 200 ℃, reaction time 6 h, the conversion can reach 98.11 %. Number-average molecular weight (M_n) of the product is 6 135. Weight-average molecular weight (M_w) of the product is 7 438. The coefficient of distribution of molecular weight (M_w/M_n) is 1.212, which indicates a narrow distribution of molecular weight. Orthogonal experiment results of rosin acid terminated reaction of dimeric fatty acid polyethylene glycol polyester showed that optimum reaction conditions were as follows: molar ratio of materials n(DFA/PEG polyester) : n(rosin acid) 1 : 1.30, dosage of catalyst $SnCl_2$ 0.20 % of polyester, reaction temperature 215 ℃. After 2.8 h, termination ratio of the end hydroxyl groups of polyester reached 62.75 %. Rosin acid terminated DFA/PEG polyester surfactant has excellent emulsification properties, emulsification stability, power to disperse calcium soap as well as performances of defoaming and inhibiting foaming.

Key words: rosin acid terminated dimeric fatty acid/polyethylene glycol polyester; dimeric fatty acid; rosin acid; non-ionic polymeric surfactant

CLC number: TQ351.471 **Document code**: A **Article ID**: 0253 - 2417(2006)02 - 0007 - 06

松香酸封端的二聚脂肪酸/聚乙二醇聚酯的合成及性能表征

冯光炷[1,3], 崔英德[2], 卢 奎[3,1], 渠 海[3], 李和平[3]

(1. 西北工业大学 材料学院, 陕西 西安 710072; 2. 仲恺农业技术学院, 广东 广州 510225; 3. 河南工业大学 化学化工学院, 河南 郑州 450052)

摘 要: 以妥尔油脂肪酸二聚酸为原料,先与聚乙二醇 (PEG 400) 缩聚后得到聚酯,然后再用松香对聚酯封端,制备了松香基聚酯醚型非离子高分子表面活性剂,并对其性能进行了研究。聚酯适宜的制备工艺条件:减压条件下,反应物二聚酸与聚乙二醇的摩尔比为 1 : 1.20,催化剂 $SnCl_2$ 用量为二聚酸质量的 0.30 %,反应温度 200 ℃,反应时间 6 h,酯化率达到 98.11 %。产物的数均相对分子质量(M_n) 6 135,重均相对分子质量(M_w) 7 438,相对分子质量分布系数(M_w/M_n)为1.212且呈好的窄分布状态。正交试验优化后的松香封端反应的条件为:再补加聚酯质量 0.20 % 的催化剂 $SnCl_2$,聚酯与松香物质的量之比为 1 : 1.30,反应温度 215 ℃,反应时间 2.8 h,封端率达 62.75 %。红外光谱验证了目标产物的存在。性能研究表明,产物具有很好的钙皂分散力、消泡和抑泡力、乳化性和乳化稳定性。

关键词: 松香酸封端的二聚脂肪酸/聚乙二醇聚酯; 二聚脂肪酸; 松香酸; 非离子型高分子表面活性剂

Received date: 2005 - 10 - 26

Foundation item: 河南省自然科学基金资助课题(0511021000)

Biography: 冯光炷(1961 -),男,河南光山人,教授,主要从事功能高分子材料和表面活性剂的合成与应用研究;
E-mail: fgzhu@371.net

* **Correspondence Auther**: 崔英德,教授,博士生导师,主要从事功能高分子材料的研究。

Dimeric fatty acid (DFA) was synthesized usually from tall oil fatty acid which has two active carboxyls and long-chain alkyl radical, and its chemical property is similar to fatty acid. Because of its excellent reaction activity, DFA has been widely used as intermediate in the synthesis of a variety of organic compounds. DFA and its derivatives are safe, nontoxic and uninflammable materials, showing many specific physical and chemical properties. Thus they have been widely applied in many fields such as surfactant, paints and coatings, adhesives, lubricants, solidified fuel. Rosin is a kind of natural resin with high economic value. As an important chemical raw material, it was also widely used in surfactant, paper-making, adhesive, paint, printing ink, rubber, food and other industries. A serial of surfactants, which is similar to natural fatty acid in structure, can be synthesized by DFA and rosin acid as reactants. These surfactants have excellent application performance to benefit human being and ecotype[1].

