

Synthesis and Characterization of Long-Chain Fatty Acid Cellulose Ester (FACE)

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SYNOPSIS

Long-chain fatty acid cellulose esters (FACE) were synthesized by the acid chloride-pyridine reaction with different degrees of substitution (DS). The hydrolyzed soybean oil was used as unsaturated fatty acids, its unsaturation degree, and composition were analyzed by ^1H and ^{13}C NMR methods. The chemical structures of FACE were confirmed by solid-state ^{13}C NMR, and substitution reaction of fatty acid chloride on cellulose were analyzed by IR spectroscopy. FACE(s) are insoluble in common organic solvents, such as benzene, toluene, THF, etc., at refluxing temperature. As the DS increased, the tensile strength of extruded FACE films decreased, but elongation increased. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose is the most abundant natural polymer. It is of major commercial and scientific importance with a variety of natural and modified celluloses used industrially.

Esterification of fatty acids to cellulose can be used to make various kinds of esters. The chemistry and technology of single and mixed fatty acid esters (acetate, propionate, butyrate etc.) are well known and have been given much attention in the technical, trade, and patent literature for decades.¹⁻⁴ The longer chain saturated fatty acids up to palmitic acid ester of cellulose have also been previously prepared and characterized.⁵⁻⁷ However, no literature about long-chain, unsaturated fatty acid esters of cellulose has been reported, especially using mixed chains, such as hydrolyzed soybean oil as the fatty acid source.

Because of the polyunsaturated molecular chains of oleic, linoleic, and linolenic acid (main components of soybean fatty acids), the properties of these fatty acid cellulose esters are different from those of saturated fatty acids and could be useful as plastics, plastic additives, chromatography supports, cosmetic additives, and slow-release carriers for pharmaceuticals.

In this work, the preparation, characterization, and fabrication of fatty acid cellulose esters (FACE) using soybean fatty acids are reported.

METHODS AND EXPERIMENTS

A Thomas Hoover capillary melting point apparatus was used to observe heating behavior of FACE samples. IR spectra were recorded using an IR 1800 spectrophotometer. The solution ^1H NMR spectra were recorded at 500 MHz, and ^{13}C NMR spectra were obtained at 125.7 MHz. The fatty acid sample was prepared in CDCl_3 and was referenced to TMS as an internal standard. The solid ^{13}C NMR spectra were obtained at 100 MHz. The Randcastle microextruder (Randcastle extrusion system Inc., 31 Hopson Ave., Little Falls, NJ 07424) was used to fabricate FACE into films. The temperature in zone 1, zone 2, zone 3, and die of the extruder was 320°F with a screw rotating speed of 200 rpm. The mechanical properties of the FACE films were tested using a SINTEC 10 tensile tester.

Chemicals

Pyridine, benzene, and *N,N*-dimethylformamide (DMF) were all analytical grade reagents. Pyridine was dried with sodium hydroxide. Benzene and DMF

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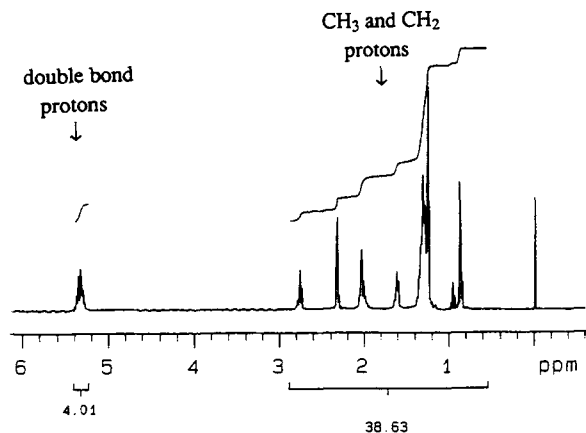


Figure 1 Partial ^1H NMR spectrum of hydrolyzed soybean oil.

were dried by anhydrous magnesium sulphate and distilled at reduced pressure.

Fatty Acids

Distilled soybean fatty acids, were kindly provided by Karlshamns USA Inc. (525 West First Ave., Columbus, OH 43215). They were dried at 65°C reduced pressure (2 mm), with stirring for 16 h under nitrogen atmosphere. The composition of the fatty acids was analyzed by NMR.

