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Synthesis and characterization of soybean oil-based waxes and their application as paraffin substitute for corrugated coating

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ABSTRACT

This study focused on modifying the structure of acyl lipid to obtain waxes with desirable properties of paraffin. Structure–function relationships were investigated and established. An increase in chain length significantly increased the hardness of esters. A hydroxyl group on the end of a linear monoester chain further increased hardness. Addition of pendent hydroxyl group increased the cohesiveness of ethylene glycol mono and diesters (EGMD). Incorporating ether groups into diester also significantly increased cohesiveness. Two potential paraffin substitutes were identified. Hydrophobic particles significantly improved water resistance and wet strength of the cardboards and a coating performance competitive to paraffin was achieved.

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Introduction

Paraffin is one of the most widely used waxes for making candles and as a water-proofing agent in the packaging and food industries. The uses of paraffin are dictated by a combination of its desirable properties including melting profile, hardness, cohesiveness, clarity, and heat stability. According to a study by The Freedonia Group, U.S., demand for waxes is to grow at a rate of 1.8% annually through 2019. However, paraffin as a petroleum-based product is not sustainable, and fibers treated with it are not recyclable or biodegradable. The demand for “green” material continues to increase due to the environmental issue of 3 billion lbs of paraffin-coated corrugated paper products going to landfills

every year. Many are seeking alternatives, and vegetable oil has been studied as a desirable raw material for the production of waxes having comparable properties to paraffin's.

Paraffin is a mixture of saturated hydrocarbons containing 80–90% linear chains with an average of 20–30 carbons [1]. The properties of refined paraffin depend on the proportion of linear and branched chains. High content of branched chain leads to an undesirable oily surface and can negatively affect physical properties such as hardness, friction resistance, melting point, consistency, and clarity [1].

The physical properties of vegetable oil triacylglycerols (TAGs) are dependent on the length of fatty acyl chains, the amount and type of unsaturation in the chains, and the distribution of fatty acyl groups among sn-positions of the TAGs [2]. Vegetable oil-based waxes are typically obtained by modifying the composition or structure of fatty acids, such as partial or full hydrogenation, and interesterification to achieve desired physical properties. Other chemical modifications are also used to attach functional groups on the acyl chain to obtain certain properties. Several studies have reported that incorporating hydroxyl groups, branched chains, and short-chain fatty acids could significantly improve the cohesiveness of vegetable oil-based waxes [3,4]. However, very few studies systematically studied structure–function relationships. Despite the efforts made in these modifications, vegetable oil-based waxes still are not widely used on commercial scale because of the

Abbreviations: EGD, ethylene glycol diester; EGD-OH, ethylene glycol diester with pendent hydroxyl groups; EGMD, ethylene glycol monoester/diester; EGMD + wt%OH, a mixture of ethylene glycol monoester and diester with wt% pendent hydroxyl group; EOA, epoxidized oleic acid; FHSO, fully hydrogenated soybean oil; HFFA, hydroxylated free fatty acid; 1,4DM, 1,4-diol monoester; 1,16DM, 1,16-diol monoester; 1,16DD, 1,16-diol diester; 1,16DD-OH, 1,16-diol diester with pendent hydroxyl groups; 1,16DD + wt%OH, a mixture of 1,16-diol diester with wt% pendent hydroxyl group; PEG200 or 400D, polyethylene glycol (molecular weight of 200 or 400) diester; PEG, polyethylene glycol; PEGD, polyethylene glycol diester; SAM, stearyl alcohol monoester; SFFA, saturated free fatty acids.

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limitations in delivering desired physical properties. Fully hydrogenated soybean oil (FHSO) alone is not suitable for coating because of its brittle texture. Although introducing branched groups into the fatty acyl chain by epoxidation, ring opening, and esterification improved cohesiveness, such materials had significantly lower hardness and melting point compared to commercial paraffin [5]. Increasing structure heterogeneity and the amount of hydroxyl group or other functional groups using partial acylglycerols may also improve cohesiveness by interfering with orderly packing, and improving intermolecular interaction. A study showed that incorporating acetyl and hydroxyl groups in FHSO improved its cohesiveness; however, hardness suffered in the acetylated FHSO [6]. Also, the use of stearyl alcohol for deriving long and linear esters did improve hardness, but it lowered cohesiveness [6]. Nonetheless, an optimization of the amount of hydroxyl group is essential for optimal hardness and cohesiveness. To date, no ideal green or biorenewable material for replacing petroleum-based paraffin has been identified and there is a need to design and evaluate practical lipid modification methods to obtain a range of materials with appropriate cohesiveness and hardness suitable for a variety of applications.

The overall goal of this study was to develop feasible modification methods using soybean oil as feedstock to deliver properties of petroleum paraffin. Saturated free fatty acids (SFFA) derived from FHSO were used to study structure–function relationships. We hypothesized that (1) a significant increase of chain length will lead to higher hardness, while a polyether group in the linear structure may provide the material elasticity, and thus cohesiveness; (2) a hydroxyl group on the end of a linear chain can further improve hardness by promoting molecular alignment or apparent chain lengthening via hydrogen bonding, while a pendent hydroxyl group can improve cohesiveness by improving intermolecular interaction; (3) an aromatic ring structure may also serve as weak hydrogen bond acceptors and may improve cohesiveness by improving intermolecular interactions with hydrogen bond donors; (4) hydrophobic particles may interact with the wax esters or physically block the surface pore, improving water resistance of the material. The following specific objectives were proposed to test these hypotheses:

1. To determine the impact of ether group and chain length in diesters on hardness and cohesiveness;
2. To determine the influence of adding different functional groups (hydroxyl group at terminal position, pendent hydroxyl group, and ring structure) on hardness and cohesiveness;
3. To determine the relationships between structure and other physical properties such as water repellency, melting point, and coefficient of surface friction; and
4. To determine the effect of hydrophobic particles on water resistance of wax esters.

