

Interesterification of Soybean Oil and Lard Blends Catalyzed by SBA-15-pr-NR₃OH as a Heterogeneous Base Catalyst

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ABSTRACT: A novel heterogeneous SBA-15-pr-NR₃OH catalyst has been prepared by reactions of dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride with mesoporous SBA-15 materials. The solid base catalysts were characterized by using Fourier transform infrared spectra, thermogravimetric analysis, nitrogen adsorption–desorption, and elemental analysis techniques. By using the solid catalyst, an environmentally benign process for the interesterification of soybean oil and lard blends in a heterogeneous manner was developed. The interesterification was investigated regarding the slip melting point (SMP), iodine value (IV), triacylglycerols (TAGs) profile, fatty acid composition at the sn-2 position in TAGs, and differential scanning calorimetry (DSC). The obtained results revealed that the solid base catalyst was capable of catalyzing TAG interesterification. It was shown that interesterification significantly modified the physicochemical properties of the oil and fat blends. The interesterified products had lower SMPs than their corresponding physical blends. These changes in melting behaviors were mostly due to the alterations in TAG compositions. The DSC cooling and melting thermograms showed an obvious change in thermal properties after the interesterification reaction.

KEYWORDS: *heterogeneous catalyst, interesterification, lard, soybean oil*

INTRODUCTION

The physicochemical characteristics of oils and fats are determined by their chemical compositions (chain length, degree of unsaturation of fatty acid (FA) residues, and distribution of FA residues on the glycerol backbone). To improve the physicochemical properties of fats and oils, chemical and physical modifications can be applied. Fractionation, hydrogenation, and interesterification are the main processes available to tailor the physicochemical properties of food lipids. These methods can be used to produce new oil products (such as margarines, shortenings, and confectionery fats) with some special functions or usability so as to meet the increasing demands of food industries.¹

Partial hydrogenation, a traditional oil processing method, has been commonly employed for the modification of edible oils. However, this process has some drawbacks mainly owing to the substantial formation of undesirable *trans* FA residues, which can act as increased risk factors of coronary artery disease by modulating the synthesis of blood cholesterol acting on the eicosanoids.^{2–4} Several nutritional studies have suggested a direct relationship between the intake of *trans* FAs and the incidence of coronary heart disease and other related diseases.⁵ *trans* FAs have been reported to be able to raise the level of low-density lipoproteins (LDL) and lower the level of high-density lipoproteins (HDL) in human blood.⁶ Besides, the hydrogenation process destroys essential polyunsaturated FAs and creates non-natural isomers of saturated fats. Therefore, in consideration of the detrimental health effects of hydrogenated fats, the demand for plastic fats and structured lipids with zero *trans* FAs is increasing and becoming more important for the edible oil industry.

Recently, interesterification has attracted considerable attention as an alternative method to obtain plastic fats with desired physicochemical properties.⁷ The interesterification

between an oil and a fat involves the exchange of a triacylglycerol (TAG) with another TAG (ester–ester exchange), with a concomitant change in physicochemical properties of the end-products with *trans*-free FA residues. It can modify the physicochemical properties of oils and fats by rearranging the distribution of FAs on the glycerol backbone, where the improved plasticity and compatibility of the final product are achievable as compared to the physical blends of oils having similar FA compositions.^{8,9} In general, interesterification can be achieved through either enzymatically or chemically catalyzed processes, and there is no possibility for *trans* FA formation.¹⁰ Enzymatic interesterification (EIE) is more specific and requires milder reaction conditions.^{11–13} However, the development of EIE reactions on an industrial scale is limited by the high cost associated with the lipase used. Chemical interesterification (CIE) is a tried-and-true approach, as it has been around for a long time and relevant industrial procedures and equipment are readily available. Hence, from cost reduction and large-scale application points of view, CIE, although leading to a random distribution of FA residues on the glycerol backbone of TAGs, seems to be the most attractive method for practical use in the edible oil industry.

The CIE process is generally promoted by chemical catalysts to improve the physicochemical properties of oils and produce distributed FA residues among TAG molecules.¹⁴ Sodium metal and sodium alkoxide are usually used as catalysts for the CIE processes, mainly thanks to their low cost and high efficiency at relatively low temperatures.^{14–16} However, the removal of these homogeneous catalysts after the reaction is

Received: January 15, 2013

Revised: March 19, 2013

Accepted: March 19, 2013

Published: March 19, 2013

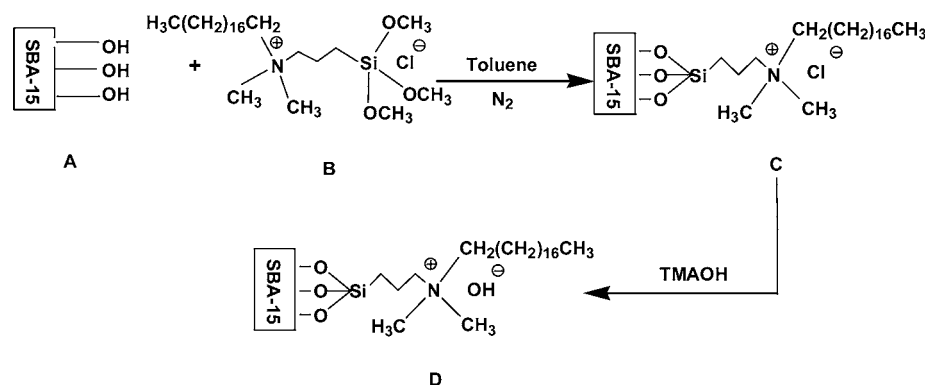


Figure 1. Synthesis of SBA-15-pr-NR₃OH solid base catalyst.

particularly problematic, requiring aqueous quench and neutralization steps that themselves generate undesired wastewater. More recently, the replacement of homogeneous catalysts by heterogeneous ones has gained increasing attention owing to the advantages of green or sustainable chemistry for catalyst recovery, easier operation, reactivation, and reutilization. Heterogeneous catalysts can be easily recovered by decantation or filtration, offering an opportunity for continuous operation in liquid flow reactors.¹⁷ Diverse basic heterogeneous catalysts have been developed, including metal oxides, hydroxides, and salts supported on high surface area materials (such as alumina, SBA-15, and MCM-41), zeolites, and ion-exchange resins.^{17–20} Supported organic bases, for example, guanidines anchored on polymers or encapsulated in zeolite cages, have been employed as heterogeneous catalysts for biodiesel production from vegetable oils.^{21,22} However, to the best of our knowledge, the solid base catalyst has not been reported to be used for the CIE reaction, despite their proven catalytic efficiency in a variety of other organic reactions.^{20–22} In this sense, the use of solid base catalysts in the interesterification is expected for developing a green and economical process.