Fatty Acid Chloride (FACl)

Preparation of FACl followed a modified method from Youngs et al.⁸ To 1200 mL of benzene in a 3-L, three-necked round bottomed flask was added 460 g of fatty acids with stirring under nitrogen purge. Phosphorous pentachloride (380 g) was added slowly over 20 min. During this addition the temperature rose to about 42°C due to the exothermic reaction. The mixture was refluxed at 85°C under nitrogen for 1 h. The solution was cooled to room temperature and washed twice with ice water. Excessive shaking was avoided and the water layer was drawn off as soon as it separated to minimize hydrolysis of the fatty acid chloride. The organic phase was dried with anhydrous magnesium sulphate and the benzene was removed under reduced pressure to give 508 g of product. The reaction products (FACl) were analyzed by IR spectroscopy and contained less than 1.5% free fatty acids.

Activated α -Cellulose

The α -cellulose (Sigma) was activated by mercerization method.⁹

Fatty Acid Cellulose Esters

FACl (15, 25, and 45 g) were slowly added to three 500 mL, three-necked round bottomed flasks each containing 90 mL of DMF, 90 mL of pyridine, and 4.05 g of activated α -cellulose with stirring under nitrogen at room temperature. After several minutes, the temperature of reaction mixtures rose to about 43°C , due to the exothermic reaction. Nitrogen was continuously purged slowly from one neck, and excess gas went out through a drying tube packed with Drierite set on another neck. The reaction mixtures were heated to 90°C and kept at this temperature for 24 h with stirring. The reaction mixtures were cooled to about 40°C , and 180 mL of anhydrous methanol was added to precipitate products. The mixtures were stirred for 10 min and filtered. The solids were collected and washed with 180 mL of fresh anhydrous methanol and filtered. The wash filter process was repeated another three times with acetone. Finally, the products were dried in a desiccator over phosphorus pentoxide under reduced pressure (2 mm) at room temperature for 20 h. The three reactions, named A, B, and C, yielded 9.9 g, 17.3 g, and 21.2 g of light yellow colored products.

DS (Degree of Substitution) Determination

A modification of Genung's method¹⁰ was used to determine the DS of each product. FACE sample (0.5 g) was placed in a 250 mL Erlenmeyer flask. Sodium hydroxide (40.0 mL of 0.25 N) in 95% ethanol was added to each flask, and also to two empty flasks as blanks. These flasks were sealed and kept at 30°C in a water bath for 24 h with occasional swirling. The samples were then titrated with 0.32 N HCl to a pH 7.0 and kept for 3 h. The excess HCl was then back titrated with 0.129 N sodium hydroxide to a pH of 9.0. The percent of fatty acids in

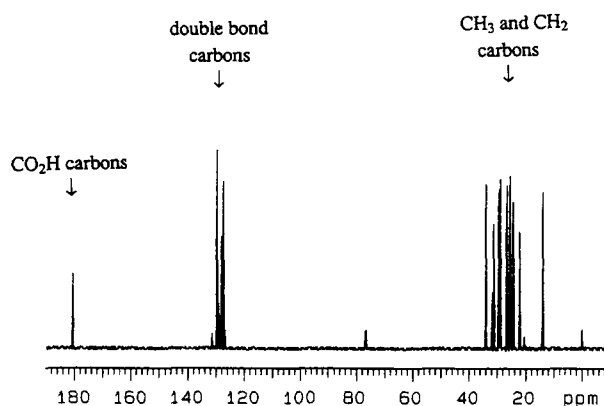


Figure 2 ^{13}C NMR spectrum of hydrolyzed soybean oil.