Polymeric surfactant has many excellent application performances, such as emulsification, lime-soap dispersion, solubility enhancement, and so on. These good performances were related to the structure and molecular weight of polymeric surfactant[2-4]. Generally, molecular weight of the DFA/PEG 400 polyester was controlled by adjusting the molar ratio of DFA and PEG 400. The molecular weight became larger when molar ratio is closer to 1, but the hydrophilic property of polyester is worse[3-5].

In this study, controlling molar ratio of reactants, a new kind of polyester with appropriate molecular weight, was synthesized by condensation polymerization using DFA and PEG 400 as raw materials, then using rosin acid to terminate the end-hydroxyls of this polyester in order to adjust the hydrophilic-lipophilic balance (HLB) of non-ionic polymeric surfactant. This polymeric surfactant has rigid, space sterically hindered lipophilic groups and hydrophilic polyether chains, therefore this polyester shows composite performance of aliphatic alcohol surfactant and polyether surfactant, and has good performance in emulsification and emulsion stability, power to disperse calcium soap, defoaming foam and inhibiting foaming, wetting power and solubility enhancement. It could be used in daily chemical industry, food industry, pesticide industry, metal-processing, etc. It is a non-ionic polymeric surfactant which is low noxious to human being, with good biodegradability and environment affinity.

1 Materials and methods

1.1 Materials

DFA was purchased from Zhejiang Yongzai Chemical Industry Corporation. PEG 400 was purchased from Tianjin Bodi Chemical Industry Company. Rosin acid was purchased from Guangxi Wuzhou Pine Chemicals Ltd. Other chemicals are of analytical grade, and they were used without further purification.

1.2 Analysis[6]

Acid value (AV) was determined according to GB 12008.5 – 1989; Hydroxyl value (HV) was determined according to GB 12008.3 – 1989; Molecular weight of polyester was determined by GPC, using a laser light-scattering mass detector (LC10A-Waters 510, DAWNEOS), and the conditions are as follows: chromatographic column, SHIM 800p, mobile phase THF, flow rate 0.5 mL/min; Shimadzu Prestige 21 FT-IR was employed for IR studies.

1.3 Calculations

$$ER = (AV_0 - AV)/AV_0 \times 100\ \% \qquad TR = (HV_0 - HV)/HV_0 \times 100\ \%$$

1.4 Determination of surface activity

Surface tension and critical micelle concentration (CMC) were measured by TX-550A (Bowing Interna-

tional Company). The performances of defoaming and inhibiting foaming ER—esterification ratio, AV_0—initial acid value, TR—termination ratio, HV_0—initial hydroxyl value, emulsifying power, power to disperse calcium soap were measured according to literature[6]. The system of water/soybean oil was used to measure emulsifying efficiency.

2 Experimental

2.1 Synthesis of DFA/PEG polyester[7-8]

Put PEG into a 100 mL flask and heated in an oil bath at 110 ℃ for 0.5 h, to remove water absorbed by PEG. Fixed quantities of DFA and PEG 400 were put into a 100 mL flask, added suitable amount of catalyst. Mixed enough, put flask in an oil bath. Kept mixture reacting under stirring for definite time at 0.097 MPa to obtain the product.

Purification of polyesters: 3 g product was dissolved in 30 mL acetic ester, using 30 mL salt water to extract water-solubles. Then removed acetic ester in water bath at 85 ℃, and put product into vacuum drying oven (65 ℃, 0.097 MPa) and vaporized solvent to obtain purification product.

2.2 Preparation of rosin acid terminated DFA/PEG polyester

Rough rosin should be refined. Rough rosin (25 g) and 10 mL hydrochloric acid were added into 100 mL ethanol, refluxed about 0.5 h at 85 ℃, then stewed 4 h at −5 ℃. The light-yellow solid product was obtained after filtering, having acid value 165.17 mg/g.

