



Effects of the addition of dimer acid alkyl esters on the properties of ethyl cellulose



Sangjun Lee^{a,b}, Kwang-Hwan Ko^c, Jihoon Shin^a, Nam-Kyun Kim^a, Young-Wun Kim^{a,b,*}, Joon-Seop Kim^{c,*}

^a White Biotechnology Research Group, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon 305-600, South Korea

^b Department of Green Chemistry and Environmental Biotechnology, Korea University of Science & Technology, 113 Gwahak-ro, Yuseong-gu, Daejeon 305-600, South Korea

^c Department of Polymer Science & Engineering, Chosun University, 309 Pilmun-daero, Dong-gu, Gwangju 501-759, South Korea

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ABSTRACT

In this study, we synthesized dimer acid (DA) esters, having short to long alkyl chains, (DA- C_n) by the Diels–Alder reaction and subsequent esterification reaction of fatty acids that were prepared by the hydrolysis of waste vegetable oil. It was found that the DA- C_n were thermally more stable than common petroleum-based plasticizer DOP. When the DOP, DA, or DA- C_n with short alkyl chains were added to ethyl cellulose (EC), the optical clarity and SEM images of the samples showed their good miscibility with those additives in a micro-scale. It was also found that the rubbery modulus of the EC decreased with increasing amount of additives; the type of the additives did not affect the rates of the decrease in the rubbery modulus. The main transition temperatures of the EC containing either DA or DA- C_1 or DA- C_4 decreased with increasing amounts of those additives and were comparable to that of the DOP-containing EC. The above findings suggested that the DA and its esters with short alkyl chains could act as effective plasticizer and, thus, could be used instead of the DOP. In addition, the results obtained from tensile testing and leaching experiments implied that the DA might be better plasticizer than the DA- C_1 and DA- C_4 , at least in some cases, because of hydrogen-bonding with the EC.

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1. Introduction

In the 20th century, petroleum-based materials had become main row materials and chemicals in the field of material science and technology; however, eventually, they were recognized as a major cause of carbon dioxide emissions that is, now, widely blamed for global warming (Rem, Olsen, Welink, & Fraunholz, 2009; Halden, 2010). In addition, the upsurge in oil prices due to the depletion of oil resources has also led us to the reduction of the use of petroleum-based fuel. Thus, many researchers continue and spur the development of materials from bio-based resources instead of petrochemical resources. Most of these eco-friendly bio-based materials made from renewable resources are bio-plastics and have

the merits of solving the oil depletion problems and environmental pollution problems caused by plastics waste (Qin & Wang, 2010; Chen & Patel, 2012). The typical examples of the bio-plastics are poly(lactic acid) and poly(hydroxyalkanoate). However, the bio-plastics have the drawbacks of very high unit costs of production and deteriorating physical properties such as poor heat resistance (Lunt, 1998; Luckachan & Pillai, 2011). To overcome these shortcomings, many researchers have been actively studying composite materials that consist of relatively cheap, abundant and renewable natural polymers (e.g. cellulose, starch, chitosan, etc.) and inorganic filler.

Ethyl cellulose (EC) is one of cellulose derivatives, some of the hydroxyl groups of the glucose units of cellulose are converted into ethyl ether groups, and shows excellent mechanical properties, stability, and biocompatibility (Rekhi & Jambhekar, 1995; Gupta & Sahoo, 2001). However, the hydrogen bonds between the hydroxyl groups of the repeating units make the processing of the EC difficult, which limits its applications (Bodmeier & Paeratakul, 1994). In plastics industry, phthalate plasticizers (e.g. di(2-ethylhexyl)phthalate (DOP) and diisodecyl phthalate) have been applied to weaken the intermolecular interactions and enhance the mobility of polymer

* Corresponding authors at: White Biotechnology Research Group, Korea Research Institute of Chemical Technology, 141 Gajeong-ro, Yuseong-gu, Daejeon 305-600, South Korea and Department of Polymer Science & Engineering, Chosun University, 309 Pilmun-daero, Dong-gu, Gwangju 501-759, South Korea.

