

The friction and wear behaviors of vegetable oil-based waxes, natural beeswax, and petroleum paraffin wax

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Abstract

Quantitative analyses on the coefficient of friction of common coating waxes are necessary and essential for designing systems for coating, conveying, packaging operations, transporting and storing of papers and paperboards, while analyses on wear behavior can be helpful for predicting performance durability of the coating surface. In this study, we investigated the friction and wear behaviors of six waxes including four commercial waxes and two soybean oil-based wax developed in our lab for bulk coating on cardboard. The effect of normal load, sliding velocity, and environmental temperature was evaluated. The friction coefficient of different waxes varies with sliding conditions. Higher normal load, sliding velocity, and environmental temperature resulted in significantly greater wear loss. Crystalline morphology and crystallinity were affected by environmental temperature, and they correlate to the variations in friction coefficient and wear loss of these materials. Overall, the Estercoat developed in our lab had comparable frictional properties and much less wear than paraffin wax under tested conditions and can be a good substitute for paraffin wax.

Keywords:

Coating waxes; friction and wear behavior; effect of sliding conditions; crystalline morphology and crystallinity

Highlights:

- Friction coefficient and wear loss of different waxes varies with sliding conditions.
- Crystalline morphology and crystallinity were affected by environmental temperature.
- The changes in crystalline morphology and crystallinity correlate with the variations in friction coefficient and wear loss.
- The soybean oil-based Estercoat developed in our lab has friction and wear properties comparable or better than paraffin wax under tested conditions.

Introduction

Waxes are commonly used for paper and corrugated coating. As a coating, surface properties including friction and wear behavior are critical factors as they are related to many issues regarding printing runnability, print quality, sliding, durability and storage. Friction is defined as the resistance to motion that occurs whenever a solid body contacts with another, and wear represents the damage to or removal of material from one or both side of solid surfaces that are in contact during motion [1]. Friction and wear are all consequences of materials' interaction at the contact point, and a better understanding of how different waxes response to such interaction leads to rational design of methods for applying coatings or new applications in which they can be utilized.

Currently, the major market for waxes is still packaging which represents 30% of the total 3 billion pounds annual North American wax consumption according to American Fuel & Petrochemical Manufacturers [2]. Regarding papers used for printing, high friction is typically desired since it helps maintain good printing register [3]. While for paperboard or corrugated coatings, the friction of coating material must be carefully optimized since too high or too low surface friction can lead to many problems. During the manufacture of packages, too little friction can cause packages to slip off the inclined conveyor belts and cause problem to the downstream processing. Lack of friction may also cause storage problems as packages can slide off the stacks or pallets. While too much friction can significantly slow down the packaging progress at the delivery chutes [4]. To correctly design systems for coating, conveying, packaging operations, transporting and storing of papers and paperboards, quantitative analyses on coefficient of friction of commonly used coating waxes are essential. Whereas, studies on wear behavior of the waxes can be helpful to predict performance durability of the coating surface.

Commonly, the simplest friction “law” (Amontons’s law) is used to describe friction, and it is stated that force of friction F , is proportional to the normal force FN , meaning ideally coefficient of friction ($\mu=F/FN$) only depends on the nature of the surface. However, Coulomb in 1821 has found that the coefficient of sliding friction depends on sliding speed and normal force, while coefficient of static friction depends approximately logarithmically on time (Persson, 2000). Temperature is another important factor that could significantly affect μ of materials. When the temperature rises, the thermal movement ability of moving units could be improved and the space between molecules is increased due to thermal expansion. Consequently, physical properties such as μ can be significantly affected. The sliding velocity, normal load and environmental temperature all closely relate to the practical situations that the wax coating can experience. Thus, a study on how these factors affect the μ of different wax coating materials would be of a significance to the coating industries. However, a literature search indicated that most of the studies were performed on materials such as metals, and very few information was available on wax coatings. Therefore, a systematic study on wax coating materials is needed. In this study, we investigated the frictional and wear behaviors of waxes and tried to better understand the relationship between frictional and wear behavior and physical and thermal properties of materials. We hypothesized that the friction coefficient of these coating materials will be affected by their hardness positively related to normal load and sliding speed. We also hypothesized that the coefficient of friction is related to the waxes’ melting profile and crystal structure and will increase as the surface temperature of the materials increases.