Weighed fixed quantities of polyester and rosin acid, put them into 100 mL flask. Controlled the reaction time, amount of catalyst and molar ratio of the reactants, keeping them in an oil bath and reacting under definite temperature for definite time, then the yellow viscous liquid was obtained[2].

3 Results and discussions

3.1 Synthesis conditions of DFA/PEG polyester

Main influencing factors are the kinds and amount of catalysts, reaction time, reaction temperature and ratio of reactants. The effects of these factors on synthesis of polyester were studied.

3.1.1 Influence of the kind of catalysts The catalysis effect of different catalysts were shown in Table 1, at temperature of reaction 180 ℃, molar ratio of reactants 1 ∶ 1.20, and reaction time 4 h.

Table 1 Effects of different catalysts on esterification conversion

catalysts	amount/%	esterification conversion/%	color
none	0	63.71	fawn
concentrated sulfuric acid	0.3	94.02	jet black
toluene-*p*-sulfonic acid	0.3	94.38	carmine
$SnCl_2$	0.3	93.85	fawn

It can be showed from Table 1 that using stannous chloride as catalyst, the conversion ratio of product is not the highest, but the color of product is fawn and the lightest. DFA has double bond which is easy to be oxidized at high temperature. Stannous chloride is a kind of antioxidant which can reduce the incidence rate of secondary reaction and increase the ratio of esterification effectively. Meanwhile, stannous chloride is a kind of acid-catalyst, which can increase the concentration of hydrogen ion in reaction system, so the speed of whole reaction can be increased effectively. Thus choosing stannous chloride as catalyst is suitable.

3.1.2 Influence of amount of catalyst The conditions of experiment are: temperature 180 ℃, molar ratio of reactants 1 ∶ 1.20, reaction time 4 h. By analyzing acid value of sample at different times, and calculate the degree of reaction. The influence of catalysts amount was showed in Table 2.

It can be showed in Table 2, when the amount of catalysts is added to 0.25 %–0.30 %, esterification

ratio is over 90 %. When amount of catalysts is added further, esterification ratio also reaches more than 90 %, but the transparency of product decreases. So the amount of catalyst is 0.30 %.

3.1.3 Influence of ratio of reactants Under the conditions of: amount of catalyst 0.30 %, temperature 200 ℃, reaction time 4 h, the influence of the ratio of reactants was studied. If PEG was excessive, the end group of polyester is mainly hydroxyls.

As shown in Table 2, when molar ratio of reactants is 1∶1.20, esterification ratio can reach 96 %. Continuous increase of PEG amount influenced the molecular weight of product, so suitable ratio of reactants is 1∶1.20.

3.1.4 Influence of reaction temperature Increasing temperature can increase the reaction velocity and enhance the rate of conversion. Under the conditions of: amount of catalyst 0.30 %, molar ratio of reactants 1∶1.20, reaction time 4 h, the influence of reaction temperature can be seen from Table 2.

It can be seen from the result that esterification ratio increases with increased reaction temperature. However, reactants would be decomposed at higher temperature. At reaction temperature above 200 ℃, the color of product would darken obviously, the possible reason is cross-linking or degradation of reactants or product. So the suitable reaction temperature is 200 ℃.

3.1.5 Influence of reaction time According to reaction kinetics theory, esterification ratio can be enhanced by increasing reaction time. However, during extended reaction time, secondary reaction, such as degradation, can occur, which may influence the performance of product. Under the conditions of: molar ratio of reactants 1∶1.20, reaction temperature 200 ℃, amount of catalyst 0.30 %, it can be seen from Table 2, the reaction rate is high at the beginning of reaction, but after 6 h, the reactio n rate becomes slow, so the suitable reaction time of esterification is 6 h.