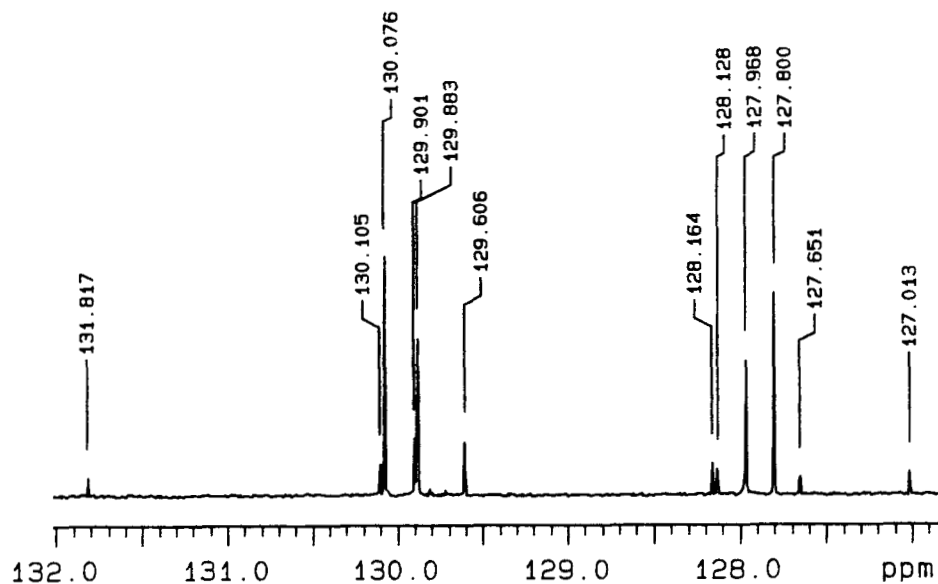


Figure 3 An expansion of ^{13}C NMR spectrum in the double bond range.

FACE (%FA) and DS were calculated as follows. The average equivalent weight of the five fatty acids in the hydrolyzed soybean oil calculated was 278.46 (see composition of fatty acids in the Results and Discussion section).

%FA = (blank acid equivalent

– sample acid equivalent) 278.46/sample weight

DS = (%FA/278.46)/[(1 – %FA)/162]

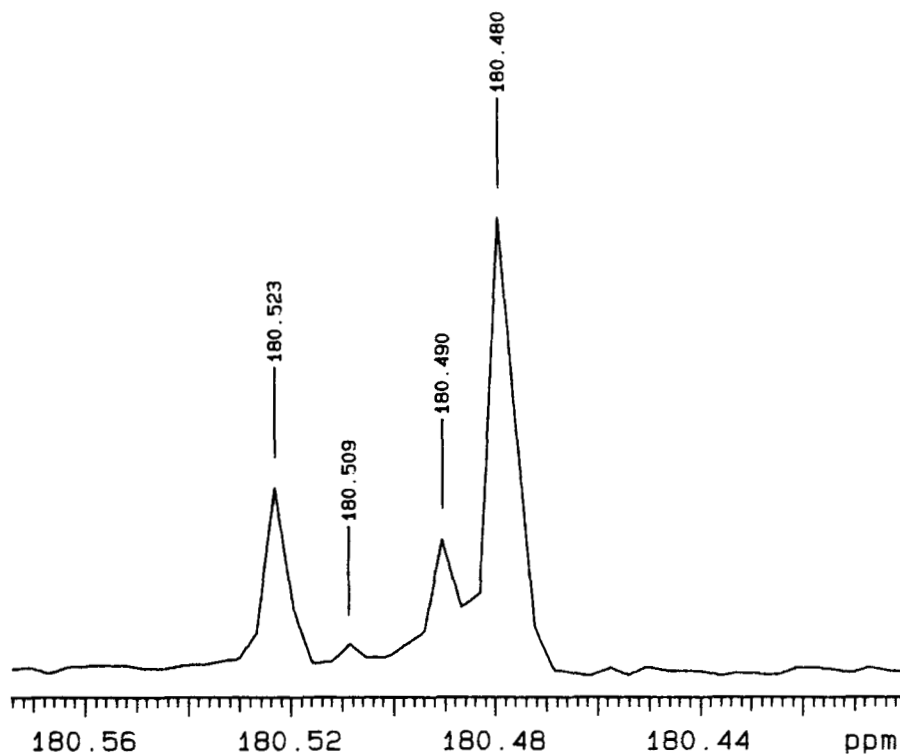


Figure 4 An expansion of ^{13}C NMR spectrum in the carboxylic carbon range.