Tel.: +82 42 860 7605/+82 62 230 7211; fax: +82 42 860 7669/+82 62 232 2474.

E-mail addresses: ywkim@kRICT.re.kr (Y.-W. Kim), joon@chosun.ac.kr (J.-S. Kim).

chains, which leads to the easier processing of brittle polymer such as EC (Rahman & Brazel, 2004). Recently, however, it has been reported that some of the phthalates are endocrine disruptors and toxic. In addition, sometimes external plasticizers leach out of plastics in a certain period of time. Thus, in some countries the use of some of phthalates as external plasticizers has been strictly restricted for use in medical plastics, toys for children and child care items (Peña, Hidalgo, & Mijangos, 2000; Krauskopf, 2003), which urges the development of eco-friendly plasticizer (Labrecque, Kumar, Davé, Gross, & McCarthy, 1997). In this case, the eco-friendly plasticizer should meet the strict requirements in terms of better biocompatibility, biodegradability, and renewability, compared to petroleum-based plasticizer (Rahman & Brazel, 2004).

Dimer acid (DA), a yellow viscous liquid at room temperature, is renewable materials that can be synthesized by dimerization of fatty acids obtained from vegetable oils. The DA has non-crystallinity, high molecular weights and more than two reactive functional groups, and thus, the useful applications of the DA have been as oil additives, lubricants, and materials used in the preparation of resins, hot-melt adhesives, surfactants, inks or coatings (Fan, Deng, Waterhouse, & Pfromm, 1998). Furthermore, bio-based and non-toxic properties of DA allow its usage as eco-friendly materials. Thus, in the present work, we attempted to study DA and its ester forms that can be used as the eco-friendly plasticizer for the EC. Thus, we synthesized DA, using waste soybean oil as a raw material, and dimer acid derivatives, i.e. dimer acid alkyl ester (DA-C_n, here *n* = the number of carbon atoms of alkyl group), and characterized them, and prepared the EC materials containing DA or DA-C_n. Then, the thermal and mechanical properties and leachability of the EC materials were investigated.

2. Experimental

2.1. Materials

The reagents such as ethyl cellulose, di(2-ethylhexyl)phthalate (99%), methanol (anhydrous, >99.8%), 1-butanol (anhydrous, 99.8%), 2-ethylhexan-1-ol (>99%), and *p*-toluenesulfonic acid monohydrate (>99%) were purchased from Sigma-Aldrich. Isotridecanol (>99%) was purchased from Sasol. Toluene (HPLC grade) and chloroform (HPLC grade) were obtained from Samchun. The reagents and solvents were used without further purification. The number-average molecular weight (*M_n* = 20,000) and molecular weight distribution (MWD = 2.22) of ethyl cellulose (viscosity 4 cP, 5% in toluene/ethanol 8/2 (v/v)) were determined at 35 °C using an Agilent 1260 LC system with one PLgel guard column (5 μm, 50 × 7.5 mm) and three PLgel Mixed-C columns (5 μm, 300 × 7.5 mm) connected in series with CHCl₃ as the solvent (flow rate of the eluent = 1 mL/min). Shodex SM-105 polystyrene standards were used for alibration of the columns. The degree of substitution (DS) of EC sample (2.45–2.57) was calculated using the ethoxyl labeling (48–49.5%) given by the manufacturer as follows:

$$DS = \frac{(\text{ethoxyl content} \times (246.3 - 29.1 \times 3))}{(45.1 - \text{ethoxyl content} \times 29.1)} \quad (1)$$

here 246.3 = molecular weight (*M_w*) of fully substituted ethyl cellulose unit, 45.1 = *M_w* of ethoxyl group, 29.1 = *M_w* of ethyl group.

