Simple Synthesis Hydrogenated Castor Oil Fatty Amide Wax and Its Coating Characterization

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Abstract: A simple method for incorporating amine groups in hydrogenated castor oil (HCO) to produce wax for beeswax or carnauba wax substitution in packaging and coating was developed. From the conversion rate of the products, HCO was reacted with ethanolamine at 150°C for 5 h, and the molar ratio of HCO and ethanolamine was 1:4. The hardness of the final product was seven times higher than that of beeswax, the cohesiveness of the final product was 1.3 times higher than that of beeswax and approximately one half of that of carnauba wax, and the melting point of the final product is 98°C. The Fourier transform Infrared spectroscopy showed that the amide groups were incorporated to form the amide products. In coating application, the results showed that the force of the final product coating cardboard was higher than that of beeswax and paraffin wax and less than that of carnauba wax. After 24 h soaking, the compression forces were decreased. HCO fatty acid wax can be an alternative wax for carnauba wax and beeswax in coating applications.

Key words: hydrogenated castor oil, fatty amide, physical properties, coating

1 Introduction

Wax use at the global level has reached up to 4, 250 kt in 2015¹. The major applications of waxes are candles and packaging materials, followed by synthetic wood. Other uses include corrugated board, coatings, food, cosmetics and pharmaceuticals, crayons, and inks. Wax sources can be generally categorized as petroleum-based, synthetic, and natural waxes, with petroleum-based waxes dominating the market (> 85%)². Wax plays an important role in the global industrial process, such as lighting, packaging, farming, chemical rubber, and medicine and homecare products². However, petroleum waxes have gradually lost market share in a few applications because of environmental concerns, such as depleting oil reserves and highly variable price of crude petroleum. Natural waxes (derived from plants and animals) have the advantages of being renewable, biodegradable, and nontoxic and are particularly important in areas wherein waxes are in contact with food and humans³.

Among natural waxes, carnauba wax and beeswax are two economically important types because of their excellent physical and textural properties. Carnauba wax, which is extracted from the leaves of the carnauba tree (Copernicia prunifera) (Miller) H. E. Moore; a Brazilian palm, consists of a complex mixture of esters, free alcohols, aliphatic acids, aromatic acids, free hydroxy carboxylic acids, hydrocarbon (paraffin), and triterpene diols⁴. Esters are the main component of carnauba wax, corresponding to more than 80% of the composition, which mostly comprises aliphatic esters and cinnamic acid diesters. Carnauba wax is hard and has one of the highest melting points for natural wax at approximately 84°C. Carnauba wax is extensively used in paper coatings, automobile waxes, shoe polishes, and food products, such as sweets. Beeswax is a complex mixture of chemical compounds predominantly based on straight-chain monohydric alcohol compounds with carbon chains from C₂₄ to C₃₆ and straight-chain acids with carbon skeletons up to C₅₆, including a few C₁₄ hydroxyl acids, such as esters, diesters, and triesters⁵. Beeswax has good cohesiveness in natural wax. In addition, beeswax has been used for applications in food products as glazing and coating agents and can be applied as a texturizer for chewing gum base and as a carrier for additives, thus rendering beeswax organogels the adequate properties for application in future fat-based foods⁶-⁹. Studies also showed the ability of beeswax organogels to maintain aroma characteristics through time, as volatile compounds were successfully incorporated⁹.

