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Soybean oil as feedstock for the synthesis and characterization of a carnauba substitute and a study of the structure–function relationships

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ABSTRACT

A soybean oil-based carnauba substitute was developed, and structure–function relationships were established. Amide derivatives of saturated fatty acid showed higher hardness and melting point than ester derivatives having the same chain length. Increasing chain length using diacids increased hardness. The cinnamic ring was confirmed to contribute to surface shininess and smoothness. The addition of long-chain fatty alcohols increased the hardness of a C52 (carbon chain length of 52) diester. Overall, a material consisted of C52 polyamide (76.3 wt%), C38 diamide (11.3 wt%), and C29 diamide with a ring structure (12.4 wt%) showed comparable hardness and surface properties as carnauba wax.

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Introduction

The limited resource for carnauba wax that has high hardness, high melting point (82–86 °C), and desirable surface properties has led to the search for alternatives. Wax derived from vegetable oil has been an interest of innovators because of its abundant supply and low price. Using hydrogenated castor oil (HCO) and ethanolamine (ETA), a compound containing esterified alkylolamide of hydroxystearic acid can be produced and used as a carnauba wax substitute as described in a patent [1]. Fatty alkanolamides, diamides, and aralkylamides can also be synthesized directly from triacylglycerol and primary amines at low temperatures [2]; however, the hardness and surface characteristics of the amide and diamide waxes are not as good as those of carnauba wax. Using hydrogenated castor oil is also not economical, so lower-priced raw materials need to be identified. There are very few studies on developing vegetable oil-based carnauba wax substitutes, and even fewer systematically reported structure–function relationships of the amide and diamide waxes.

Abbreviations: AFM, atomic force microscopy; ETA, ethanolamine; ETD, ethylenediamine; FHSO, fully hydrogenated soybean oil; HCO, hydrogenated castor oil; R-diamide, diamide with cinnamic ring attached; SFFA, saturated free fatty acid.

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The effects of different functional groups on physical properties have remained relatively unknown.

Carnauba wax is mainly produced by mechanically recovering the coating from the leaves of one type of palm trees that almost exclusively grow in northeastern Brazil. The composition of this wax was reported by Vandenburg and Wilder [3] as follows: hydrocarbon (0.3–1%), aliphatic esters (38–40%), monohydric alcohols (10–12%), ω -hydroxy aliphatic esters (12–14%), *p*-methoxycinnamic aliphatic diesters (5–7%), *p*-hydroxycinnamic aliphatic diesters (20–23%), a triterpene type of diol (0.4%), free fatty acids, and other unknown constituents (5–7%). Other authors have also reported that carnauba wax mainly consists of hydrocarbon (0.1–0.7%), wax esters (60–65%), free fatty acids (7–8%), and free fatty alcohol (28–33%) [4]. The esters have carbon numbers between 44 and 66 [5], the alkanes have carbon numbers between 16 and 34 [3], and the free fatty acids and free fatty alcohols have carbon numbers between 16 and 30, and 28 and 34 [4]. The presence of long-chain esters is believed to contribute to the high melting point and hardness of carnauba wax. In addition to the esters, the mixtures of substituted long-chain aliphatic hydrocarbons, free fatty acids, and primary and secondary alcohols also play an important role [6].

It is believed that different functional groups contribute to the different physical properties of carnauba wax. Fatty alcohols and ω -hydroxy fatty acids probably contribute to the cohesiveness or internal strength of the wax. Wang and Wang [7] reported that incorporating hydroxyl groups into hydrogenated soybean oil can improve its cohesiveness and suggested a positive relationship

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between the quantity of hydroxyl groups and degree of cohesiveness. The aromatic ring structure that cinnamic acid brings to the diesters was believed to be responsible for the desirable surface properties of carnauba wax [8].

This study aimed to develop soybean oil-based wax materials with physical properties similar to those of carnauba wax. Such a wax substitute would significantly increase the availability of the high-priced hard wax. A systematic structure–function relationship study was conducted using free fatty acids from fully hydrogenated soybean oil. The established relationship can be used for tailored synthesis of vegetable oil-based wax materials. We hypothesized that: (1) amide bonds will create a high melting point and high hardness compared to ester bonds, and linking two free —NH_2 groups of monoamide with a diacid will increase carbon chain length and thus further increase the hardness; (2) introducing a proper amount of cinnamic ring to the structure can improve surface shininess and reduce the surface friction of the material; and (3) blending long-chain fatty alcohols (C28–C34), which are the major components of carnauba esters, can significantly increase the hardness of long-chain diesters. To test these hypotheses, different molar ratios of reactants were used and mixtures of monoamide and diamide were synthesized and further reacted with diacids and cinnamic acid. Long-chain fatty alcohols were extracted from carnauba wax and blended with the selected long-chain fatty acid esters at various percentages. The physical properties of these mixtures were compared and an optimal soybean oil-based carnauba wax substitute was identified.