Mesoporous silica materials, such as SBA-15 molecular sieves, have generated much interest as a catalyst support in heterogeneous catalysis because of their high specific surface area, ordered mesoporous structure, and large pore volume.²³ The functionalization of organic base groups on the surface of these materials by grafting or co-condensation can be used to create efficient solid base catalysts with improved catalytic properties as compared to conventional homogeneous and heterogeneous catalysts.^{23–26} In the present work, an efficient heterogeneous catalyst, SBA-15-pr-NR₃OH, was prepared and used for the interesterification reaction. To covalently anchor organic bases on the SBA-15 surface, the surface grafting could be employed to attach organic functional groups to mesoporous silica frameworks without the risk of pore blockage. The anchoring procedure of organic base involved the functionalization of the SBA-15 material with dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride, followed by the exchange of chloride ions with hydroxyl anions. The prepared solid catalysts were characterized by using Fourier transform infrared (FT-IR) spectra, thermogravimetric analysis (TGA), nitrogen adsorption–desorption, and elemental analysis techniques. The interesterification of different ratios of soybean oil to lard was carried out in a batch reactor by using this solid base catalyst. Besides, FA residues and TAG compositions of the interesterified products were determined

by high-performance liquid chromatography (HPLC) and gas chromatography (GC) methods. Moreover, the physicochemical properties of the end-product mixtures were also evaluated in terms of the slip melting point (SMP) and thermal behaviors.

MATERIALS AND METHODS

Materials. Refined soybean oil and lard used in this work were purchased from local commerce. Pluronic copolymer P123 (EO₂₀PO₇₀EO₂₀, average molecular weight of 5800), dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride, and tetraethylorthosilicate (TEOS, 98%) were obtained from Aldrich. All other materials used were of either analytical or chromatographical grade.

Catalyst Preparation. Mesoporous silica SBA-15 was prepared according to the approach described previously.²⁵ In a typical preparation, 10 g of amphiphilic triblock copolymer P123 was dispersed in 75 mL of water and 300 mL of 2 mol/L HCl solution. Thereafter, 21 g of TEOS was added to the P123 solution. The resulting solution was continuously stirred at 40 °C for 24 h and subsequently crystallized in a Teflon-lined autoclave at 100 °C for 48 h. After crystallization, the solid product was centrifuged, filtered, then washed with deionized water, and finally dried in air at room temperature. The formed SBA-15 powder was obtained by calcining the materials in air at 550 °C for 6 h to remove the template. The mesoporous SBA-15 silica was used as a parent material for preparation of the heterogeneous catalyst.

The procedure for preparation of the solid base catalyst is illustrated in Figure 1. Initially, 1.2 g of SBA-15 material (A) was activated at 500 °C for 6 h. Afterward, 1.5 g of dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (B) and 15 mL of dry toluene were added to the activated SBA-15 and allowed to reflux under nitrogen at 120 °C for 48 h. After cooling, the formed solid (C) was filtered off and washed thoroughly with methanol. Thereafter, the intermediate was suspended in 0.21 mol/L methanolic solution (100 mL) of tetramethylammonium hydroxide (TMAOH), and then the suspension was stirred for 4 h at room temperature to exchange chloride ions with hydroxyl anions. The prepared solid base was extracted in a Soxhlet apparatus using diethyl ether/methylene chloride mixture (v/v, 1:1) for 6 h for removal of excess reactants. Finally, the solid catalyst SBA-15-pr-NR₃OH (D) thus prepared was dried under vacuum at 60 °C for 12 h. The extent of functionalization for the SBA-15 material could be determined from the elemental analysis results.

Catalyst Characterization. The KBr pellet technique was applied for determining the IR spectra of the samples. Spectra were recorded on a Shimadzu IR-Prestige-21 spectrometer with 4 cm⁻¹ resolution. The scanning range was from 400 to 4000 cm⁻¹.

TGA was performed on a TA Instrument TG 2050 thermogravimetric analyzer with a heating speed of 20 °C/min under air atmosphere with a flow rate of 100 mL/min.

The carbon, hydrogen, and nitrogen contents of the samples were determined by a Carlo-Erba 1106 elemental analyzer. The amount of

incorporated organic groups was calculated through the nitrogen content determined by the elemental analysis.

The textural properties of the solid catalysts were measured by nitrogen adsorption–desorption isotherm method at liquid nitrogen temperature ($-196\text{ }^{\circ}\text{C}$) using a Quantachrome NOVA 1000e instrument. Specific surface areas were calculated from the isotherm data by using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were measured by using the Barrett–Joyner–Halenda (BJH) analysis applied to the desorption branch of the isotherms.

Interesterification Procedures. Binary blends of lard and soybean oil were designed at ratios of 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, and 20:80 (w/w) and were used as the starting fat mixture. The blend samples were prepared after complete melting of the fats at $80\text{ }^{\circ}\text{C}$, and the mixtures were stored in a refrigerator (ca. $4\text{ }^{\circ}\text{C}$) prior to use.

Portions of 100 mL of the samples were previously dried under reduced pressure in a flask fitted with a rotary evaporator in a water bath at $90\text{ }^{\circ}\text{C}$. The CIE reaction of different blends of lard and soybean oil was carried out by the addition of 1.5 wt % of SBA-15-pr-NR₃OH as a catalyst. The lard and soybean oil blends were interesterified under reduced pressure at $100\text{ }^{\circ}\text{C}$ in a 150 mL stoppered flask in a water bath with magnetic stirring ($\sim 750\text{ rpm}$) for a time frame of 3 h. At the end of the reaction, the interesterified product was filtered and then stored at $-18\text{ }^{\circ}\text{C}$ for subsequent analysis.

