

Chemical Modification of Partially Hydrogenated Vegetable Oil to Improve its Functional Properties for Candles

Liping Wang · Tong Wang

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Abstract Partially hydrogenated vegetable oil (PHVO) has recently been used to make vegetable oil-based candles. However, its use is limited primarily to container candles because of its inherent physical properties, such as brittleness when a hard material is produced, and greasiness when it is soft by low degree of hydrogenation. Such material lacks the most desired cohesiveness and elasticity compared to the commercial petroleum paraffin and beeswax. To improve the cohesiveness and thermal properties of PHVO, epoxidation, ring-opening reaction, and esterification were conducted to introduce new functional groups into the fatty acyl chain of PHVO. These newly synthesized derivatives or waxes were also mixed with the fully hydrogenated soybean oil (FHSO) or PHVO base materials. Hardness and cohesiveness of the new waxes and the mixtures were measured with a texture analyzer. Their thermal properties were analyzed with a differential scanning calorimetry (DSC). It was found that the introduction of hydroxyl (OH) group significantly improved the cohesiveness of PHVO. The melting range of PHVO also increased after the reactions. However, the hardness of the new wax was lower than those of commercial paraffin wax or beeswax. For wax mixtures, the hardness of dihydroxy wax was significantly improved by the addition of FHSO, however, the cohesiveness was negatively affected by the amount of FHSO added. Both the melting and the crystallization ranges were widened by mixing the derivatives with the base materials.

Keywords Candles · Cohesiveness · Crystallization · Epoxidation · Hardness · Melting point · Partially hydrogenated vegetable oil

Introduction

Petroleum paraffin wax is used in most commercial candles. It is the by-product from fractionation and refining of the fossil fuel crude oil. Although candles made from paraffin wax are typically inexpensive, consumers are becoming more interested in using products that are from domestic and renewable sources. Fats of animal origin have long been used for making candles, but such candles are typically of lower quality because of the greasy texture, rancid odor, and sooting during burning. Partially hydrogenated vegetable oil (PHVO) may provide a promising replacement of petroleum wax and the traditional tallow wax because of its more desirable environmental and combustion properties [1]. However, the inherent chemical structure and physical properties of PHVO limit its wide use in making variety types of candles. For example, it may be either too greasy or too brittle depending on the degree of hydrogenation, and it lacks the cohesiveness that petroleum wax and beeswax possess [2]. Few researches have been reported on fundamental improvement of crystallization and textural properties of PHVO by chemical modification, although various formulations have been made to suit particular applications. Currently, candles made from PHVO are primarily the container type. By modifying the physical properties, the derivatized material may be used in making other forms of candles. The new materials with increased cohesiveness are also expected to replace paraffin in other applications, such as coating waxes.

L. Wang · T. Wang (✉)
Department of Food Science and Human Nutrition,
Iowa State University, 2312 Food Sciences Building,
Ames, IA 50011-1061, USA
e-mail: tongwang@iastate.edu

The main defect of PHVO as candle material is its poor elasticity or cohesiveness, also referred to as kneadability, compared to beeswax or paraffin wax. This may be attributed to the highly homogeneous molecular composition of the PHVO. The introduction of branched structure on the acyl chain may lead to stronger intermolecular interaction and discourage ordered structural packing and crystallization. Therefore, we hypothesized that if we add side chain or functional groups to the triacylglycerol structure, the cohesiveness of the material will increase.

Theoretically, we could synthesize true wax, the structure of beeswax which is esters of long chain fatty acids and long chain alcohols with minor component of free long chain fatty alcohols. Such esterification reaction requires a large excess amount of long chain alcohols so the reaction would be expensive. In addition, the separation of the product from the long chain alcohols can be difficult and cost prohibitive. Whereas, chemical modification of on the triacylglycerol acyl chain is quite feasible. The epoxidation of double bonds of vegetable oil is a well-developed reaction in the paint and plastic industries [3]. The further ring-opening reaction of the epoxide can introduce hydroxyl groups and other functional groups can then be added onto the triacylglycerol molecules to increase the intra- and inter-molecular interactions. The di-hydroxy groups can be reacted with acid to form ester side chains.

We also hypothesized that when the newly synthesized fats or waxes are incorporated into the base material, they will interfere with the crystal network formation thus improving the cohesiveness or plasticity of the mixture. Therefore, the objectives of this research were to chemically modify the PHVO, and to evaluate the physical properties of the synthesized products alone and when they are used in combination with the base fat materials.

Experimental Procedures

Materials

A commercial PHVO with 27.9% palmitic, 24.1% stearic, and 48.0% oleic acids (referred to as KLX in this report) was provided by Loaders Croklaan (Channahon, IL, USA) and fully hydrogenated soybean oil (FHSO) (11.6% palmitic and 88.4% stearic acids) was obtained from Uniqema (Chicago, IL, USA). Beeswax was provided by Strahl & Pitsch Inc. (West Babylon, NY, USA). Commercial paraffin (Cparaffin) candles were purchased from a local grocery store. Commercial soywax (Csoywax) was provided by Soyawax International (Cedar Rapids, IA, USA).

Hydrogen peroxide (H₂O₂, 30% aq.), glacial acetic acid, perchloric acid (70% aq.), acetic anhydride, potassium hydroxide, hydrogen bromide (40–48% aq.), ammonium

chloride, and organic solvents were from Fisher Scientific (Pittsburgh, PA, USA). Butyric anhydride, Amberlite IR-120 H, dimethylaminopyridine (DMAP), and triethylamine (Et₃N) were all purchased from Sigma-Aldrich (St. Louis, MO, USA).