Materials and methods

Fully hydrogenated soybean oil (FHSO) was provided by Stratas Foods (Memphis, TN). Carnauba wax was provided by Michelman, Inc. (Cincinnati, Ohio). Ethylenediamine (ETD), cinnamic acid, dodecanedioic acid, and other chemicals were purchased from Sigma–Aldrich (St. Louis, MO).

Preparation of saturated free fatty acid (SFFA) from FHSO

SFFA was produced from FHSO by using a modified saponification reaction and then acidification process [9]. FHSO was mixed

with aqueous sodium hydroxide solution (4 M) with a molar ratio of oil to sodium hydroxide of 1:3. The mixture was heated at 100°C for 1 h under reflux with vigorous mixing to form a soap solution. Hydrochloric acid was then added to acidify the soap solution at the molar ratio of soap to HCl of 1:1.5. The mixture was heated at 100°C for 1 h and then cooled to room temperature. SFFA was collected upon solidification and vacuum oven dried. This SFFA contained 11 wt% C16 and 89 wt% C18 fatty acid. For the simplicity of expression and discussion, carbon chain length of 18 is used for this material.

Preparation of monoamide, diamide, polyamide, diester, long-chain fatty alcohol, and their mixtures

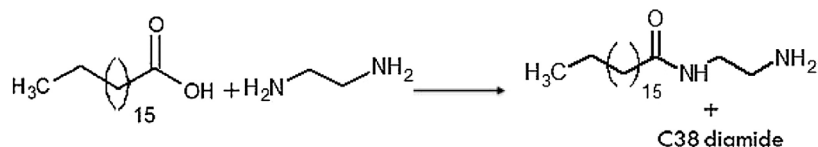
The SFFA prepared was used to react with ETD to form fatty acid monoamide and diamide. Molten SFFA was slowly added to ETD at an equivalent molar ratio (COOH to NH_2) of 1:2, 1:3, and 1:4 in a round-bottom flask connected with a reflux condenser, and the system was heated at 90, 110, 130, and 150°C for 3 h to determine the effect of temperature on reaction completeness. After the reaction, the flask was disconnected and heated at 120°C for another 30 min to evaporate any ETD residue. The mixture of monoamide and diamide was characterized using ^1H NMR and the proportion of monoamide and diamide was determined.

To attach a ring structure, cinnamic acid was used to react with the monoamide in the mixture obtained from the steps above. To evaluate the effect of diacid that can react with the free —NH_2 group and the effect of chain length on textural properties, adipic acid (C6) and dodecanedioic acid (C12) were selected to link two units of monoamide. The reactants were mixed in a round-bottom flask (molar ratio of —NH_2 group in monoamide to —COOH of 1:1) and then heated at the best conditions identified. The overall reaction design is shown in Scheme 1.

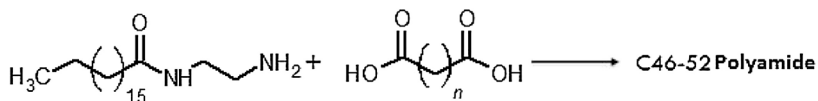
The starting material for Reactions (2) and (3) was the mixture generated in Reaction (1); thus, all the reactions generated mixtures, which are described below:

1. Mixture of monoamide with a free amine group and C38 diamide from Reaction (1) (Scheme 1).

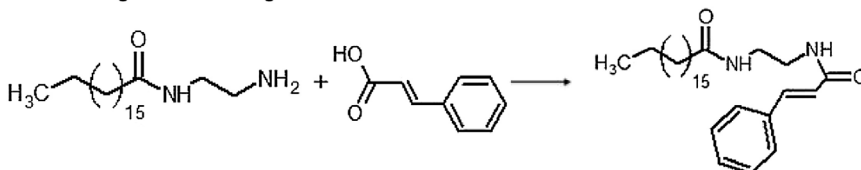
1. Formation of monoamide and diamide



2. Linkage of two monoamide by C6 or C12 diacid ($n=4$ or 10)



3. Attaching a cinnamic ring to monoamide



Scheme 1. Chemical reactions for the synthesis of carnauba wax substitute.

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