Determination of Total FA Profiles. FA compositions of the interesterified products were determined after complete conversion of FA residues into their corresponding fatty acid methyl esters (FAMES) according to the method described by Hartman and Lago.²⁷ Analyses of FAMES were carried out on an Agilent gas chromatograph (model 6890N), fitted with a split injection port, a flame ionization detector, and a software package for system control and data acquisition (Model Star Chromatography Workstation, version 5.5). Injections were performed in a 120 m fused silica capillary column (i.d. = 0.25 mm) coated with 0.25 μm of BPX-70 (SGE, Australia) using nitrogen as carrier gas at a flow rate of 1.2 mL/min with a split ratio of 1:20. The injector and detector temperatures were set at 260 and $300\text{ }^{\circ}\text{C}$, respectively. The oven temperature was initially held at $160\text{ }^{\circ}\text{C}$ for 5 min, programmed to increase to $200\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$, and then held isothermally for another 42 min at the final temperature. The FAME composition was identified by comparing the retention time of the peaks with the respective standards of FAME. The relative FAME content was obtained by area normalization and expressed as mass percentage.²⁸ All samples were analyzed in triplicate, and the reported values are the average of three determinations.

sn-2 Positional Analysis of FA Residues. The FA compositions at the sn-2 position of the interesterified product were determined by using pancreatic lipase in accordance with the method described in the literature.²⁸ The pancreatic lipase can be applied to hydrolyze selectively the TAGs and can release FAs from the sn-1,3 positions of TAGs. Briefly, a known amount of oils and an appropriate amount of pancreatic lipase were placed in a stoppered flask. Afterward, 2 mL of Tris-HCl buffer (1 mol/L, pH 8.0), 0.5 mL of 0.05% sodium cholate solution, and 0.2 mL of 2.2% calcium chloride solution were added to the mixture. To emulsify the sample, the mixture was vortexed for 2 min. Thereafter, the samples were incubated in a water bath at $40\text{ }^{\circ}\text{C}$ for 3 min. To quench the hydrolysis reaction, 1 mL of 6 mol/L HCl solution and 4 mL of diethyl ether were added, vortexed for 2 min, and centrifuged at 1000 rpm for 3 min. The diethyl ether layer containing the lipid component was passed through an anhydrous sodium sulfate column, and the solvent was subsequently evaporated under nitrogen to obtain the concentrated sample containing the hydrolysis product 2-monoacylglycerol (2-MAG). Next, the concentrated samples were spotted on TLC plates and then developed with a solvent system of hexane/diethyl ether/formic acid mixture (70:30:1, v/v/v). The developed plates were sprayed with 0.2% 2,7-dichlorofluorescein in methanol, and 2-MAG bands were identified with 2-oleoylglycerol as a standard. After that, the bands corresponding to 2-MAG were scraped from the silica plates and then extracted with 5 mL of ethyl ether. The

extracted solution could be used for the sn-2 positional analysis of FA residues in the TAGs by GC techniques after methylation as described previously.

TAG Analysis. The variation of TAG profile occurred during the interesterification reaction was evaluated using reversed-phase high-performance liquid chromatography (RP-HPLC). The interesterified products were dissolved in chloroform (10 mg/mL) and used for the TAG analysis. Of these solutions, 20 μL aliquots were injected into the HPLC system. The mobile phase was dichloromethane/acetonitrile (HPLC grade) system at a gradient composition from 35% acetonitrile increasing to 55% dichloromethane in 45 min. The flow rate of mobile phase was 1.2 mL/min. A commercially packed Genesis C18 HPLC column (15 cm length \times 4.6 mm) was used to separate the TAGs. The column temperature was held at $40\text{ }^{\circ}\text{C}$. The TAG species were detected by an Alltech 500 evaporative light scattering detector. The sample injection volume was 20 μL . Individual peaks were identified tentatively by comparing the retention times with those of pure TAG standards and according to Adhikari et al.²⁹ The equivalent carbon number (ECN) method was applied to predict the elution order of TAGs according to AOCS Official Method Ce 5b-89.²⁸ Some standard TAGs such as tripalmitin, tristearin, triolein, and 1,2-dioleoyl-3-palmitoylglycerol, were chromatographed to help determine the TAG components.

Iodine Value (IV) and Slip Melting Point (SMP). The IV for the interesterified product was determined from the FA composition according to the procedure described in AOCS Official Method Cd 1c-85.²⁸

The SMP was measured by the open capillary tube method, according to AOCS Official Method Cc 3-25.²⁸ The capillary tubes filled with the samples were kept in a refrigerator overnight before the measurements. Three replicates of this measurement were performed.

Thermal Properties Analysis. The melting and crystallization characteristics of the interesterified products were determined on a DSC 4000 Perkin-Elmer Thermal Analyzer fitted with an automatic liquid nitrogen cooling system. The instrument was calibrated using indium and lead. An empty aluminum pan was employed as a reference, and each sample was accurately weighed (about 3–5 mg) for DSC analysis.

The following temperature program was used according to AOCS Official Method Cj 1-94.²⁸ For crystallization curves, the sample was heated to $80\text{ }^{\circ}\text{C}$ and kept for 10 min to eliminate all crystal nuclei. Afterward, the temperature was decreased to $-60\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and then held at this temperature for 30 min. The melting curves were obtained by heating from -60 to $80\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$. All data were treated using the Pyris software program.

RESULTS AND DISCUSSION

Catalyst Characterization. High concentrations of silanol groups are found on the framework surface of the mesoporous SBA-15 silica materials.²⁵ Because the surface hydroxyls can react easily with the alkoxy groups of silane by silylation reaction, these silanol groups act as anchoring sites for organic moieties. In the present work, the solid base catalysts were prepared in two steps (Figure 1). First, the surface grafting technique was employed for incorporating dimethyloctadecyl-[3-(trimethoxysilyl)propyl]ammonium chloride into the SBA-15 mesoporous molecular sieves. In the next step, for exchanging chloride ions with hydroxyl anions, the modified materials were treated with a methanolic solution of TMAOH. For identification of the solid base catalysts, FT-IR spectroscopy, TGA, nitrogen adsorption–desorption, and elemental analysis techniques were used to characterize the solid catalyst.