Table 2 Effects of reaction conditions on esterification conversion

reaction conditions		esterification conversion/%
catalyst amount/%	0.20	80.62
	0.25	89.24
	0.30	90.11
	0.35	84.39
	0.40	82.85
	0.50	83.46
	0.70	85.38
	1.00	91.09
reaction temp./℃	160	62.40
	170	83.31
	180	93.48
	190	95.67
	200	96.02
	210	96.02
	220	96.03
n(DFA)∶n(PEG)	1∶1.00	91.39
	1∶1.10	93.11
	1∶1.20	96.38
	1∶1.30	97.21
	1∶1.40	96.96
	1∶1.50	96.63
reaction time/h	2	78.60
	4	94.40
	6	98.11
	8	98.70
	10	98.70

3.2 Synthesis of rosin-terminated DFA/PEG polyester

According to esterification mechanism and some preparatory experiments, factors which affect termination ratio are mainly reaction temperature, amount of catalysis, ratio of reactants and reaction time. These factors have been studied respectively.

3.2.1 Effect of reaction temperature on termination ratio Under conditions of: molar ratio of reactants 1∶1.50, amount of catalysis 0.20 %, reaction time 3 h, the results of reaction at different temperatures are showed in Table 3.

From Table 3, when reaction time is 3 h, the terminated ratio increases with the rising of reaction temperature, and reaches the maximum at 220 ℃. When temperature is over 220 ℃, termination ratio would decrease, secondary reaction would increase and the product would darken. So the appropriate temperature of 220 ℃ was used in following experiments.

3.2.2 Effects of ratio of reactants on termination ratio　Temperature 220 ℃, amount of catalysis 0.20 %, reaction time 3 h, the effect of ratio of reactants on esterification conversion of end-hydroxyl is showed in Table 3.

It is obvious from Table 3 that termination ratio increases with the amount of rosin increasing. When molar ratio of reactants is 1 ∶ 1.30, termination ratio reaches the maximum 60.53 %, therefore molar ratio of reactants 1 ∶ 1.30 was used for the following experiments.

3.2.3 Effect of amount of catalysis on termination ratio　Under the conditions of: temperature 220 ℃, molar ratio of reactants 1 ∶ 1.30, reaction time 3 h, the results of reaction at different amounts of catalysis are showed in Table 3.

From Table 3, the effect of amount of catalysis on the termination ratio is small and unconspicuous, this is because DFA/PEG polyester included about 0.30 % of catalyst $SnCl_2$. When 0.20 % catalyst $SnCl_2$ (0.20 % of DFA/PEG polyester amount) is added to reaction system, termination ratio reaches 60.65 %, so the amount of catalysis 0.20 % was used in the following experiments.

3.2.4 Effect of reaction time on termination ratio　Under the conditions of: temperature 220 ℃, molar ratio of reactants 1 ∶ 1.30, amount of catalysis 0.20 %, the results of reaction at different times are showed in Table 3.

It is obvious from Table 3 that termination ratio reaches the maximum (60.56 %) when reaction time is 3 h. If the time is longer, the ratio of terminated end-hydroxyl decreases since secondary reactions increase.

Table 3　Effects of reaction conditions on termination ratio

reaction conditions		termination ratio/%
reaction temp./℃	190	28.92
	200	40.00
	210	55.30
	220	60.69
	230	42.64
	240	37.20
n(DEA/PEF polyester) ∶ *n*(rosin acid)	1 ∶ 1.10	33.38
	1 ∶ 1.20	46.84
	1 ∶ 1.30	60.53
	1 ∶ 1.40	60.60
	1 ∶ 1.50	60.60
	1 ∶ 1.10	33.38
catalysis amount/%	0	49.05
	0.10	38.42
	0.20	60.65
	0.30	59.10
	0.40	59.10
reaction time/h	1	23.57
	2	51.24
	3	60.53
	4	41.50
	5	31.10

3.2.5 Optimum of reaction conditions　Orthogonal experiment, of four factors and three levels, was designed in order to optimize the reaction conditions. The factors are respectively ratio of reactants, reaction temperature, reaction time and amount of catalyst. Optimum reaction conditions were as follows: molar ratio of materials *n*(DFA/PEG polyester) ∶ *n*(rosin acid) 1 ∶ 1.30, amount of catalyst $SnCl_2$ 0.20 % of polyester, reaction temperature 215 ℃, reaction time 2.8 h. According to optimum reaction conditions, termination ratio of the end hydroxyl group is 62.75 %.