Epoxidation of KLX

The method reported by Park et al. [4] was used for the synthesis of epoxidized KLX (EPKLX) with or without the presence of solvent. The KLX (121 g, 0.14 mol), glacial acetic acid (7.8 g, 0.13 mol), and the catalyst Amberlite IR-120 H (25 g) were placed in a round-bottomed, three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The mixture was heated to 55 °C, then 30% aq. H₂O₂ (23.8 ml, 0.21 mol) was added dropwise from a separatory funnel and the reaction was allowed to remain at 55 °C for 7 or 24 h. After the reaction was complete, the crude product was filtered immediately to remove the catalyst. The liquid was washed with hot distilled water several times till the pH was approximately 7.0. When the reaction was conducted with solvents, such as benzene, hexane, and acetonitrile (40 mL), the solvent was removed with a vacuum evaporator. To calculate the epoxide conversion rate, the oxirane oxygen value was measured using the standard method AOCS Cd9–57 [5], and the calculated oxirane oxygen was based on the oleic acid content. Therefore,

$$\text{Epoxide conversion, \%} = \frac{\text{Measured oxirane oxygen}}{\text{Calculated oxirane oxygen}} \times 100$$

In this study, sulfuric acid was also tested as a catalyst in the non-solvent reaction system because it is a cheap and readily available catalyst. The amount of sulfuric acid added was 0.1% of KLX.

Ring-Opening Reaction of EPKLX

A ring-opening reaction was conducted to produce dihydroxy EPKLX (OHKLX) using the method reported by Sharma et al. [6] with modification. The reaction was carried out by refluxing EPKLX in perchloric acid (2% of EPKLX) aqueous solution at 95 °C. Perchloric acid was added drop-wise under constant stirring. Two reaction parameters, time and amount of water, were examined. Samples were taken at various reaction times (0–48 h) to determine optimal time for the reaction when water to EPKLX ratio of 20 was used. The other factor examined was the water to EPKLX ratio (0.8–20) at 16 h of reaction. The optimal conditions were used to synthesize a large

quantity of OHKLX for testing the physical properties and for further reactions.

The OH values of OHKLX were measured to monitor the reaction using the AOCS official method Tx 1a-66 [5].

Esterification of OHKLX with Butyric Acid Anhydride

To synthesize butyric ester of OHKLX (BuoKXLX), OHKLX (0.1 mol) was dissolved in dry methylene chloride (CH_2Cl_2 , 100 ml) and stirred at ambient temperature. Butyric anhydride (0.4 mol) was added followed by 4-dimethylaminopyridine (DMAP) (0.01 mol) as a catalyst and tri-ethylamine (0.4 mol) as base. After 6 h, the reactants were quenched with saturated aqueous NH_4Cl and the mixture washed with water. The solvent was removed by rotary evaporation.

Structural Confirmation by NMR

The structure of the synthesized waxes was characterized using a Varian VXR 400 NMR instrument (Varian, Palo Alto, CA, USA) with a Bruker Magnet (Bruker BioSpin, Billerica, MA, USA). ^1H NMR (400 MHz, CDCl_3): KLX, $\delta = 5.3$ ppm (3H, $-\text{CH}=\text{CH}-$), $\delta = 5.23$ ppm (1H, $-\text{CH}_2-\text{CH}-\text{CH}_2$ of glycerol backbone); EPKLX, $\delta = 2.6$ – 2.9 ppm (3H, epoxy group), $\delta = 2.3$ ppm (6H, $\text{O}=\text{C}-\text{CH}-$), $\delta = 5.23$ ppm (1H, $-\text{CH}_2-\text{CH}-\text{CH}_2$ of glycerol backbone); OHKLX, $\delta = 3.5$ ppm (2.6H, $\text{OH}-\text{HC}-\text{HC}-\text{OH}$); BuoKXLX, $\delta = 5.23$ ppm (1H, $-\text{CH}_2-\text{CH}-\text{CH}_2$ of glycerol backbone), $\delta = 5.0$ ppm (2.7H, $\text{CH}-\text{OOCCH}_3$). ^{13}C NMR (400 MHz, CDCl_3): KLX, $\delta = 130$ ppm ($\text{C}=\text{C}$); EPKLX, $\delta = 58.5$ ppm (epoxide group); OHKLX, $\delta = 73$ – 75 ppm ($\text{OH}-\text{C}-\text{C}-\text{OH}$); BuoKXLX, $\delta = 172$ ppm ($-\text{OCOC}_3\text{H}_7$).

Observation of Fat Crystal Properties by Polarized Light Microscopy

The microstructure of the waxes was observed using Polarized Light Microscopy (PLM). In order to erase the crystal memory of waxes, samples were heated in an oven at 85°C for 30 min. The glass microscopy slides and capillary tubes were also preheated in the oven at 85°C . A small amount of melted wax (about 50 μL) was placed on a preheated glass slide. A second preheated glass slide was slipped over to produce a film with uniform thickness. Bubble entrapment was avoided during the slide preparation. The prepared slides were stored at room temperature until use. The slides were analyzed with a Zeiss Axioskop upright microscope (Carl Zeiss, Thornwood, NY, USA). A 20X Neofluar dry objective with numerical aperture

($\text{NA} = 0.50$) was chosen in the imaging mode. A dry turret condenser ($\text{NA} = 0.9$) was used for differential interference contrast (DIC) microscopy. Images were acquired with a camera system and presented with Adobe Photoshop software.

Hardness and Cohesiveness Measurements

The most important physical or textural properties to be modified and measured in this research are hardness and elasticity or cohesiveness which is the ability to deform under applied force [7]. To measure the hardness and cohesiveness of waxes, a TA.XT2i Texture AnalyzerTM (Stable Micro Systems, Godalming, UK) was used with a TX plate probe to measure the force during compression. The parameters of the method are as follows: pre-test and post-test speed of 2.0 mm/s, probe movement speed of 0.5 mm/s, and compression distance of 2.0 mm. Bulk waxes and wax mixtures were individually melted at 80°C and formed into 13.8 mm \times 5 mm (diameter \times thickness) sample disks using the bottom plate of a tube rack as a mold. The disks were stored at 4°C for 24 h before use. The highest compression force was taken as the hardness measurement. The rate of deformation (slope of the curve, after reaching the peak) and the force ratio between the lowest and the highest points (valley to peak ratio, VTP) during deformation were used as the cohesiveness or brittleness measurement of the wax. The lower the value of the slope and the higher the value of VTP ratio, the more cohesive the material is. Two batches of wax materials were prepared and three wax discs were made from each material for triplicate sample measurements.