The FT-IR spectra of SBA-15 and SBA-15-pr-NR₃OH are presented in Figure 2. In the IR spectrum of SBA-15, the broad absorption band centered at 3460 cm^{-1} was mostly ascribed to the stretching vibration of framework hydroxyl groups and adsorbed water molecules, and the peak at 1635 cm^{-1} was

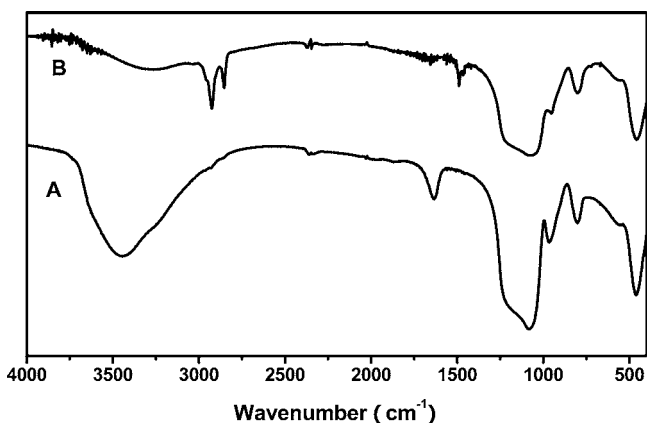


Figure 2. Fourier transform infrared spectra of SBA-15 (A) and SBA-15-pr-NR₃OH (B) catalyst.

attributed to the bending mode of bound water present in the SBA-15 materials.³⁰ Meanwhile, the peak at 950 cm⁻¹ could originate from the bending vibration of defective Si-OH groups. Besides, the vibration modes of Si-O-Si in the SBA-15 silica could be seen at 1100 cm⁻¹ (asymmetric stretching) and 770 cm⁻¹ (symmetric stretching).^{30,31} After the organofunctionalization, the IR characteristic peaks of surface hydroxyl groups disappeared, suggesting that the surface hydroxyl groups reacted with the anchored functional groups to form the functionalized SBA-15 material. In comparison with the IR spectrum of SBA-15, new absorption bands at 2940 and 2875 cm⁻¹ due to the CH₂ asymmetric and symmetric vibration, respectively, were evident for the solid base catalyst.^{30,31} The presence of these new bands confirms the successful organofunctionalization of the SBA-15 material.

The thermogravimetric curve of SBA-15-pr-NR₃OH is depicted in Figure 3. The initial weight loss (about 7%)

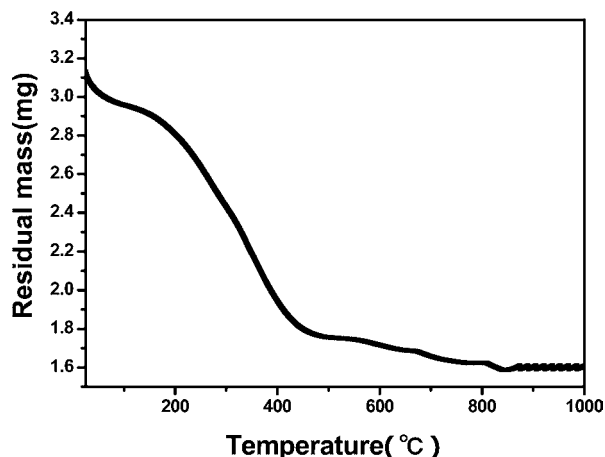


Figure 3. Thermogravimetric curves of SBA-15-pr-NR₃OH catalyst.

between room temperature and 200 °C could be attributed to desorption of physically held water from the framework of the mesoporous material. The subsequent weight loss (about 49%) event in the temperature range of 200–750 °C was mainly related to the thermal decomposition of organic functional groups. The main thermal decomposition of the organic groups occurred between 250 and 450 °C. According to the weight loss (200–750 °C), the amount of functional groups covalently anchored on the mesoporous SBA-15 silica could be estimated,

which was calculated to be 1.43 mmol/g. Above 750 °C, there was no obvious weight loss in the TG curve.

The C, H, and N elemental analysis results for the solid base catalyst are summarized in Table 1. According to the results, the

Table 1. Results for C, H, and N Elemental Analysis

sample	C (wt %)	H (wt %)	N (wt %)
SBA-15	NF ^a	NF	NF
SBA-15-pr-NR ₃ OH	20.34	3.23	1.95

^aNF, not found.

loading of functional groups on the SBA-15-pr-NR₃OH catalyst amounted to 1.39 mmol/g, which was in line with the result obtained from thermogravimetric measurements.

The nitrogen adsorption–desorption isotherms of SBA-15 and SBA-15-pr-NR₃OH are shown in Figures 4 and 5,

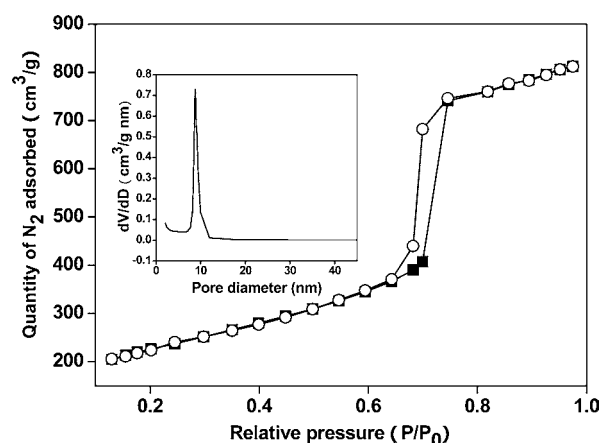


Figure 4. Nitrogen adsorption/desorption isotherms and pore size distribution profiles of SBA-15 material.

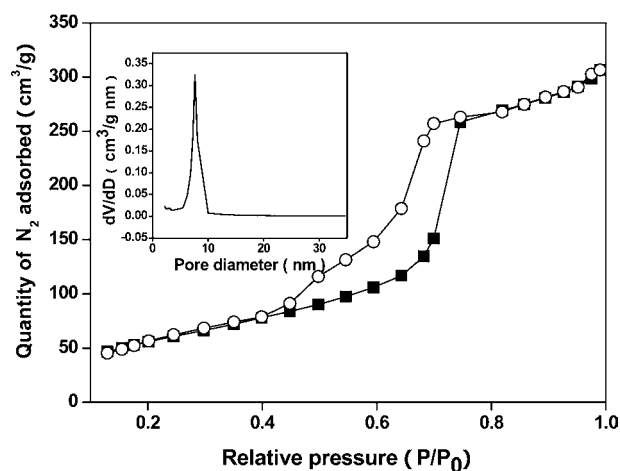


Figure 5. Nitrogen adsorption/desorption isotherms and pore size distribution profiles of SBA-15-pr-NR₃OH catalyst.

respectively. For the SBA-15 material and SBA-15-pr-NR₃OH catalyst, the adsorption isotherm showed an increase in the adsorbed amount of nitrogen in the p/p_0 range of 0.64–0.75, characteristic of mesoporous molecular sieves with narrow pore size distributions as usually reported for this kind of material.²⁶ This result suggested that the mesoporous structure of SBA-15 was preserved after functionalization with the organic base.