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However, larger fluctuations in price and availability have led to the search for alternative and renewable solutions for natural wax substitution\textsuperscript{13,14}. Wax derived from vegetable oil has been the focus of interest of innovators because of its relatively abundant supply and low price\textsuperscript{3,11}. Castor oil is obtained from extracting or expressing the seed of a plant that has the botanical name *Ricinus communis* of the family Euphorbiaceae. Castor oil is not only a naturally occurring resource but is also inexpensive and environmentally friendly. Castor oil is a viscous, pale yellow non-volatile and non-drying oil with a bland taste and is frequently used as a purgative. It has a slight characteristic odor, whereas crude oil tastes slightly acrid with a nauseating aftertaste. Moreover, it has a good shelf life and does not turn rancid unless subjected to excessive heat compared with other vegetable oils. India, China, and Brazil are the largest exporters of castor oil in the world\textsuperscript{12}. Castor oil is not edible but an important renewable resource; it could be substituted in many industrial application areas where edible oils are used. An awareness of the various uses (paints, coatings, inks and lubricants) of the oil can be used to make a strong case for an increase in its production as a vital raw material for the chemical industries\textsuperscript{13,14}. The double bonds of unsaturated fatty acid of castor oil react with hydrogen gas to produce hydrogenated castor oil (HCO). HCO is a triacylglycerol and is a derivative of castor oil\textsuperscript{13,15}. HCO is a hard, waxy substance with a unique structure, which works with other waxes in the formula to harden the stick, thus preventing it from crumbling when used. In addition, HCO is commonly used as a lubricant and can be found in coatings, carbon paper, cosmetics, and polish products. Kelley et al. invented hydroxylated compounds containing saturated and esterified alkylolamines as hard wax substitute by using castor oil and ethanolamine as raw materials\textsuperscript{16}. Feairheller et al. reported that a direct low-temperature synthesis of fatty alkylamides, diamides, and alkylamides for triglycerides and primary amines provides an essentially quantitative yield of various products\textsuperscript{17}. These works focused on fatty amide preparation, thus lacking the properties of products. The objective of this study was to develop a simple synthesis method for incorporating amine groups in HCO and to examine the effect of the reactant ratio on the physical and textural properties of wax. Carnauba wax and beeswax, as well as HCO, were used as controls for comparisons with the new castor oil-based waxes in box coating application.

2 Materials and methods

2.1 Sample materials and chemicals

HCO was purchased from Acme-Hardesty Co. (Blue Bell, PA, USA). Ethanolamide, chloroform, and other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA). Carnauba wax was purchased from Sigma-Aldrich (St. Louis, MO, USA). Beeswax was purchased from Blue Corn Naturals (Ridgway, CO, USA). Corrugated cardboards were cut out of the same box, measuring 8.5 cm long and 4 cm wide. These cardboards were coated with different waxes.

2.2 Syntheses

HCO and ethanolamine were mixed in various molar ratios, and the mixtures were agitated at temperatures ranging from 90°C to 150°C for a certain time under refluxing. After the reaction, the final products were transported to the container and were cooled down to room temperature for further analysis. The complete reaction of HCO with ethanolamine is presented in Scheme 1:

![Scheme 1](Image)

The effects of the HCO and ethanolamine molar ratio, reaction temperature, and reaction time on the amide value of the final products were examined. The HCO and ethanolamine molar ratios were set at 1:1, 1:2, 1:3, 1:4, and 1:5. The reaction temperature was set at 90°C, 120°C, and 150°C. The reaction time was set at 1 h, 3 h, 5 h, and 7 h. Three synthesis replicates were employed for each treatment.

2.3 Chemical analyses

2.3.1 Determination and analysis of the amine value

The amine value (AV) of crude HCO amide was determined by using the ASTM D 2074-2007 method, by boiling the sample with alcohol and then titrating with hydrochloric acid in the presence of bromphenol blue indicator.

2.3.2 Conversion rate

The AV represents ethanolamine in the crude HCO amide. The conversion rate (CR) was used to represent the reaction process. The reaction rate was calculated with Eq. (1):

\[
CR(\%) = \frac{AV_0 - AV}{AV_0} \times 100
\]

(Eq. 1)

where \(AV_0\) is the amide value of the HCO and ethanolamine mixture and \(AV_i\) is the amide value of the crude HCO amide.