Melting and Crystallization Properties

A differential scanning calorimeter (DSC 6200, Seiko Instruments, Inc., Shizuoka, Japan) equipped with a cooling controller using liquid N_2 was used to measure melting and recrystallization properties. A wax sample of 6.0–9.0 mg was used. The temperature program reported by Rezaei et al. [2] was adopted in this experiment. Briefly, an initial 2 min hold at 30°C was followed by $30^\circ\text{C}/\text{min}$ heating to 90°C and with a second 5 min hold at 90°C . Then the sample was cooled to -20°C at $10^\circ\text{C}/\text{min}$ rate with a 10 min hold at -20°C . Heating was applied at a $10^\circ\text{C}/\text{min}$ rate to 90°C . The data collected in the last two steps were used to analyze the crystallization and melting properties of the waxes. Each sample was measured once, and all treatments (individual waxes or mixtures) were duplicated.

Effect of the Newly Synthesized Waxes on the Physical Properties of the Base Materials

OHKLX was mixed with individual KLX and FHSO in weight percentages from 0 to 100. Similarly, BuoKLX was also mixed with individual KLX and FHSO. Each mixing and formulation was performed in duplicate. All physical and thermal properties described above were evaluated for these samples.

Statistical Analysis

ANOVA of the Statistical Analysis System (SAS) 9.1 (SAS institute, Cary, NC, USA) was used for data analysis [8]. The mean and standard deviation were determined and presented.

Results and Discussion

Synthesis of EPKLX

In commercial epoxidation processing of soybean or other oils, hydrogen peroxide is reacted with formic acid without a catalyst if hydrogen peroxide is concentrated (50–70%), or with acetic acid using a strong acid as a catalyst [3]. The two most common catalysts for peroxyacetic acid formation are sulfuric acid and cross-linked polystyrene sulfonic acid cation-exchange resins. Sulfuric acid is the cheapest catalyst used on a commercial scale. However, it causes molecular cleavage and waste disposal problems [3]. Acidified cation exchange resin can be removed by filtering after the reaction and can be recycled on a large scale reaction. Solvents are not ordinarily used in industry scale production. But in most reported epoxidation reactions, benzene and toluene are widely recommended as dilute agents, particularly when sulfuric acid is used as the catalyst [4, 9]. Any amount of solvent residue may be a toxic emission during candle burning or when the material is used for other purposes, therefore, a solvent is not desirable in this reaction.

In this study, three solvents and two catalysts were selected and compared, and the oxirane value was determined to optimize the epoxidation reaction (Table 1). When Amberlite IR-120H was used as the catalyst, the highest epoxide conversion (98.4%) was obtained in a non-solvent system, whereas a 90.3% conversion was obtained using the method reported by Park et al. (2004), in which benzene was used as the solvent or dilute agent. The epoxide conversion was only 79.4% using sulfuric acid as a catalyst in a non-solvent system. Hexane and acetonitrile were also used to replace benzene, however, the epoxide

Table 1 Epoxidation reaction of KLX with different solvent and catalyst

Catalyst	Solvent	Reaction time (h)	Conversion (%)
Amberlite IR-120H	Benzene	7	90.3
	Hexane	7	49.2
	Acetonitrile	7	62.7
	Acetonitrile	24	87.0
	No solvent	7	98.4
Sulfuric acid	No solvent	7	79.4

conversions were both lower than that of benzene after 7 h of reaction. This result may be due to the slower reaction rate because the epoxide conversion increased by 25% as the reaction time was extended to 24 h using acetonitrile as solvent.

Swern (1971) reviewed the industrial procedures of epoxidation of soybean oil and pointed out that solvent was generally not required in epoxidation reactions utilizing ion-exchange-resin catalysts. In this study, EPKLX was prepared on a large scale using Amberlite IR-120H as the catalyst in a non-solvent system. The oxirane oxygen value of this product was $2.35 \pm 0.02\%$. The oxirane conversion was $98.4 \pm 0.8\%$. ^1H NMR of EPKLX also showed that the epoxidation reaction was practically complete. The C=C ($\delta = 5.3$, 3H) disappeared and epoxide group ($\delta = 2.6$ – 2.9 ppm, 3H) was produced.

Synthesis of OHKLX

The oxirane ring is more reactive than C=C and can be hydrolyzed into two OH groups in a hot acidic solution. In the method reported by Sharma et al. [6], epoxidized vegetable oil was reacted with a large amount of water (20:1, water: EPKLX, wt/wt) at 100 °C for 48h using perchloric acid as the catalyst. To improve the reaction efficiency, the reaction time and amount of water were optimized in this study. The OH values of products were measured to monitor the reaction. The OH value of OHKLX was at its highest at 16 h, and then decreased after prolonged reaction (data not shown). The longer reaction time may have caused molecular cleavage under the hot acidic conditions [10]. By comparing the ^1H -NMR data of individual OHKLX samples, the hydrogen number at $\delta = 3.5$ ppm (OH–HC–HC–OH) was lower for the 48-h product (2.3H) than for the 16-h product (2.6H). The OH value decreased considerably as the amount of water was reduced to below about five times the amount of EPKLX (data not shown). The difference in the concentration of perchloric acid may partially account for such a result. As a strong oxidizing agent, perchloric acid at high

concentration might enhance the degradation of the newly formed OH group.

In the method reported by Sharma et al. [6], chloroform was used to extract the organic material. Such a toxic solvent has to be completely removed after the extraction. It took a considerable amount of time to remove the solvent from OHKLX and it foamed during the process. In our preliminary experiment, we also found that the OH value and viscosity of the final product decreased as OHKLX was evaporated with the solvent at high temperature (80 °C) for a long time. The possible reason is the degradation of the OH group when heated. In this study, washing with water and crystallization in cold water were used to avoid the use of a solvent and any side reaction and for improved production efficiency.

Synthesis of BuoKXLX

Sharma et al. [6] synthesized the butyric ester of dihydroxy soybean oil in pyridine, which was used as both the solvent and the base catalyst. The odor from any residual pyridine would make this process highly unsuitable for candle application. In this experiment, methylene chloride was used as the solvent and DMAP as the catalyst. The butyric anhydride complexed with DMAP to form an acyl pyridinium ion, which was the reactive acyl group. Reaction of the hydroxy group and acyl pyridinium ion regenerated DMAP and formed the ester plus a butyric acid which was

neutralized by Et₃N. The esterification reaction was terminated by adding aqueous NH₄Cl which is a weak acid used to neutralize the excess amount of Et₃N. A soft yellowish product was produced by this process. The reaction was complete as suggested by NMR data. The peak for OH–HC–HC–OH at $\delta = 3.5$ ppm disappeared whereas the peak for –CH–OCC₃H₇ at $\delta = 5.0$ ppm was observed after the reaction.