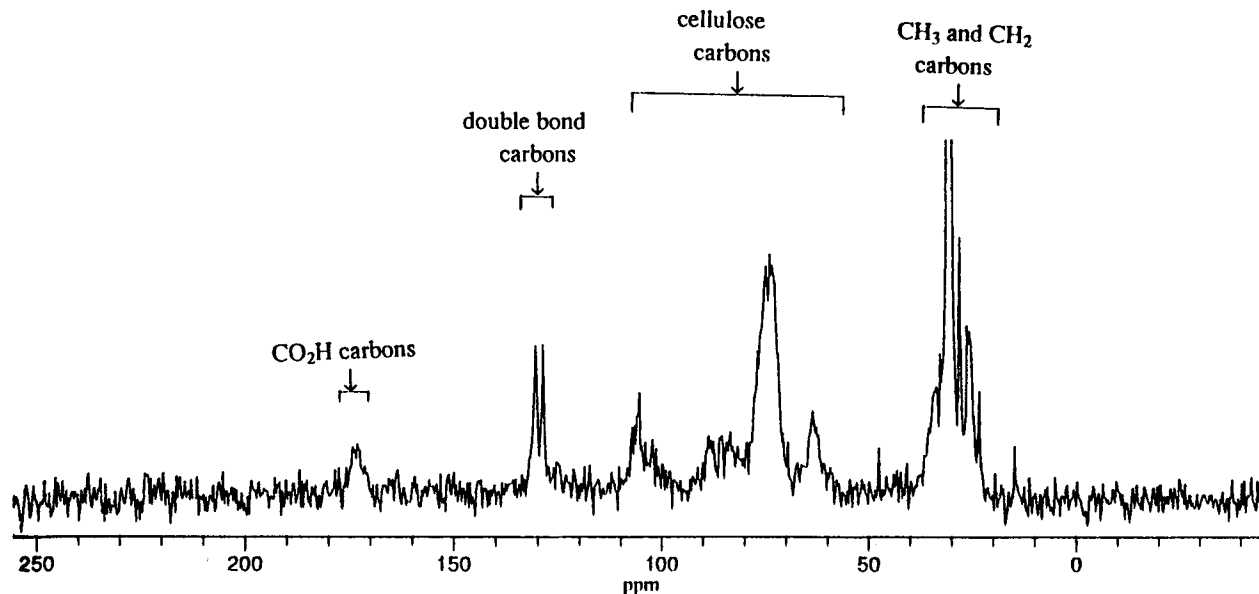


Figure 5 Solid-state ^{13}C NMR spectrum of FACE with DS = 0.8.

RESULTS AND DISCUSSION

NMR Analysis of Fatty Acids

The distilled hydrolyzed soybean oil was analyzed by nuclear magnetic resonance spectroscopy (NMR). The ^1H NMR spectrum is shown in Figure 1.

The chemical shifts of methyl and methylene protons and double-bond protons are at 0.8–2.9 ppm

and 5.2–5.4 ppm, respectively.¹¹ It was reported¹² that general distilled hydrolyzed soybean oil composition was palmitic acid (16 : 0) 11%, stearic acid (18 : 0) 4%, oleic acid (18 : 1) 29%, linoleic acid (18 : 2) 51%, and linolenic acid (18 : 3) 5%. Based on these data, the average numbers of methyl methylene protons and double-bond protons are 28.72 and 2.92, respectively, with a ratio of 9.84. From Figure 1 it can be found that the integration values (representing numbers of protons) of methyl meth-