The textural properties of the samples are listed in Table 2. The SBA-15 material had a high surface area of 807 m²/g and a

Table 2. Textual Characteristics of SBA-15 and SBA-15-pr-NR₃OH Catalyst

sample	S_{BET}^a (m ² /g)	V_p^b (cm ³ /g)	D_{BJH}^c (nm)
SBA-15	807	1.25	6.65
SBA-15-pr-NR ₃ OH	225	0.48	5.49

^aBET surface area. ^bPore volume. ^cAverage pore diameter from BJH desorption.

pore volume of 1.25 cm³/g, which were consistent with the literature.^{30,31} In the case of SBA-15-pr-NR₃OH catalyst, the surface area and pore volume were 225 m²/g and 0.48 cm³/g, respectively, and the pore size distribution was narrow with a mean pore diameter of 5.5 nm. Obviously, as compared to the SBA-15 material, the BET surface area, pore volume, and pore diameter of SBA-15-pr-NR₃OH catalyst were decreased upon the modification reaction, which may be caused by the presence of anchored organic groups on the framework channel of the SBA-15 material. Besides, the powder X-ray diffraction pattern for the functionalized SBA-15 material (not shown here) was similar to the pattern of the SBA-15 material, implying that the mesoporous structure of the support remained virtually unchanged after the organofunctionalization reaction.

Total FA Compositions and Iodine Value. The total FA compositions of lard, soybean oil, and interesterified product are presented in Table 3. It can be seen from this table that the major FA in lard was oleic acid, which accounted for 38.9% of the total FAs, followed by palmitic acid (25.5%), linoleic acid (18%), and stearic acid (12.9%). Saturated FAs of lard constituted about 40% of the total FAs, and thus the lard was readily solid state at room temperature. By contrast, soybean oil contained 55% linoleic acid, 22.2% oleic acid, and 11.9% palmitic acid as major FAs. Besides, linolenic acid (7.6%) and stearic acid (3.4%) were also present in the soybean oil as minor FAs. Due to the high proportion of unsaturated FAs, soybean oil exhibited a liquid state at the measured temper-

atures. The FA compositions of lard and soybean oil are in accordance with those reported in the literature.³²

As shown in Table 3, the CIE reaction did not significantly affect the degree of unsaturation or cause isomerization of the FA residues, as expected. No remarkable alteration in the total FA profile was observed between the initial blend and the interesterified product. However, the distribution pattern of FAs in TAG molecules can influence the physicochemical behaviors and nutritional properties.

The IVs of lard, soybean oil, and the binary blends before and after the CIE reaction are indicated in Table 3. The IV can be used to measure the degree of unsaturation of oils without defining the specific FAs. A higher IV means a higher degree of unsaturation in the oils. From Table 3, the IV of the blends was increased with increasing amount of soybean oil in the blend. Moreover, the IVs of the blends remained almost unchanged after the CIE, revealing that the amount of unsaturated FAs was not varied during the interesterification.

Regiospecific Distribution. The FA compositions of sn-2 position for soybean oil and lard and their blends in various ratios, before and after the CIE catalyzed using the solid base catalyst, are shown in Table 4.

The sn-2 position of lard mainly contained 75.9% palmitic acid, 9.7% oleic acid, 5.0% stearic acid, and 4.0% myristic acid, with a small amount of linoleic acid (2.9%) and palmitoleic acid (2.4%). Besides, the oleic acid (54.0%), linoleic acid (23.4%), palmitic acid (16.4%), and stearic acid (6.3%) were predominately located at the sn-2 position of soybean oil. The positional distribution of these FAs was comparable to those reported previously.^{32,33}

Interesterification is generally employed to produce structured lipids that have improved functionality by rearranging the FAs on the glycerol backbone. As can be seen, compared to noninteresterified sample, the FA compositions at the sn-2 position were altered in all cases after the interesterification. The reason for this change is considered to be due to the redistribution of FAs after the CIE reaction. Notably, *trans* fatty acids were not detected during the interesterification under our experimental conditions. As can be observed from Table 4, 80:20, 70:30, 60:40, and 50:50 blends showed a decrease in

Table 3. Total Fatty Acid Composition (Percent) and Iodine Values of Lard, Soybean Oil, and Their Blends in Various Ratios before and after Chemical Interesterification^a

LA/SO ratio	myristic	palmitic	palmitoleic	stearic	oleic	linoleic	linolenic	IV
LA	1.4 ± 1.0	25.5 ± 1.2	1.8 ± 0.6	12.9 ± 0.2	38.9 ± 1.5	18.0 ± 0.3	0.6 ± 0.1	67.9
80:20 (before)	1.3 ± 0.0	25.4 ± 0.7	1.4 ± 0.1	16.7 ± 0.4	30.7 ± 0.6	7.8 ± 1.1	0.3 ± 0.0	42.0
80:20 (after)	1.3 ± 0.0	26.2 ± 0.0	1.5 ± 0.0	17.3 ± 0.1	31.1 ± 0.1	8.2 ± 0.1	0.3 ± 0.0	43.2
70:30 (before)	1.1 ± 0.1	28.1 ± 0.6	1.3 ± 0.0	19.0 ± 0.3	36.2 ± 0.3	11.9 ± 0.5	0.6 ± 0.0	54.5
70:30 (after)	1.3 ± 0.0	27.5 ± 0.0	1.2 ± 0.1	19.3 ± 0.0	36.8 ± 0.0	12.4 ± 0.1	0.6 ± 0.0	55.8
60:40 (before)	1.1 ± 0.1	27.2 ± 0.8	1.3 ± 0.0	17.1 ± 0.0	35.8 ± 1.3	14.6 ± 1.2	0.7 ± 0.0	59.1
60:40 (after)	1.1 ± 0.0	26.5 ± 0.1	1.3 ± 0.0	17.7 ± 0.0	36.6 ± 0.2	13.9 ± 0.0	0.7 ± 0.0	58.6
50:50 (before)	1.2 ± 0.0	25.5 ± 1.1	1.2 ± 0.1	14.2 ± 0.4	35.7 ± 0.7	20.5 ± 0.8	1.3 ± 0.0	70.7
50:50 (after)	0.9 ± 0.2	24.4 ± 0.0	1.1 ± 0.0	15.6 ± 0.1	36.1 ± 0.0	19.9 ± 0.2	1.1 ± 0.2	69.4
40:60 (before)	0.8 ± 0.0	23.6 ± 0.0	0.9 ± 0.0	14.3 ± 1.1	35.9 ± 0.0	21.9 ± 0.0	1.2 ± 0.0	72.8
40:60 (after)	0.8 ± 0.0	23.9 ± 0.0	0.9 ± 0.0	15.3 ± 0.0	35.7 ± 0.0	21.2 ± 0.7	1.0 ± 0.2	70.9
30:70 (before)	1.0 ± 0.0	22.8 ± 1.1	0.8 ± 0.0	12.7 ± 0.5	35.8 ± 0.8	25.2 ± 0.0	1.4 ± 0.6	78.9
30:70 (after)	1.0 ± 0.0	23.3 ± 0.1	0.9 ± 0.1	13.2 ± 0.0	36.3 ± 0.0	24.4 ± 1.1	1.1 ± 0.2	77.2
20:80 (before)	0.5 ± 0.3	20.9 ± 0.7	0.6 ± 0.0	10.7 ± 0.0	35.0 ± 0.7	29.3 ± 0.3	1.7 ± 0.0	85.9
20:80 (after)	0.8 ± 0.0	21.3 ± 0.6	0.7 ± 0.1	10.5 ± 0.2	35.7 ± 0.0	28.6 ± 1.2	1.4 ± 0.3	84.6
SO	0.0 ± 0.0	11.9 ± 0.2	0.0 ± 0.0	3.4 ± 1.2	22.2 ± 1.6	55.0 ± 1.3	7.6 ± 0.4	134.2