Observation of Wax Crystallines by Polarized Light Microscopy (PLM)

PLM images were captured to compare the crystallization of the waxes (Fig. 1). FHSO had the most ordered crystallization. Beeswax had a fine and somewhat random crystallization. KLX and EPKLX had more ordered crystallization than Csoywax. Csoywax seemingly had a similar image to beeswax, but it is much softer and has a lower-melting point. After EPKLX is hydrolyzed to give hydroxy derivatives, the OHKLX had much finer and more random crystallization than the EPKLX, and it had similar image as that of beeswax. Few studies have been reported on PLM images of fats and waxes. Edwards [11] studied the crystal habit of paraffin wax. Dorset [12, 13] demonstrated that beeswax had a disordered lamellar interface. Although PLM does not provide quantitative and definitive comparison among materials from different sources and with a wide melting range, it does give a

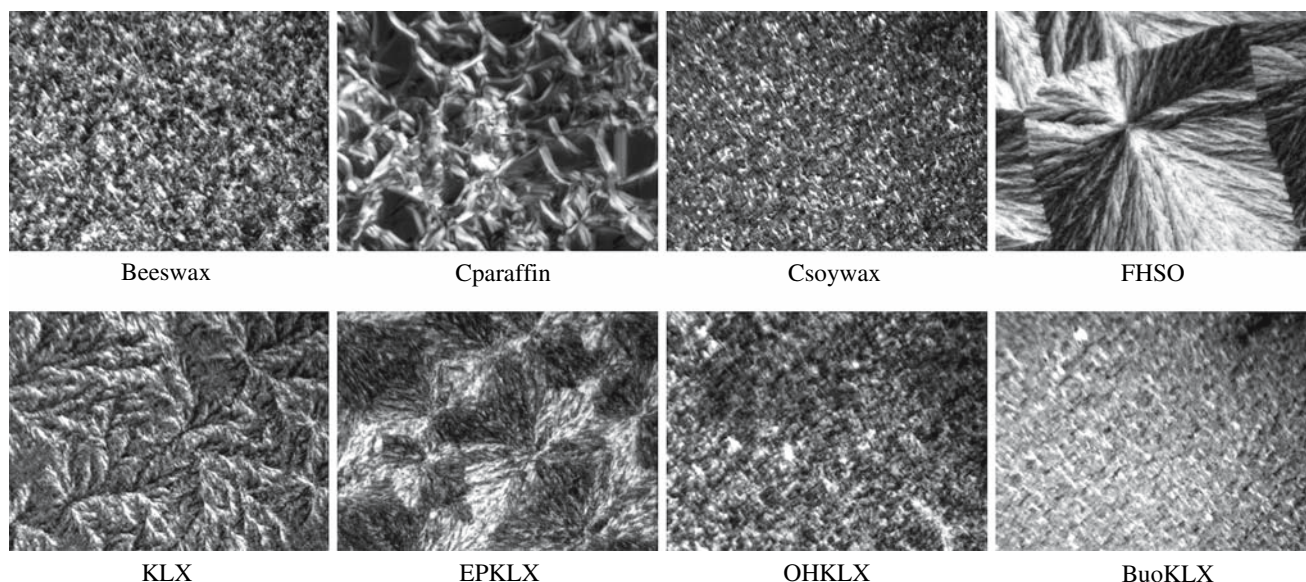


Fig. 1 Polarized light microscopic (PLM) images of selected waxes. *Cparaffin* commercial paraffin wax; *Csoywax* commercial soybean wax; *FHSO* fully hydrogenated soybean oil; *KLX* partially hydrogenated

vegetable oil; *EPKLX* epoxidized KLX; *OHKLX* ring-opened EPKLX; *BuoKXLX* butyric ester of OHKLX

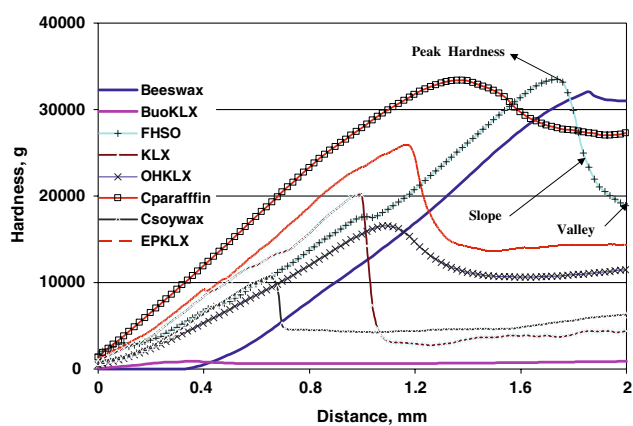


Fig. 2 Deformation profiles of waxes measured by a texture analyzer. See Fig. 1 caption for abbreviations

visual microscopic observation that may relate to the wax's physical properties.

Hardness and Cohesiveness

The hardness and deformation properties of bulk waxes are shown in Figs. 2 and 3. The peak value of the deformation curve in grams was used to represent the hardness of the waxes (Fig. 2). Because our wax samples were hard and brittle, their cohesiveness could not be determined with the cone penetrometry method as used in the measurement of the rheological properties of cheese or butter [14]. In our plate compression method, the ratio between the valley value (lowest force) and the peak value (VTP ratio) and the absolute value of the slope (the deformation rate) in grams per millimeter provide a good comparison for cohesiveness and brittleness among the wax samples from our preliminary evaluations (Fig. 2) because they correlated with direct hand touch evaluation. A wax having a higher VTP ratio and lower slope value is more cohesive and less brittle than a wax with a lower VTP ratio and higher slope.