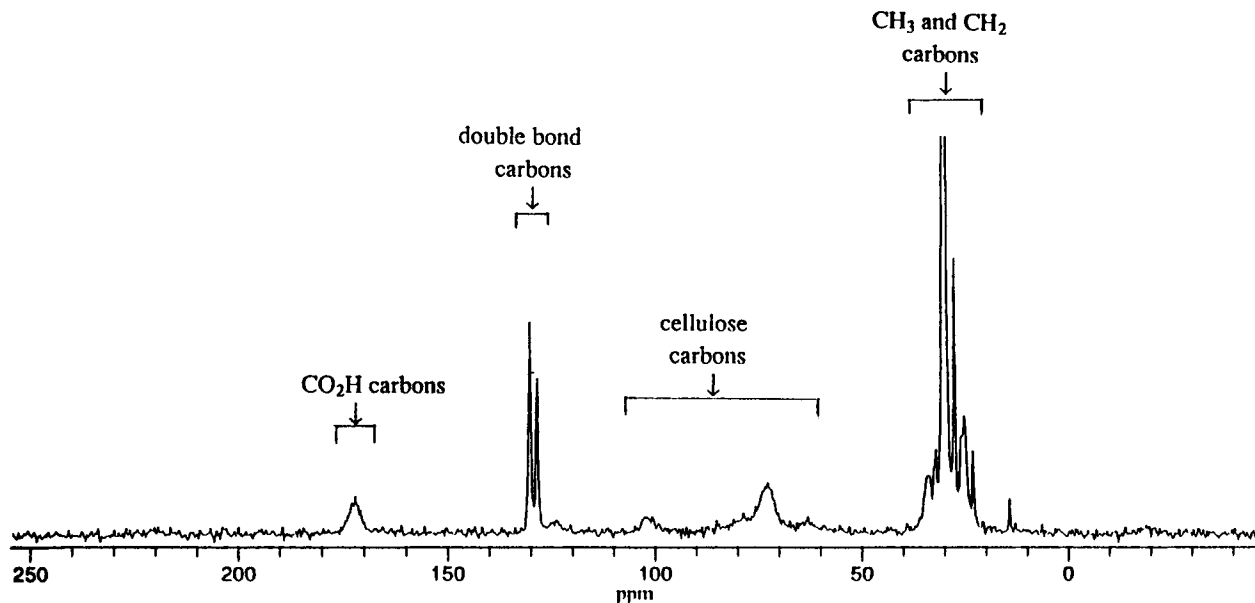


Figure 6 Solid ^{13}C NMR spectrum of FACE with DS = 2.7.

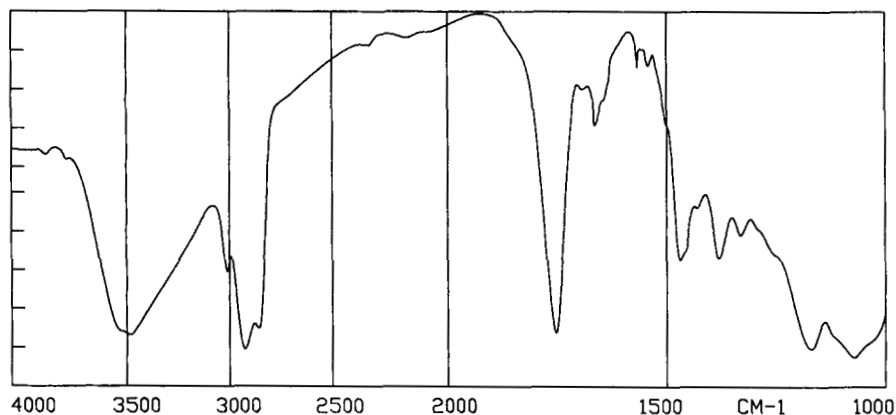


Figure 7 IR spectrum of FACE with DS = 0.8.

ylene and double bond protons are 38.63 and 4.01. Their ratio is $38.63/4.01 = 9.63$. This ratio value is almost the same as that reported for soybean oil (9.84). This analysis indicates that the soybean fatty acids used here have the same unsaturation level as general soybean oil. The ^{13}C NMR spectrum is shown in Figure 2.

As shown in Figure 2, the methyl methylene carbons are located at 12–38 ppm, double-bond carbons at 127–132 ppm, and carboxylic acids at 180 ppm.¹¹ The expansions of the spectrum ranges are shown in Figures 3 and 4.

As shown in Figure 3, there are 12 double-bond carbons, six lowest peaks at 127.013, 127.651, 128.128, 128.164, 130.105, and 131.817 ppm are from linolenic acid (18 : 3), four high peaks at 127.800, 127.968, 129.883, and 130.076 ppm are from linoleic acid (18 : 2), two intermediate peaks at 129.606 and 129.901 ppm are from oleic acid (18 : 1). In Figure 4, the four carboxylic carbons of the five fatty acids can be observed. The fifth peak is overlapped by the larger peaks. These NMR data clearly demonstrate

that the soybean fatty acids used in this experiment are representative of soybean oil.

FACE NMR Analysis

The chemical structure of the prepared FACE has been confirmed by solid ^{13}C NMR. The spectra are shown in Figures 5 and 6. From Figure 5 it can be observed that the peaks at 12–40 ppm, 127–133 ppm, and 168–178 ppm are from methyl methylene carbons, double-bond carbons, and carboxylic carbons of the fatty acids, respectively. The peaks at 57–110 ppm are from the carbons of cellulose.¹³ The ratio of the signal intensities from cellulose and fatty acids in Figure 6 is much smaller than that in Figure 5, due to higher DS.

FACE IR Analysis

The DS of the three samples from reaction A, B, and C were found to be 0.8, 1.7, and 2.7, respectively.