^aValues are the mean ± standard error. LA, lard; SO, soybean oil; IV, iodine value.

Table 4. sn-2 Fatty Acid Compositions (Percent) of Lard, Soybean Oil, and Their Blends in Various Ratios before and after Chemical Interesterification^a

LA/SO ratio	saturated acid	oleic acid	linoleic and linolenic acid
80:20 (before)	60.1 ± 0.6	23.6 ± 0.3	14.0 ± 0.1
80:20 (after)	58.4 ± 0.4	16.5 ± 0.1	23.1 ± 0.5
70:30 (before)	55.2 ± 0.3	23.9 ± 0.2	18.8 ± 0.3
70:30 (after)	45.6 ± 0.2	18.9 ± 0.3	33.8 ± 0.5
60:40 (before)	51.9 ± 0.4	24.4 ± 0.1	22.4 ± 0.4
60:40 (after)	44.9 ± 0.2	18.3 ± 0.0	35.2 ± 0.6
50:50 (before)	59.3 ± 0.5	22.9 ± 0.4	17.7 ± 0.2
50:50 (after)	36.1 ± 0.4	17.1 ± 0.8	39.3 ± 0.4
40:60 (before)	37.7 ± 0.3	29.2 ± 0.5	31.9 ± 0.5
40:60 (after)	39.2 ± 0.2	34.4 ± 0.3	22.1 ± 0.0
30:70 (before)	32.7 ± 0.5	29.8 ± 0.1	36.1 ± 0.2
30:70 (after)	32.9 ± 0.1	38.1 ± 0.3	27.3 ± 0.1
20:80 (before)	28.1 ± 0.0	30.3 ± 0.1	40.6 ± 0.2
20:80 (after)	31.9 ± 0.3	36.6 ± 0.2	30.4 ± 0.0

^aValues are the mean ± standard error. LA, lard; SO, soybean oil.

saturated FAs at the sn-2 position after the CIE, whereas for 40:60, 30:70, and 20:80 blends the levels of saturated FAs at the sn-2 position were increased when compared to their physical mixed counterparts. For example, for the trial involving a weight ratio of lard to soybean oil equal to 50:50, the saturated FA, oleic acid, linoleic, and linolenic acid at the sn-2 position of the blend were varied from 59.3, 22.9 and 17.7 to 36.1, 17.7, and 39.3% after the CIE. Such a result suggested that the FA compositions on the glycerol backbone were changed

after the interesterification. This observation is generally in accordance with the result obtained by using CH₃ONa as a catalyst, but certainly some differences also exist.³⁴ As a consequence, the solid catalyst was shown to be active for the CIE of soybean oil and lard.

According to the literature,³² human milk fat showed 78.3% of saturated FAs, 12.8% oleic acid, and 9% linoleic and linolenic acid at the sn-2 position of TAGs, whereas the sn-1,3 positions were mainly occupied by unsaturated FAs. This unique TAG could improve the adsorption of FAs and calcium in infant bodies. Therefore, from a nutritional standpoint, the blends containing predominately lard (80:20 and 70:30) after the CIE were shown to have interesting distributions of FAs as a human milk fat substitute, because their main saturated FAs were located at the sn-2 position, whereas the unsaturated FAs were predominately presented at the sn-1,3 positions.

Triacylglycerol Composition. The TAG compositions of lard, soybean oil, and their binary blends before and after CIE are illustrated in Table 5. As observed, the most abundant TAGs in lard were StOL (33.8%), PStO (10.6%), StLL (9.2%), OLL (8.1%), PPO (7.8%), POL (6.1%), and OOL (5.1%). The soybean oil consisted of appreciable amounts of LLLn (25.3%), LLL (20.3%), OLLn (15.5%), PLL (11.7%), OLL (10.1%), and LLnLn (5.2%). A similar composition of TAGs in soybean oil and lard was previously described in the literature.^{35,36} The TAG species of the original mixtures varied when different weight ratios of lard to soybean oil were employed. As indicated in Table 4, some changes in the TAG composition of the blends were observed after the CIE compared to their physical blends. As an example, for the 60:40 blend the interesterified

Table 5. Triacylglycerol Compositions of Lard, Soybean Oil, and Binary Blends before and after Chemical Interesterification^a