2.4 Sample purification

The crude HCO amide was dissolved in hot chloroform.
and placed in a reparator funnel to isolate the lower layer and the mixture of glycerol and excess ethanolamine from the fatty amide. The final products were obtained from the hot chloroform layer by crystallization at 20°C and were re-crystallized from hot acetone to produce a yellow powder.

2.5 HCO amide analysis

2.5.1 FTIR analysis

Approximately 0.1 g of HCO amide sample was dissolved in 10 mL chloroform. Then, 0.5 mL was deposited onto the surface of the salt plate using a micropipette and subsequently uniformly spread using the tip of the micropipette. The amide solid film was formed after the solvent evaporated. The spectra were recorded with a Bruker Tensor 37 FTIR spectrometer with air as background. Each recorded spectrum was obtained by averaging 32 scans at a resolution of 4 cm⁻¹.

2.5.2 Textural analysis

The wax was heated to melt; thereafter, approximately 16 g of hot wax was poured into a tin container (3.81 cm diameter and 2.54 cm height) for the penetration test with three replicates for subsampling or testing. Then, 2.5 g of wax was melted for the bend test (with six replicates for subsampling) in a hexagonal weighing boat as the mold for the hexagon shape (4 mm thickness \(\times\) 28 mm length), which was formed upon cooling to ambient temperature for 12 h before analysis.

A Texture Analyzer (TA.XT2i, Stable Micro Systems, Godalming, UK) was used to determine the hardness and cohesiveness/brittleness of the waxes. Hardness was determined by the penetration test with a TA-212 cylinder probe (3 mm diameter). The test speed was 0.2 mm/s, and the probe traveled 10 mm into the wax. The peak force (kg) in the penetration test was defined as the hardness \(H^\prime\).

The bend test was conducted with a blade (70 mm). A custom-built three-point accessory was used in the bend test. The wax disk was placed on two vertical support bars 20 mm apart. A third bar attached to the crosshead of the instrument was driven perpendicular to the sample at a speed of 0.2 mm/s, with 5 mm of travel distance. The area under the force curve before the wax was broken was recorded as the wax resistance to fracture, which was defined as cohesiveness (kg.mm)².

2.5.3 Thermal analysis

The melting and crystallization properties of the waxes were analyzed using a differential scanning calorimeter (DSC) (DSC-7, Perkin-Elmer, Norwalk, CT, USA) equipped with an Intracooler II system. Solid wax (3–5 mg) was weighed in an aluminum pan (Perkin-Elmer, Norwalk, CT, USA) and sealed. Indium was used as the reference standard. The temperature program started with a 10 min hold at 20°C, followed by 10°C/min rapid heating to 200°C and a 5 min hold at 200°C. Then, the sample was cooled to 20°C at 40°C/min. The completion of melting or the melting point was determined during the heating step and calculated using the Pyris software (Perkin-Elmer, Norwalk, CT, USA) as the intersection of tangent lines drawn from the high-temperature side of the melting peak of the highest temperature and the baseline. Two replicates from each wax sample were analyzed.

2.6 Wax cardboard coating analysis

2.6.1 Wax absorption

The cardboard samples were weighed before and after coating, and the difference in weight was the quantity of wax retained on the cardboard. This experiment was repeated 18 times for the four types of waxes.

2.6.2 Analysis of the resistance to high temperatures

All the cardboard samples were first placed in an oven at 40°C. After 30 min, the samples were weighed, replaced in the oven at 50°C for 30 min, and weighed again. This procedure was repeated for 60°C, 70°C, 80°C, and 90°C. The difference in weight before and after the test determined the quantity of wax that was removed during the test.

2.6.3 Analysis of wax loss and compression force change

The coated cardboards were placed directly in a beaker for 24 h and stored at room temperature. As the cardboards floated, weights were placed on top to ensure that the samples would remain under water at all times. After soaking, the cardboards were air-dried and the wax loss and compression forces of the cardboards were analyzed.