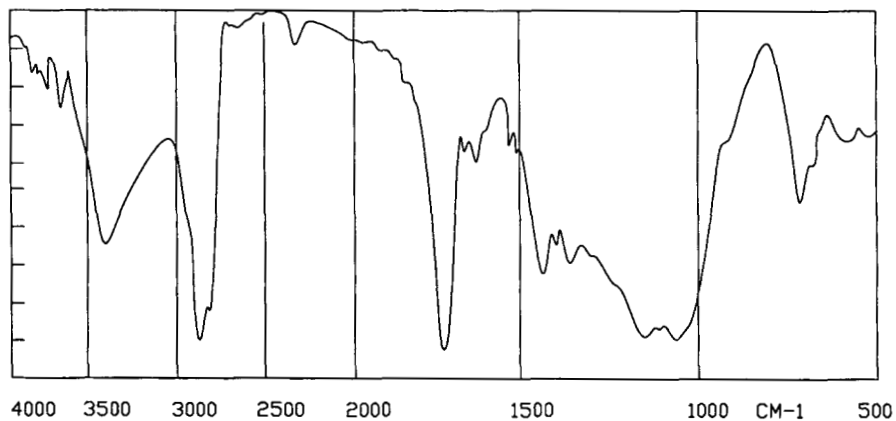


Figure 8 IR spectrum of FACE with DS = 1.7.

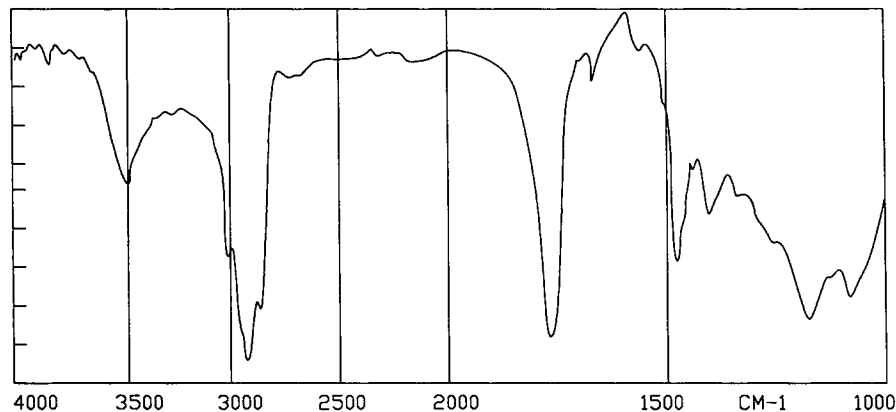


Figure 9 IR spectrum of FACE with DS = 2.7.

The substitution reaction on hydroxyl groups of the anhydroglucosyl units of cellulose was also detected by IR spectroscopy. The absorption of hydroxyl groups on the glucosyl units¹⁴ is at about 3500 cm^{-1} . Pure fatty acids do not absorb in this range. Based on the titration results, the three FACE samples contain 41.1%, 25.4%, and 18.0% (w/w) cellulose material. In the IR sample preparations, 1.0, 1.6, and 2.3 mg of samples all contained same amount of cellulose (0.41 mg) were combined with the same amount of potassium bromide (100 mg). The semi-quantitative IR analysis procedure was used. The three IR spectra were in the Figures 7–9.

From the three IR spectra it can be observed that as the DS of the FACE increased, the absorption intensity at 3500 cm^{-1} decreased, indicating fewer availabilities of O-H groups.

Solubility of FACE

The solubility of the DS = 2.7 FACE sample was determined in some common organic solvents. Samples were added to 54.0 mL of solvent. The mixtures were stirred at refluxing temperature for 4 h under nitrogen, then immediately filtered while the mixtures were hot. The filtrates were evaporated,

the solids left (soluble parts) were dried and weighed, and the solubilities calculated. The insoluble solids were refluxed with the same procedure twice more. The results from the three tests were listed in Table I.

It was found that FACE is essentially insoluble in the solvents listed except some low molecular weight products that made up 2.6–6.0% (w/w) of total FACE material. These results indicate that in the preparation of FACE the final washing with organic solvents should be carried out at refluxing temperature for longer time to reduce impurities to minimum.

In *n*-dodecane at refluxing (216°C) for 20 h, the samples were decomposed. After removal of the solvent, the solid left was a soft paste, rather than a powder.