TAG	LA	80:20		70:30		60:40		40:60		30:70		20:80		SO
		before	after	before	after	before	after	before	after	before	after	before	after	
LLnLn	0.0	0.5	0.6	0.9	1.1	1.5	1.8	2.7	2.9	3.4	2.8	4.5	2.2	5.2
LLLn	0.0	2.8	2.4	4.8	5.8	8.2	7.8	14.4	13.7	17.3	16.4	20.3	12.2	25.3
LLL	0.5	4.8	2.5	4.1	3.9	6.8	6.5	11.9	11.3	13.9	13.7	15.1	15.6	20.3
OLLn	0.5	0.3	2.7	4.0	3.9	5.9	5.8	9.4	9.1	11.0	10.9	13.2	11.4	15.5
PLLn	0.8	2.1	2.2	3.0	4.3	4.2	5.2	6.4	6.4	7.4	7.5	8.5	8.2	0.3
MLO	1.1	0.9	0.7	0.6	0.7	0.8	0.5	0.6	0.4	0.2	0.3	0.2	0.1	0.0
OLL	8.1	9.0	8.8	9.8	9.6	10.5	11.6	11.6	11.3	11.7	12.2	12.5	9.8	10.1
PLL	1.9	1.8	1.9	1.8	1.9	1.7	2.0	1.8	1.9	1.5	1.9	2.4	2.1	11.7
POO	2.2	2.5	2.4	2.8	2.8	3.8	3.0	3.1	3.2	3.6	3.5	4.5	3.8	1.4
OOL	5.1	21.3	22.8	21.9	23.5	18.6	19.3	1.3	1.4	1.6	2.4	2.7	2.2	3.3
OOM	1.4	1.3	1.5	2.8	2.5	3.5	3.1	4.1	3.2	2.6	2.3	2.5	2.1	0.0
POL	6.1	4.7	4.5	4.2	3.9	3.1	3.4	15.3	15.5	12.0	14.8	14.1	10.2	1.9
PPO	7.8	6.6	6.8	5.9	5.7	5.1	4.8	4.2	4.1	3.8	3.7	2.1	1.9	1.7
P _o PSt	1.7	1.6	1.5	1.4	1.2	0.9	0.7	0.6	0.8	0.7	0.5	0.4	0.2	0.0
StLL	9.2	7.0	6.5	6.3	6.4	5.3	5.3	3.3	3.5	2.7	3.4	2.0	3.8	3.5
OOO	3.3	2.8	2.9	2.6	3.2	2.4	1.6	1.8	2.2	1.7	2.6	2.1	2.9	0.4
StOL	33.8	32.6	30.3	28.7	24.8	22.7	18.4	14.4	15.2	10.0	14.3	8.1	15.2	0.6
PPL	3.2	0.9	1.5	0.8	0.9	0.7	1.2	0.5	0.6	0.5	0.4	0.4	0.3	0.3
PStO	10.6	3.5	3.8	3.1	3.7	2.5	2.1	1.5	1.9	1.3	2.2	1.1	2.7	0.0
PStSt	2.4	2.1	1.1	1.2	1.1	1.2	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ECN														
40	0.0	2.8	2.4	4.8	5.8	8.2	7.8	14.4	13.7	17.3	16.4	20.3	12.2	25.3
42	1.8	7.3	7.4	11.1	12.0	16.9	17.4	27.7	26.8	32.3	32.1	36.8	35.2	36.1
44	13.3	14.3	13.7	15.0	14.9	16.8	17.1	17.2	16.8	17.0	17.9	19.6	15.8	23.2
46	23.9	34.3	34.8	35.1	36.3	30.6	31.1	24.1	24.5	15.9	22.9	21.3	18.3	8.648
48	46.6	43.6	44.5	34.6	35.9	31.1	35.5	21.1	12.3	15.2	11.1	12.7	10.2	2.7

^aLA, lard; SO, soybean oil.

product showed that the proportions of the TAGs, such as LLnLn, PLLn, OLL, OOL, and PPL, were increased from 1.5, 4.2, 10.5, 18.6, and 0.7 to 1.8, 5.2, 11.6, 19.3, and 1.2% after CIE, whereas the proportions of the other TAGs in the same blend such as LLLn, POO, OOO, StOL, and PStO were found to reduce from 8.2, 3.8, 2.4, 22.7, and 2.5 to 7.8, 3.0, 1.6, 18.4, and 2.1%. Similar results were also reported for the CIE of palm stearin and palm kernel olein in different ratios from 20:80 to 80:20.³⁷

The TAG compositions of the samples, before and after interesterification, could be divided into different classes according to their ECN. The ECN value of TAGs is calculated as $ECN = cn - 2(db)$, where *cn* is the number of carbons in the constituent FA and *db* is the number of double bonds. As observed from Table 5, for the lard there was a high content of higher molecular weight TAGs with C46 and C48, whereas soybean oil showed a predominance of lower molecular weight TAGs with C40, C42, and C44. The physical blends were a mixture of lower and higher molecular weight TAGs. After the CIE, an increase in the C42 and C48 groups for 80:20, 70:30, and 60:40 blends and an increase in the C46 group for all samples except for the 20:80 blend were observed. Besides, the CIE reaction also resulted in a decrease in the C42 and C48 groups for the 20:80, 30:70, and 40:60 blends. This result showed that TAG compositions were changed during the interesterification reaction, implying that the solid base catalyst was active for the CIE reaction.

Slip Melting Point. The TAG compositions in the blends of lard and soybean oil can contribute to the melting and crystallization properties. The change degree of the physicochemical characteristics such as the SMP was significantly dependent on the altered TAG compositions. In this study, the heterogeneously catalyzed CIE was employed to change the physical properties of blends to produce *trans*-free fats with desirable functions. The SMP results obtained for all samples are listed in Table 6. As observed, these fat blends displayed

Table 6. Slip Melting Points of Binary Soybean Oil and Lard Blends before and after Chemical Interesterification^a

LA/SO	SMP (°C)	
	before CIE	after CIE
80:20	44.2 ± 0.1	39.7 ± 0.1
70:30	42.3 ± 0.0	37.8 ± 0.0
60:40	40.1 ± 0.1	36.5 ± 0.0
50:50	37.8 ± 0.1	33.2 ± 0.1
40:60	37.3 ± 0.0	31.3 ± 0.1
30:70	30.5 ± 0.0	26.2 ± 0.1
20:80	25.2 ± 0.1	22.2 ± 0.0

^aValues are the mean ± standard error. LA, lard; SO, soybean oil; CIE, chemical interesterification.

SMPs ranging from 22.2 to 39.7 °C, and the SMP was increased with increasing lard amount in the blends due to the high level of saturated FAs present in lard. The interesterified products had different SMPs depending on the proportions of lard and soybean oil in the blend. The SMPs for 70:30, 60:40, 50:50, and 40:60 blends after CIE were 37.8, 36.5, 33.2, and 31.3 °C, respectively. Interestingly, the interesterified blends tended to have lower values of the SMP for all samples as compared to their corresponding noninteresterified blends. The highest reduction in SMPs caused by the CIE was observed when the lard/soybean oil ratio was 40:60. The decrease in the

SMP of the interesterified blends could be due to the reduced amount of high-melting TAGs originating from the FA redistribution occurring during the CIE process. For example, the content of the trisaturated TAGs was observed to decrease after the CIE. Moreover, the melting range of the interesterified products was narrower than that of noninteresterified blends. This result can be considered as further evidence for the catalyst activity.