2.7 Wax cardboard coating analysis

Three batches of waxes were synthesized for each treatment. Each batch of wax was used to provide three replicates for the penetration test, five replicates for the compression test, three replicates for the bend test, and two replicates for melting point determination. The treatment effects were examined at the 5% significance level by fitting the data to a linear mixed model using the restricted maximum likelihood method and Bonferroni correction and were analyzed by the Statistical Analysis System (SAS) 9.1 (SAS Institute, Cary, NC, USA). The means and standard deviations were determined and presented.

3 Results and discussion

3.1 Effect of different molar ratios of HCO and ethanolamine on the CR of fatty amide wax

The CR at different molar ratios is presented in Fig. 1.

As shown in Fig. 1, the CR decreased when the molar ratio increased. However, the molar ratio from 1:1 to 1:4 was not significantly different because the amines were used in excess, which served as a solvent reagent and possibly as a catalyst. The amine was used in 1:4 molar ratios excess, the reagent was used as a solvent for HCO, and the formed fatty amide was used as the basic catalyst for the
reaction. The excess amine prevented the reaction mixture from solidifying and permitted the completion of the reaction. In this study, the molar ratio 1:4 was selected for further reaction.

3.2 Effect of reaction temperature on the CR of fatty amide wax

The CR at different temperatures is presented in Fig. 2. As shown in Fig. 2, the CRs were not significant \((p > 0.05)\) when the reaction temperature was higher than 130°C. However, when the reaction temperature was 150°C, the HCO fatty amide products became dark. Therefore, 130°C was selected as the reaction temperature.

3.3 Quantification of aspartic acid, glutamine, and lysine

The CR at different reaction times is presented in Fig. 3. Figure 3 shows that the CR was significantly different \((p < 0.05)\) from 2 h to 4 h. The CR was not significantly different \((p > 0.05)\) when the reaction time was more than 5 h. Therefore, the reaction time of 5 h was selected.

3.4 Physical properties of fatty amide wax, carnauba wax, and beeswax

The fatty amide wax was synthesized at the optimal reaction conditions (HCO and molar ratio of 1:4, reaction temperature of 150°C, and reaction time of 5 h). After purification, the final products were analyzed by texture analyzer and DSC. The results are presented in Table 1.

Hardness is an important property of wax used in box and paper coating applications. A hard wax is usually preferred. The hardness of fatty amide wax is 12.2 kg, which is approximately eight times higher than that of beeswax (1.65 kg) and more than three times higher than that of commercial paraffin wax (3.27 kg) (Table 1). According to our research, cohesiveness, extent to which the sample could be deformed prior to erupting, and cohesiveness is defined as the work required deforming in the down movement of the probe, and force times distance was work the probe done. Therefore, a texture analyzer with a blade was used to measure force during compression testing. Beeswax has good cohesiveness properties among the natural waxes. The cohesiveness of synthetic wax is better than that of beeswax and half that of carnauba wax because more hydroxyl groups are introduced into the final product to increase the cohesiveness of waxes. The melting point (completion of melting) of the fatty amide wax was approximately 98°C. Beeswax and commercial grade paraffin wax all melted above 60°C (Table 1). The melting point of waxes increased compared with HCO (84°C). The amide groups increased the melting point of the final product.

3.5 FTIR analysis of the final product

Figure 4 shows the HCO and final product FTIR absorption spectra. Figure 4 shows that two amide peaks at 1,650
and 1,470 cm\(^{-1}\) appeared and the ester peak at 1,740 cm\(^{-1}\) disappeared in the final product compared with the HCO spectrum. In addition, the 3,500–3,300 cm\(^{-1}\) spectral region became a large board band because of the amide second overtone region. The ester peak can be used as an indicator of the extent of the completion of the reaction\(^\text{(7)}\).

Figure 4 confirmed that the product was HCO fatty amide.

3.6 Box coating application

3.6.1 Wax absorption

The wax retained in the cardboard is presented in Fig. 5. Figure 5 shows that the remaining amount of HCO amide in the cardboard was higher than that of other waxes because of the higher melting point of HCO amide. The samples rapidly solidified when the waxes were drained at room temperature.