Hardness was significantly different among the eight wax samples (Figs. 2, 3). FHSO had the hardest texture whereas BuoklX, having semi-solid texture, was the softest wax. Cparaffin wax and beeswax were harder than Csoywax, KlX, and the synthesized waxes. EPklX had intermediate hardness which was greater than those of OHklX and KlX. OHklX was significantly softer than Cparaffin wax, beeswax, and KlX, but it was harder than Csoywax. Brittleness and cohesiveness also varied significantly among waxes (Fig. 3). Cparaffin and beeswax had higher compression force for longer time than other waxes (low slope and high VTP ratio values). Csoywax and KlX, however, were deformed with the least compression in shortest time (high slope and low VTP ratio

values). The synthesized waxes OHklX and BuoklX broke down much slower (low slope and high ratio values) than other triacylglycerol type of materials. The slope and VTP ratio data shown in Fig. 3 indicate that OHklX has much improved cohesive properties compared to the unmodified vegetable waxes. If a more saturated material was used for the derivatization reaction, the hydroxy product will be harder. In addition, if a longer chain acid was used to synthesize the esters, the hardness of the ester will be higher. Thus, these reactions provide much promise for producing modified waxes with desired properties.

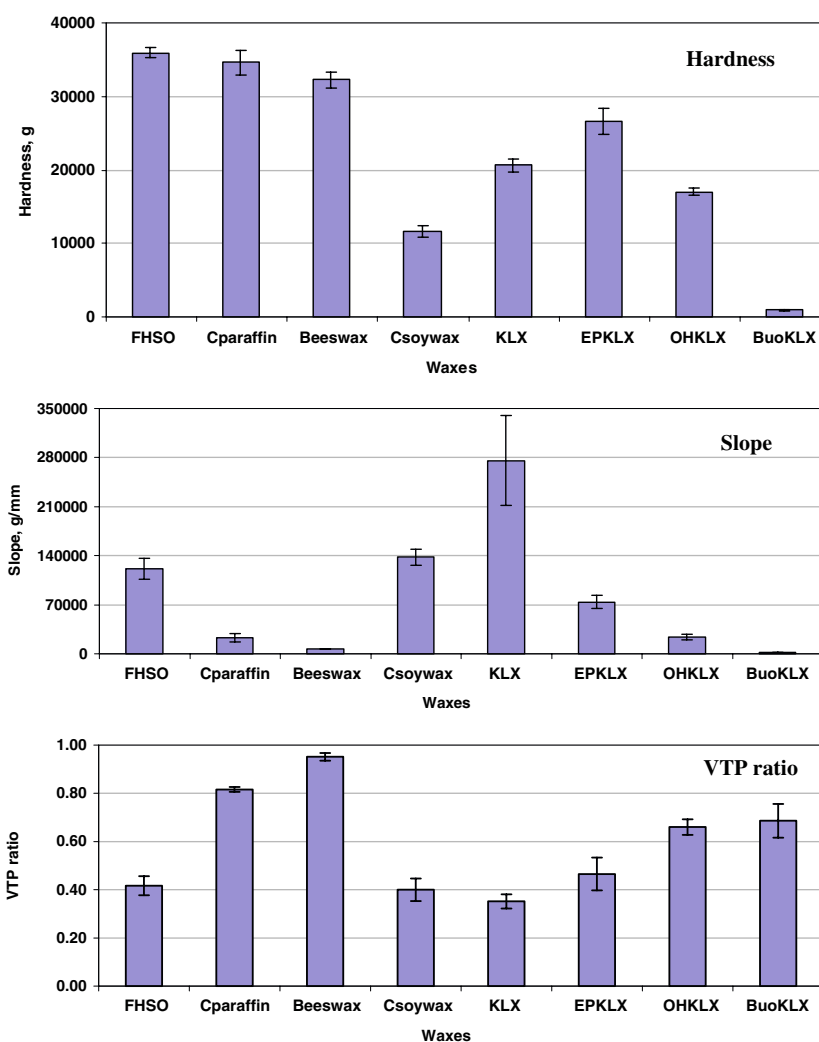
OHklX and BuoklX have proved to be possible components for candle-making since they had better cohesiveness than the unmodified KlX. However, they lack the proper hardness when used alone. To improve the hardness of the newly synthesized materials, FHSO and KlX were mixed with the two modified waxes individually. Hardness, slope, and VTP ratio were measured to evaluate the textures of the mixtures (Fig. 4). The hardness of the OHklX was significantly affected by the addition of FHSO, but it was not as significantly affected by the addition of KlX. The hardness of BuoklX was significantly improved by the addition of both FHSO and KlX. The addition of FHSO into OHklX or BuoklX increased the hardness of mixtures more significantly than the addition of KlX to the two modified waxes.

The cohesiveness of the synthesized waxes considerably decreased with the addition of FHSO or KlX. The slopes of OHklX and BuoklX with added FHSO increased much slower than those with added KlX. This suggests that to increase hardness and at the same time keep the low slope value (high cohesiveness), FHSO can be effectively used. Similarly, for the VTP ratio, adding FHSO to OHklX and BuoklX led to a slower decrease in the VTP ratio than adding KlX to the two newly synthesized materials. Therefore, using FHSO in combination with OHklX or BuoklX will produce a wax material with proper hardness and cohesiveness. Both of these two properties should be considered when formulating wax materials for candles. From our study, the proper formulation should be about 60% OHklX with 40% of FHSO for a hard wax. A mixture with about 70–90% of OHklX and 10–30% of KlX will have hardness similar to Csoywax, and its cohesiveness should be significantly better than that of Csoywax.

Melting and Crystallization Properties

The melting and crystallization profiles of KlX and its derivatives are shown in Fig. 5. From the profiles, it seems the EPklX did not have significantly altered thermal

Fig. 3 Textural properties of bulk waxes. See Fig. 1 caption for abbreviations



properties compared to KLX, however, the BuoK LX had much lower melting and crystallization temperatures.

The temperatures of onset, peak, and completion of both the melting and crystallization peaks were measured. The temperature range of these peaks and the endothermic and exothermic energy (ΔH) were also calculated and these results are presented in Table 2 and Fig. 6. Cparaffin and Beeswax absorbed and released more energy than others. The absorbed heat of Cparaffin, Beeswax, EPK LX, and FHSO during melting was similar to their released heat during crystallization. However, KLX, Csoywax, OHK LX, and BuoK LX needed more energy for melting than the energy released in crystallization. This may indicate that these materials do not crystallize as well and as fast as EPK LX and FHSO do, and crystallization may have continued during the low temperature treatment and storage. BuoK LX had the least energy exchange in a melting and recrystallization cycle, suggesting the most disordered crystalline packing. These energy data may provide insight

about how easy the wax material will be melted to supply fuel for burning of candles and how readily the wax will solidify so it will not cause excessive dripping as seen in some vegetable oil candles.