3.3 Analysis of product

3.3.1 Infrared spectrum analysis of product　From infrared spectrum it can be seen that 1740 cm^{-1} is the characteristic absorption peak of product, which is the stretching vibration of C═O; the absorption peak at 1100 cm^{-1} is the stretching vibration of C—O. These informations show that the product contains ester bond. The vibration of —OH at 3500 cm^{-1} is smaller than polyethylene glycol, namely the end hydroxyl is decreased, namely the product has been ended by rosin acid.

Table 4　Molecular weight distribution of DFA/PEG 400 polyester

samples	M_n	M_W	M_W/M_n
polyester	6088	7798	1.281
refined polyester	6135	7438	1.212

3.3.2 Analysis of molecular weight of product　Polyester and refined polyester were analyzed by GPC, the result is showed in Table 4. It is known that molecular weight of refined polyesters is increasing, showing that soluble substances have already been removed. The narrow distribution of molecular weight indicates the improved effect of refined polyester.

3.3.3 Analysis of surface activities The result of measurements of surface activities is showed in Table 5. Interfacial force and CMC of rosin terminated DFA/PEG polyester are lower. It has excellent emulsification and emulsification stability, power to disperse calcium soap, performance of defoaming and inhibiting foaming.

Table 5 Surface activities of rosin acid terminated DFA/PEG polyester

items	γ_{cmc} /(1×10^{-4} N·m^{-1})	CMC /(mmol·L^{-1})	defoaming foam /mm	inhibiting foaming /s	power to disperse calcium soap/%	emulsification power (soybean oil)/min	emulsion stability /h
product	30.21	1.07	20.0	160	9.6	25.0	9
K_{12}	38.19	8.24	186.0	3			
OP-10						24.0	8

4 Conclusion

4.1 The optimum esterification conditions for DFA/PEG polyester are as follows: molar ratio of DFA /PEG 400 1∶1.20, amount of catalyst stannous chloride 0.30 %, reaction temperature 200 ℃, reaction time 6 h, esterification ratio can reach 98.11 %. Number-average molecular weight (M_n) of the product is 6 135, the coefficient of distribution is 1.212, showing a narrow distribution of molecular weight.

4.2 The suitable synthesis conditions for rosin acid terminated polyester surfactant are as follows: 0.20 % catalyst, molar ratio of polyester/rosin 1∶1.30, reaction temperature 215 ℃, reaction time 2.8 h, termination ratio can reach 62.75 %.

4.3 A new kind of non-ionic polymeric surfactant, rosin acid terminated DFA/PEG polyester was prepared. The product is a dark yellow viscous oleo liquid, and its interfacial force and CMC are low. It has excellent emulsification property and emulsification stability; excellent power to disperse calcium soap; excellent performance of defoaming foam and inhibiting foaming; and it has poor foaming property.

References:

[1]周永红, 宋湛谦. 松香的精细化工利用(Ⅳ)——松香类表面活性剂的合成与应用[J]. 林产化工通讯, 2003, 37(1): 28-32.

[2]周永红, 宋湛谦, 许玉芝,等. 松香季戊四醇酯聚氧乙烯醚的表面活性研究[J]. 林产化学与工业, 2004, 24(增刊): 61-64.

[3]金 勇, 董 阳, 魏德卿. 高分子表面活性剂的合成[J]. 化学进展, 2005, 17(1): 151-156.

[4]王学川, 赵军宁. 高分子表面活性剂的合成及其应用进展[J]. 皮革科学与工程, 2004, 14(6): 24-30.

[5]江 龙. 胶体化学概论[M]. 北京: 科学出版社, 2002:132.

[6]毛培坤. 表面活性剂产品工业分析[M]. 北京: 化学工业出版社, 2003:396-474.

[7]O'LENICK Jr, ANTHOINY J. Capped dimer polyesters in personal care applications: US, 6800275[P]. 2004-10-05.

[8]GUO WEN-XUN, HUANG KAI-XUN. Preparation and properties of poly (dimer acid-dodecanedioic acid) copolymer and poly (dimer acid-tetradecanedioic acid) copolymer[J]. Polymer Degradation and Stability, 2004, 84: 375-381.