Materials and methods

FHSO was provided by Stratas Foods (Memphis, TN). Paraffin was provided by Michelman, Inc. (Cincinnati, Ohio). A hydrophobic silica nanoparticle product (6864HN, 10–25 nm) was purchased from SkySpring Nanomaterials, Inc. (Houston, TX, USA), and a hydrophobic silica microparticle (Dumacil 300FGK, 15 μm) product was provided by Elementis Specialties (East Windsor, NJ, USA). Epoxidized oleic acid (EOA) and hydroxylated free fatty acid (HFFA) were produced using the methods described as in the following section. Polyethylene glycols (PEG) and other chemicals were purchased from Fisher Scientific (Pittsburgh, PA) and Sigma Aldrich (St. Louis, MO).

Preparation of EOA, HFFA, and SFFA

EOA was prepared for a ring opening reaction following a method reported by Park et al. [7] with minor modifications. Oleic acid (about 56 g, 0.2 mol), glacial acetic acid (24 g, 0.4 mol), and the catalyst Amberlyst-15 (5 g) were mixed in a round-bottom, three-neck flask connected to a reflux condenser. The mixture was stirred by a mechanical stirrer and heated to 55 °C, and then 30% aqueous H_2O_2 (60 mL, 0.6 mol) was added dropwise and the reaction was allowed to take place at 55 °C for 7 h. After the reaction, the catalyst was removed by filtration and the product was washed with hot deionized (DI) water until the pH was approximately 7.0.

HFFA was produced by ring-opening EOA with water using the method reported by Chen et al. [8] with minor modification. About 30 g of EOA was mixed with DI water (molar ratio of epoxy group to water of 1:10) in a round-bottom flask with the presence of 0.1 wt% tetrafluoroboric acid as catalyst. The reaction was carried out at 95 °C for 8 h, and then the mixture was cooled to room temperature. The crude product was extracted using ethyl acetate and washed with saturated sodium chloride solution three times. Organic solvent was then removed at 80 °C using a rotary evaporator.

SFFA was produced from FHSO by a modified saponification then acidification process [9]. FHSO was mixed with aqueous sodium hydroxide solution (4.0M) at a molar ratio of 1:3 (oil: sodium hydroxide). The mixture was heated at 100 °C for 1 h under reflux with vigorous mixing to form a soap solution. Hydrochloric acid was added at a molar ratio of 1:1.5 (soap:HCl) to acidify the solution. The mixture was heated at 100 °C for 1 h and then cooled to room temperature. Saturated FFA was collected upon solidification and then vacuum oven dried.

Syntheses of fatty acyl monoesters and diesters with alcohols of different chain length and functional groups

To produce monoesters of fatty acid with different alcohols, SFFA was mixed with 1,4-butanediol, 1,16-hexadecanediol, and stearyl alcohol at a molar ratio of 1:1 in a round-bottom flask with 5 wt% of Amberlyst-15 as catalyst. The mixture was heated at 95 °C in an oil bath for 12 h. Hot filtration was used to remove the catalyst after the reaction and the collected liquid was cooled and saved in tin cans for NMR and textural analysis. The monoesters, which had a reactive hydroxyl group at the end of the linear chain, provide a functional group to conduct further esterification. To attach a benzene ring to the structure, 1,16-diol monoester (1,16 DM) was mixed with benzoic acid at a molar ratio of 1:1 and the mixture was heated at 95 °C for 12 h with 5 wt% Amberlyst-15. Hot filtration was used to remove the catalyst and the collected material was saved for further analyses. To produce 1,16 diol diester (1,16 DD), ethylene glycol diester (EGD), and PEG diester (PEGD), SFFA was esterified with 1,16 diol, ethylene glycol and PEG (200 or 400 molecular weight) at a molar ratio of 2:1. To produce 1,16 diol diester and ethylene glycol diester with a pendent hydroxyl group (1,16 DD-OH and EGD-OH), HFFA was used to react with 1,16 diol and ethylene glycol at a molar ratio of 2:1. Reaction conditions used were the same as those for synthesizing monoesters. A mixture of ethylene glycol monoester and diester (EGMD) was also synthesized using a SFFA to ethylene glycol mixing ratio of 1:0.75. For evaluating the effect of a pendent hydroxyl group, 1,16 DD-OH or EGD-OH was mixed with 1,16 DD or EGMD to form a mixture with either 0.5, 1.0, or 2.0 wt% of pendent —OH. The mixtures were then used to prepare samples for measuring hardness and cohesiveness.

A simplified and more feasible process for generating EGMD and EGD-OH mixture was also tested. The mixture was synthesized in a one-pot reaction instead of mixing individual components. A SFFA (95 wt%) and HFFA (5 wt%) mixture was reacted with ethylene

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