3.6.2 Analysis of the resistance to high temperatures

Wax loss is shown in Fig. 6, in which wax was lost around the melting point, and the loss was decreased possibly because the corrugated cardboards absorbed some of the waxes.

3.6.3 Analysis of wax loss and compression force change

Figure 7 shows that HCO amide lost approximately 12% weight of the amount of wax during 24 h soaking, which is higher than that of other waxes. HCO amide consists of amino and hydroxyl groups, which are easily soluble in water, thereby providing a method to recycle the wax from the cardboards.

Figure 8 shows that the compression forces were increased after the wax coating process, thus strengthening the structure of the cardboard. Different waxes can increase the compression forces. These results were similar to the hardness of wax, in which the force of the HCO amide coating cardboard was higher than that of beeswax and paraffin wax and lesser than that of carnauba wax. After 24 h soaking, the compression force was decreased because a few compounds of the waxes were dissolved in water.

The novelty of this successfully demonstrated method for the synthesis of HCO fatty amide wax is the use of ethanamine and its beneficial effect on the reaction and product quality. HCO not only facilitated the reaction with the amine group but also contributed to the textural prop-

| Properties               | Carnauba wax | Beeswax | Paraffin wax | HCO amide wax |
|--------------------------|--------------|---------|--------------|---------------|
| Melting point /\(\degree\)C| 84.2 ± 0.05  | 66.3 ± 0.02 | 62.4 ± 0.06  | 98.1 ± 0.03   |
| Hardness /kg             | 12.2 ± 0.87  | 1.65 ± 0.96 | 3.27 ± 0.18  | 10.1 ± 0.67   |
| Cohesiveness /kg·mm      | 2.82 ± 0.57  | 3.34 ± 0.57 | 1.38 ± 0.60  | 0.681 ± 0.69  |

Fig. 4 FTIR spectra of the final product and HCO.

Fig. 5 Wax absorption after coating.

Fig. 6 Wax loss at the evaluated temperatures.
properties of the synthase wax. The amine group may be replaced by the carbonyl group of HCO, which will probably result in waxes with different textural properties for a variety of applications\(^\text{19}\). Therefore, the modified wax from this solvent-free synthesis has significant potential for coating applications, such as packaging, boxing, and paper coatings that are in direct contact with food. The coating comparison with the commercial paraffin products has shown a similar performance. With regard to the melting point, synthetic wax had a higher melting point than commercial waxes, which is suitable for coating applications in high-temperature environments. The water resistance of synthetic wax is slightly less than that of commercial waxes, thereby providing an easier way to recycle the wax after usage. The strength of the cardboard was significantly increased after coating using synthetic wax\(^\text{20}\). The results of compression force change of different waxes showed that synthetic wax is suitable for high-moisture environment application, such as coating cardboard for vegetable/fruit transportation in low temperature.

4 Conclusions

This study was developed for incorporating amine groups in HCO to produce wax for beeswax or carnauba wax substitution in packaging and coating. The optimized reaction conditions are as follows: HCO was reacted with ethanolamine at 150°C for 5 h, and the molar ratio of HCO and ethanolamine was 1:4. The hardness of the final product was seven times higher than that of beeswax, the cohesiveness of the final product was 1.3 times higher than that of beeswax and approximately one half of that of carnauba wax in the method of the current study, and the melting point of the final product is 98°C. The FTIR spectra showed that the amine groups were incorporated to form the mono-amide products. In coating applications, the results showed that the force of the final product coating cardboard was higher than that of beeswax and paraffin wax and less than that of carnauba wax. After 24 h soaking, the compression forces were decreased. The findings of this study will facilitate the use of abundant castor oil resource and will also provide the foundation for further development in synthesizing hard wax using renewable vegetable oil for coating purposes.

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Conflict of Interest

The authors have declared no conflicts of interest.

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