As shown in Table 2, Csoywax had the lowest melting peak temperature while FHSO had the highest compared with KLX, EPK LX, and OHK LX. The melting peak temperature of BuoK LX was significantly lower than others, which agreed with the study reported by Sharma et al. [6]. They found that the butyric ester of epoxidized soybean oil could be used as a lubricant with a very low pour point.

The temperature range during melting and crystallization were also significantly different among paraffin wax, beeswax, Csoywax, and the synthesized waxes (Fig. 6). Beeswax had the widest melting range (62 °C for melting and 58 °C for crystallization) while FHSO had the narrowest range (17 °C for melting and 14 °C for recrystallization). The temperature ranges of Csoywax, KLX,

Fig. 4 Hardness and cohesiveness/brittleness of wax mixtures. The number on the X axis is the percentage of the modified waxes (OHKLX and BuoKLX) in the mixture. Four series of mixtures are presented. See Fig. 1 caption for abbreviations

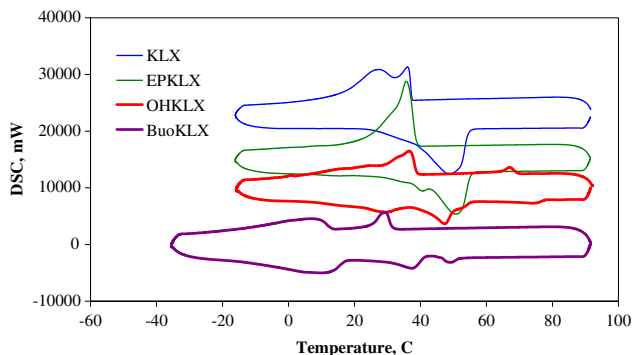
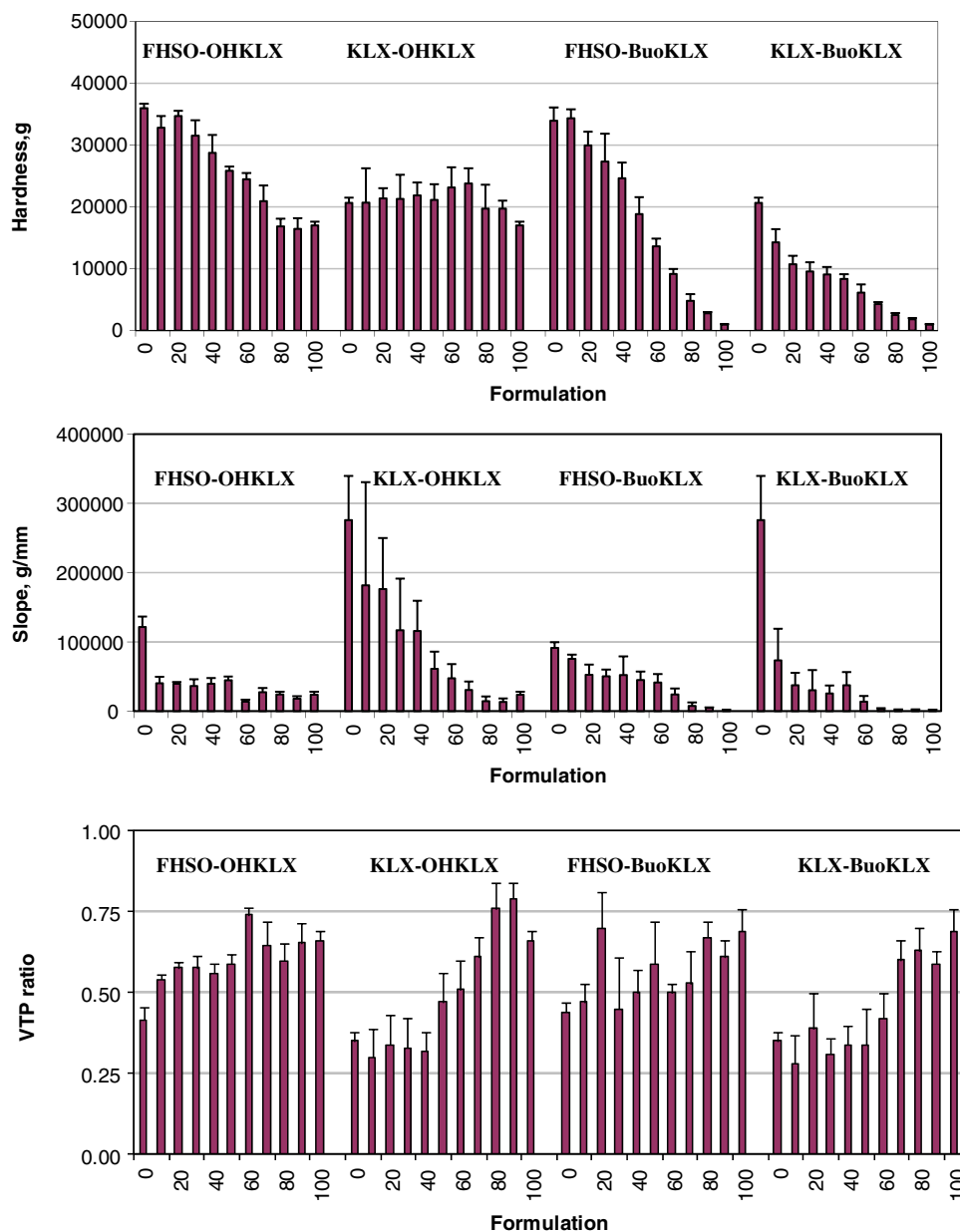


Fig. 5 DSC profiles of KLX, epoxidized KLX (*EPKLX*), hydroxy KLX (*OHKLX*), and butyl ester of *OHKLX* (*BuoKLX*)

EPKLX, and OHKLX were similar during melting, and they seem to be slightly wider than the range of Cparaffin. A proper melting and crystallization range is desired for liquid fuel formation and its containment. Candles made from materials with a narrow melting range and high onset melting temperature tended to form holes or leaky channels which have been observed in FHSO. Meanwhile, candle with low onset melting temperature, such as very soft soywax, had dripping problems. Typically, material with a wide melting range is desirable for candle-making.