Thermal Behavior

The behavior on heating of the DS = 2.7 FACE sample was examined by heating the ester in a $1.5 \times 90\text{ mm}$ glass tube in oil bath. Its temperature rise was controlled at 5°C per min. It was found that the FACE sample did not really melt to form liquid, so it has no true melting point. It started to change its

Table I Solubilities (mg/mL) of FACE (DS = 2.7) in Some Organic Solvents

Solvent Refluxing Temp. ($^{\circ}\text{C}$)	Benzene 80.1	Toluene 110.6	Tetrahydrofuran (THF) 65.4	Chloroform 61.2	Carbon Tetrachloride 76.8	Ethyl Acetate 77.1
1st	0.59	1.11	0.76	0.83	0.48	0.83
2nd	0.06	0.44	0.08	0.14	0.08	0.14
3rd	0.03	0.10	0.04	0.04	0.02	0.04

Table II The Effect of DS of FACE on the Physical Properties of the Films

DS	0.8	1.7	2.7
Tensile strength (pa)	2.0×10^6	1.4×10^6	0.8×10^6
Elongation (%)	6.9	9.0	17.2

color from light yellow at about 190°C. At about 220°C it became brown. It showed only a little bit of "sintering" at about 223°C. Above 223°C, the sample became a black, carbonaceous solid.

The FACE samples were easily oxidized if they were exposed in air at room temperature because of the reactivity of oxygen to double bonds in the fatty acid molecular chains. The FACE with the same DS value 2.7, but exposed in air for 8 weeks, changed its color to brown at 255°C, and became black at 285°C.

Physical Properties of Extruded FACE Films

Extrusion was used to make the films of FACE. The extruding temperature range was 300–340°F, with a screw rotate rate of 200 rpm. For lower substituted FACE (DS = 0.8 and 1.7), a lower extrusion temperature was used to reduce oxidation. All films extruded were flexible and transparent. The mechanical properties were tested, the tensile strength and elongation data were listed in Table II.

As shown in Table II, as DS increased, the tensile strength of films decreased, but elongation increased. The lower tensile strength and increased elongation of FACE with higher DS probably reflects decreased hydrogen bonding between FACE molecules due to fewer hydroxyl groups on the molecule.

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REFERENCES

1. V. Stannett, *Cellulose Acetate Plastics*, p. 5, Temple Press Ltd., London, 1950.
2. R. L. Smith, *Paint Varn. Prod. Manager*, **59**, 53 (1969).
3. J. W. Fisher, *Recent Advances in the Chemistry of Cellulose and Starch*, J. Honeyman, Ed., p. 188, Heywood, London, 1959.
4. C. H. Keith and R. O. Tucker, U.S. Pat. 4,192,838 (1980).
5. C. J. Malm and C. R. Fordyce, *Cellulose and Cellulose Derivatives*, 2nd ed., Part 2, E. Ott, H. M. Spurlin, and M. W. Grafflin, Eds., p. 667, Interscience, New York, 1954.
6. C. J. Malm, J. W. Mench, D. L. Kendall, and G. D. Hiatt, *Ind. Eng. Chem.*, **43**, 684 (1951).
7. C. A. Battista, A. T. Armstrong, and S. S. Radchenko, *Polym. Preprints*, **19**, 567 (1978).
8. C. G. Youngs, A. Epp, B. M. Craig, and H. R. Sallans, *J. Am. Oil Chemists' Soc.*, **34**, 107–108 (1956).
9. H. S. Kwatra, J. M. Caruthers, and B. Y. Tao, *Ind. Eng. Chem. Res.*, **31**, 2647–2651 (1992).
10. L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem. Anal. Ed.*, **13**, 369–374 (1941).
11. Frank D. Gunstone and Frank A. Norris, *Lipids in Foods, Chemistry, Biochemistry and Technology*, pp. 48–50, Pergamon Press, New York, 1983.
12. *Fatty Acids and Their Industrial Applications*, E. S. Pattison, Ed., p. 7, Marcel Dekker, Inc., New York, 1968.
13. Colin A. Fyfe, *Solid State NMR For Chemists*, pp. 434–441, C. F. C. Press, P.O. Box 1720, Guelph, Ontario, Canada, NIH 6Z9, 1983.
14. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th ed., p. 112. John Wiley & Sons, Inc., New York, 1980.

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