2.2. Characterization methods

The ¹H- and ¹³C-nuclear magnetic resonance (NMR) spectra of the compounds dissolved in CDCl₃ were obtained using a Bruker DPX-300 spectrometer (300 MHz and 75 MHz, respectively). Tetramethylsilane was used as the internal standard. The Fourier transform infrared (FT-IR) transmittance spectra of the compounds were acquired in the range of 4000 to 550 cm⁻¹ using a

Bio-RAD FTS165 spectrometer. For the gas chromatography–mass spectrometry (GC/MS) study to determine the composition of fatty acids (FAs), an Agilent Technologies 7890 A GC/MS instrument, equipped with electron ionization and HP-1 capillary GC column (30 m (length) × 0.25 mm (inner diameter)) was used. A temperature range was 50–320 °C, a heating rate was 10 °C/min, a split ratio was 1:50, and injector and detector temperatures were ca. 250 and 300 °C, respectively. The molar mass and composition of FAs were also determined using size exclusion chromatograph at 40 °C using three Styragel columns (i.e. two HR 0.5 (7.8 × 300 mm) columns and one HR 1.0 (7.8 × 300 mm) column) connected in a series, with tetrahydrofuran as the solvent. Six of polyglycerol fatty acid ester standards (molecular weight = 280, 360, 620, 880, 1200, and 1500) were used for the calibration of the columns. The high-performance liquid chromatography (Waters HPLC system) for the quantitative analysis of the DA and DA-C_n derivatives were also carried out. The total acid number (TAN) of the compounds was determined by a base titration technique (ASTM D664) using a Metrohm 888 Titrando titrator.

2.3. Synthesis of DA-C_n

As shown in Scheme 1, dimer acid (DA) (85%) containing a small amount of trimer acid (TA) (15%) were synthesized by the hydrolysis and subsequent Diels–Alder reaction of fatty acids (FAs). Then, DA and TA ester derivatives were prepared by the esterification between corresponding the DA and TA, respectively, and proper alcohols.

2.3.1. Preparation of DA

FAs were prepared by the hydrolysis of waste soybean oil at 180–200 °C. The chemical composition of the FAs analyzed by GC/MS is C16:0 (4.7%), C16:1 (0.8%), C18:0 (0.7%), C18:1c (37.0%), C18:2c (50.4%), C18:3 (6.2%), others (balance); here, the number right next to capital “C” indicates the number of carbon atoms of the molecule, and the number right next to colon indicates the number of double bonds of the molecule, and “c” indicates *cis* isomer form. The preparation method, modified from the work by Paschke, Peterson, and Wheeler (1964) and Wheeler and White (Wheeler & White, 1967), is described briefly here. For the preparation of the DA, the FAs (30 g), clay catalyst (2.4 g, 8 wt%), H₃PO₄ (0.026 g, 0.085 wt%), and deionized water (0.6 g, 2 wt%) were put in a high-pressure stainless-steel reactor equipped with a mechanical stirrer, a cooling water jacket, and a temperature controller. The reactor was sealed, evacuated for 30 min, and backfilled with N₂ four times to remove O₂ completely. The mixture in the reactor was heated to 250 °C and stirred for 12 h, and, then, cooled to room temperature and neutralized with H₃PO₄. After that, the mixture was heated again to 80 °C and stirred for 1 h. The mixture was cooled to room temperature and filtered to remove salts. The unreacted FAs in the filtrate were removed by vacuum distillation to obtain a product (27 g, yield = ca. 90%). HPLC analysis revealed that the product was composed of ca. 85 wt% of dimer acid and ca. 15 wt% of trimer acid. From now on, we use “DA” as a product notation instead of “the mixture of dimer acid (DA) and trimer acid (TA)” throughout the paper. At this point, it should be mentioned that the detailed studies on the effect of reaction conditions and source of fatty acids had already been conducted by our group and the findings have been reported elsewhere; interested readers are referred to the original article (Lee et al., 2013). For the sake of convenience, only brief results are given here. We found that the various waste vegetable oils, such as used soybean oil or by-products obtained in course of the production of edible oils, can be converted to fatty acids that can be used for synthesis of DA. Depending on oil sources, various fatty acids were obtained. With increasing the proportion of unsaturated fatty acids, overall yield percentages and the relative amount of TA were found

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