The melting and crystallization profiles of selected formulation mixtures are shown in Fig. 7. The mixing of FHSO and KLX with OHKLX and BuoKLX led to increases in temperature range for both melting and

Table 2 Melting and crystallization of bulk waxes (the first line of individual wax is the data for the main peak)

Wax	Melting							Crystallization						
	ΔH , mJ/mg	Peak temp, °C	Onset temp, °C	Complete temp, °C	Temp range, °C	ΔH , mJ/mg	Peak temp, °C	Onset temp, °C	Complete temp, °C	Temp range, °C				
Beeswax	195.5 ± 0.5	65.1 ± 0.3	11.5 ± 1.6	73.7 ± 0.0	62.2 ± 1.6	197.8 ± 0.0	59.9 ± 0.1	63.0 ± 0.6	4.8 ± 0.1	58.3 ± 0.6				
Cparaffin	206.6 ± 1.9	62.7 ± 0.4	30.2 ± 0.4	68.9 ± 1.0	38.8 ± 0.6	212.6 ± 4.2	56.4 ± 0.4	61.1 ± 0.2	27.3 ± 0.4	33.8 ± 0.1				
Csoywax	110.6 ± 3.0	46.6 ± 0.6	14.9 ± 1.2	55.0 ± 1.3	40.2 ± 2.5	80.9 ± 2.8	32.6 ± 0.2	42.8 ± 0.2	-2.3 ± 0.4	45.1 ± 0.6				
FHSO	78.9 ± 13.9	55.8 ± 0.5	42.5 ± 0.9	59.6 ± 0.4	17.1 ± 1.3	140.2 ± 6.6	48.2 ± 0.8	51.0 ± 1.1	37.1 ± 0.1	14.0 ± 1.2				
KLX	77.6 ± 11.7	65.2 ± 0.4	59.6 ± 0.4	71.9 ± 1.1	12.4 ± 0.8	100.3 ± 2.7	35.7 ± 0.3	38.0 ± 0.0	2.1 ± 1.8	36.0 ± 1.8				
EPK LX	119.1 ± 0.4	48.6 ± 0.4	20.3 ± 1.6	58.4 ± 0.0	38.1 ± 1.6	94.6 ± 3.2	36.3 ± 0.8	40.1 ± 1.5	13.1 ± 0.4	27.1 ± 1.1				
OHK LX	99.1 ± 2.4	51.6 ± 1.3	8.2 ± 0.6	58.4 ± 1.8	50.2 ± 2.4	73.6 ± 3.2	35.8 ± 0.8	40.0 ± 1.5	-1.9 ± 0.4	41.8 ± 1.1				
BuoK LX	79.7 ± 2.4	46.7 ± 1.3	7.4 ± 0.6	56.2 ± 1.8	48.8 ± 2.4	4.9 ± 0.1	68.4 ± 1.9	72.3 ± 1.3	59.7 ± 5.0	4.9 ± 6.3				
	6.9 ± 0.3	75.7 ± 0.8	57.9 ± 0.6	79.8 ± 0.4	21.9 ± 0.1	33.6 ± 0.6	7.4 ± 0.8	14.2 ± 0.2	-27.4 ± 1.1	41.5 ± 1.3				
	38.9 ± 0.8	10.8 ± 2.3	-26.2 ± 0.6	19.3 ± 0.6	45.5 ± 1.1	14.0 ± 2.4	30.8 ± 1.8	35.8 ± 1.7	14.2 ± 0.2	21.7 ± 1.9				
	23.4 ± 3.3	37.9 ± 0.8	19.3 ± 0.6	41.8 ± 0.6	22.5 ± 1.2									
	13.6 ± 2.6	49.7 ± 0.2	43.0 ± 1.1	56.6 ± 3.1	13.6 ± 4.2									

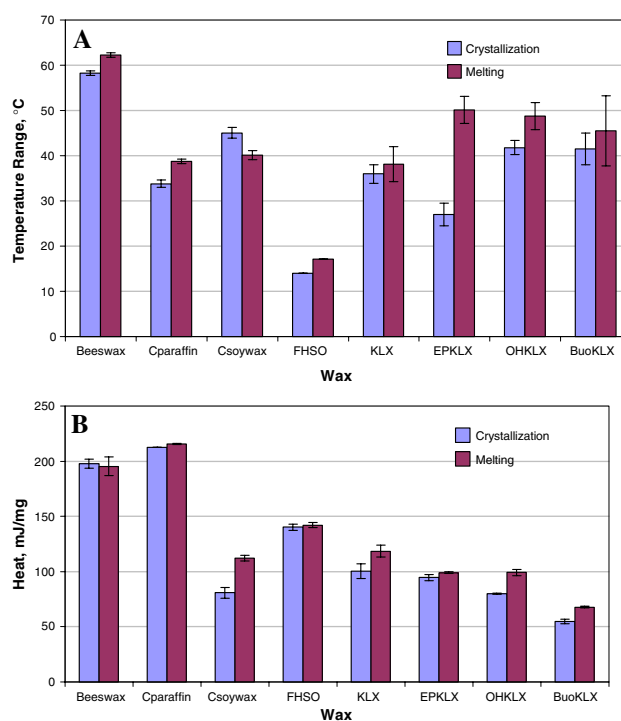


Fig. 6 Temperature range of the main DSC peak and total heat change of waxes during crystallization and melting (a Temperature range; b Total heat of fusion). See Fig. 1 caption for abbreviations

crystallization cycles, as shown in Fig. 8. It is interesting to observe that these increases are not linear and a threshold has to be passed to obtain a widened range. This widened temperature range is expected to alleviate the problem of improper melting and dripping during the burning of vegetable candles. DSC peak tailings were also observed in wax mixtures and the synthesized waxes. Narine et al. [15] reported fat peak tailing in their study of the thermal properties of fat and suggested that the tailing indicated a gradual crystallization that may be attributed to disorder in a system.