Melting and Cooling Characteristics. Generally, the change in TAGs caused by interesterification can be reflected in the DSC curves before and after interesterification. The DSC profiles of lard, soybean oil, and their blends before and after CIE are shown in Figures 6 and 7. It can be seen that the DSC

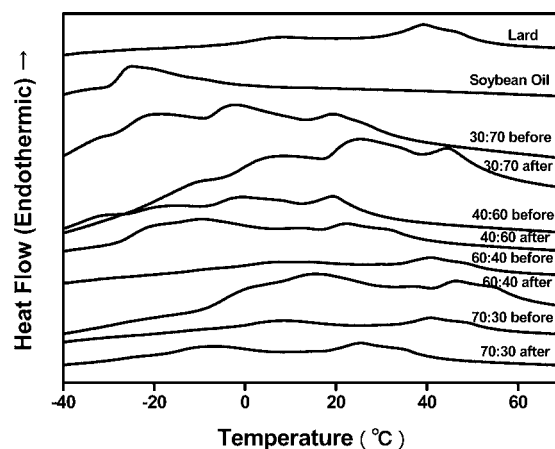


Figure 6. Differential scanning calorimetry heating thermograms of lard, soybean oil, and lard/soybean oil blends before and after chemical interesterification.

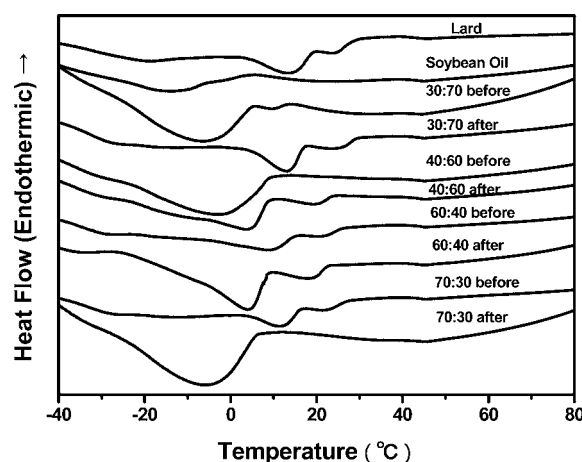


Figure 7. Differential scanning calorimetry cooling thermograms of lard, soybean oil, and lard/soybean oil blends before and after chemical interesterification.

curves of the final products were different depending on the different ratios of soybean oil to lard. The difference in thermal behaviors among the samples may be due to the different molecular species of their TAGs. As seen from Figure 6, the melting thermogram of lard was characterized by an endothermic peak at a temperature of 49 °C, resulting from the presence of high levels of higher melting TAGs. Besides, the soybean oil had few endothermic peaks, which were joined together to form a broad peak at lower melting temperatures

(−25 to −8 °C), mostly due to high levels of lower melting TAGs present in soybean oil. The broadening endothermic band with a wide temperature of melting process was attributed to the wide distribution of TAG compositions. In the case of lard and soybean oil blends (30:70 and 40:60) before CIE, there was one endothermic peak at a lower temperature range (approximately −15 to 5 °C), and the other peaks were observed at high temperatures (25–30 °C). These curves were correlated well with the combination of the thermograms of lard and soybean oil, suggesting that these blends were composed of the higher and lower melting TAGs. As the content of lard increased for the blends before the CIE, the peak areas at lower temperatures were decreased concurrently with the increase of peak areas at higher temperatures, and the endothermic peaks were found to shift to higher temperatures. Moreover, compared to the noninteresterified sample, the thermograms of the interesterified lard and soybean oil blends showed more endothermic peaks at the medium temperature range (approximately 20–40 °C). The decrease in higher and lower melting endothermic peaks indicated that the interesterification factually took place in the heterogeneous reaction process.

In the crystallization thermogram curves (Figure 7), lard exhibited two exothermic peaks at temperatures between 15 and 26 °C, whereas there was an obvious exothermic peak in the thermogram of the soybean oil at a temperature of −18 °C. From the crystallization thermogram profiles, two exothermic peaks were observed in the thermograms of lard and soybean oil blends before the CIE except for the 40:60 blend sample, where the first peak ranged from −10 to 15 °C and the second one appeared at 15–25 °C. After the interesterification, a significant change in the crystallization thermogram profile was observed between the interesterified and noninteresterified samples. All of the interesterified blends tended to exhibit exothermic peaks at temperatures between −5 and 15 °C, and fewer peaks at lower and higher temperatures were observed in the DSC curves for the interesterified product as compared to noninteresterified samples. This result showed that the interesterified product contained more medium molecular weight TAGs than the original blends, suggesting that the exchange of FAs on the glycerol backbone could be conducted during the interesterification with a variation in physicochemical properties of the interesterified product.

In conclusion, a new heterogeneous catalyst, SBA-15- $\text{pr-NR}_3\text{OH}$, was prepared and used as a heterogeneous catalyst for the interesterification of lard and soybean oil. All of the characterization results of the solid catalysts indicated the successful anchoring of organic base on the framework channel of mesoporous SBA-15 materials. Binary blends of lard and soybean oil were interesterified using the solid base catalyst. From the HPLC analysis and sn-2 positional analysis results, the CIE could result in the rearrangement of FAs in TAG species. The interesterified products displayed lower values of SMPs when compared with the blends before CIE. Analysis of the results of melting and cooling characteristics showed a significant change in the thermal properties after the interesterification process.

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Funding

This work was financially supported by research grants from the National Natural Science Foundation of China (Project 21276066).

Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

CIE, chemical interesterification; EIE, enzymatic interesterification; AOCS, American Oil Chemists' Society; DSC, differential scanning calorimetry; IV, iodine value; TG, thermogravimetric analysis; FT-IR, Fourier transform infrared; SMP, slip melting point; TAG, triacylglycerol; FA, fatty acid; LDL, low-density lipoproteins; HDL, high-density lipoproteins; HPLC, high-performance liquid chromatography; GC, gas chromatography; TEOS, tetraethylorthosilicate; TMAOH, tetramethylammonium hydroxide; BET, Brunauer–Emmett–Teller; BJH, Barrett–Joyner–Halenda; TLC, thin-layer chromatography; FAME, fatty acid methyl ester; 2-MAG, 2-monoacylglycerol; P, palmitic acid; P_O, palmitoleic acid; O, oleic acid; L, linoleic acid; St, stearic acid; Ln, linolenic acid

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