The total heat released or absorbed during crystallization and melting decreased significantly with the addition of OHK LX or BuoK LX to FHSO and KLX (Fig. 9), and these relationships were relatively linear compared to those in Fig. 7. The heat tended to level off when the content of OHK LX was greater than 50% in the mixture, however, it decreased continuously with the addition of BuoK LX. The reduction in heat change may suggest that the wax mixture will melt and solidify easier and faster than the initial unmodified material, and this is a significant quality improvement of candle wax.

The chemical reactions used to modify fats will probably increase the cost of the wax material, especially during the early stages when such waxes are produced in small quantities and as niche products. However, we hope that

Fig. 7 Melting and crystallization curves of wax mixtures. See Fig. 1 caption for abbreviations

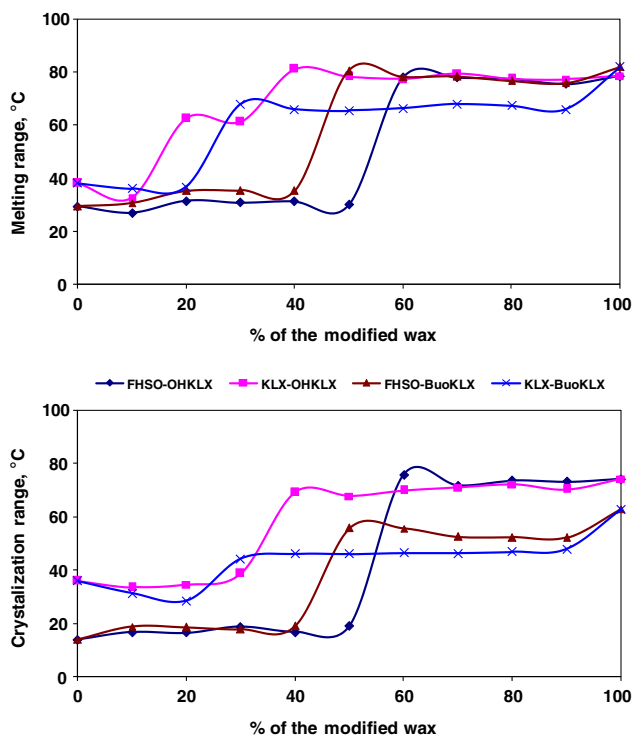
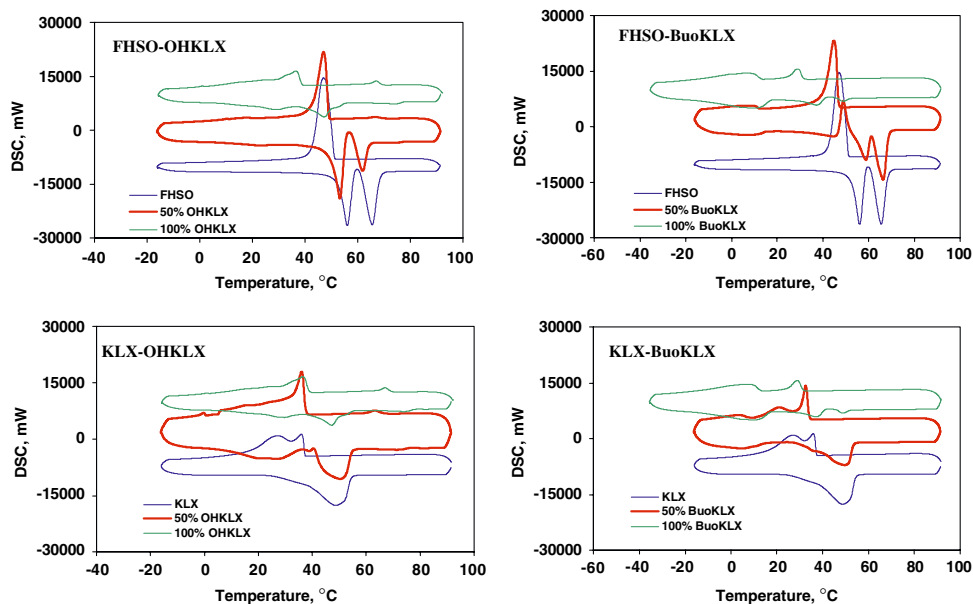


Fig. 8 Melting and crystallization temperature ranges of wax mixtures as affected by the percentage of modified wax. See Fig. 1 caption for abbreviations

the functionality improvement of the wax will justify the production costs.

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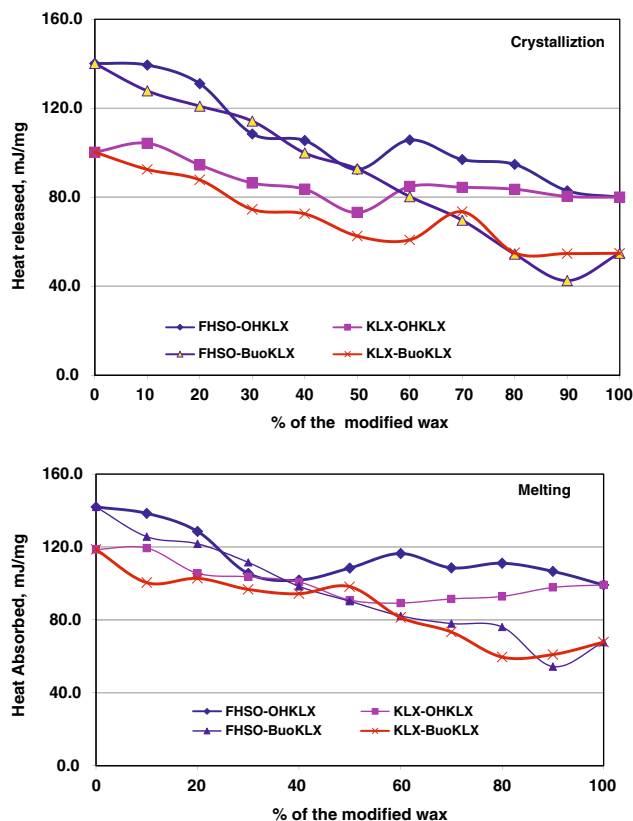


Fig. 9 The total heat released or absorbed by the wax mixtures during crystallization and melting. See Fig. 1 caption for abbreviations

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