To test our hypotheses, we compared friction coefficient and wear loss of 6 waxes at different normal load, sliding velocity and environmental temperature, and characterized their physical and thermal properties. These waxes are paraffin wax, beeswax, fully hydrogenated soybean oil (FHSO), hydrogenated castor oil (HCO), ethylene glycol mono/diester (EGMD) and Estercoat as described later. Although approaches for characterization of the friction and wear behavior are dependent on the scale and complexity of the system under investigation [5-7], and field tests are necessary, such model study can serve as a guide for further improving material surface properties and for industries to better design their systems if similar materials and tribological situations are encountered.

Materials and Methods

FHSO was provided by Stratass Foods (Memphis, TN). Paraffin wax and beeswax were provided by Michelman, Inc. (Cincinnati, OH). HCO was purchased from Acme-Hardesty Co. (Blue Bell, PA). EGMD and Estercoat was synthesized using the method described as in the following section.

2.1 Synthesis of EGMD and Estercoat

EGMD and Estercoat are soybean oil-based wax like materials developed in our lab for corrugated coating [8]. It was synthesized following the method reported in our previous study [8] with minor modifications. Stearic acid and ethylene glycol were mixed in a round bottom flask at a molar ratio of 1:0.6 with 1 wt% of amberlyst-15 as catalyst. The mixture was heated at 95 °C in an oil bath for 8 hours to synthesize a mixture of ethylene glycol mono and diester (EGMD). Hot filtration was used to remove the catalyst after

the reaction and the collected liquid was cooled and saved. Mono and diacylglycerol (50/50) mixture of 5 wt% was then mixed into the previously collected EGMD at 75 °C to form the Estercoat. Both the EGMD and Estercoat were used for tribological tests.

2.2 Measurement of coefficient of friction

The selected waxy materials were melted at 5 °C higher than their melting point and pool into a cylindrical mold (40 mm in diameter × 25 mm in height). The molten waxes were allowed to solidify under room temperature (23 °C) for 2 hours before removed from the mold. The wax disc was then taped on the platform of a Discovery Hybrid Rheometer (TA Instruments, New Castle, DE) equipped with tribo-rheometry accessories for measurement of coefficient of friction. The test was conducted following the procedures reported by Krasnik and Schlattmann (2015) [9] except that a three-ball on plate setup (Figure 1) was used. Normal load (F_{Load}), sliding velocity (v) and temperature were varied to determine their influence on friction and wear behaviors of different waxes. The bottom surface of samples in contact with glass were tested. When testing the effect of normal load, normal load of 5, 10 and 15 N were used at a fixed sliding velocity of 5 rad/s under room temperature (25 °C). For evaluating the effect of sliding velocity, 1, 5 and 10 rad/s were used with fixed normal load of 5 N under room temperature. For evaluating the effect of temperature, environment temperature of 0, 25 and 50 °C were tested at fixed normal load (5 N) and sliding velocity (5 rad/s). Three samples were prepared for each test, and each sample was measured once.

2.3 Measurement of wear loss

The depth of the wear track was measured as the indicator of wear loss, by using a laser microscope (S-neox, Sensofar Metrology, Scottsdale, AZ) following the method reported by Yamamoto et al. (2013) [10] with minor modifications. The laser wavelength used was 530 nm and the resolution was 75 nm. The depth of the wear track and the cross-sectional area profile were precisely determined. Figure 2 shows typical data of the wear track profile obtained from the laser microscope.

Observation of wax crystallization using Polarized Light Microscopy

To determine how the environmental temperature affects the crystal structures and subsequently physical properties such as coefficient of friction and wear, the microstructure of the coating materials was observed using PLM. Samples were prepared following the method reported by Fei et al. [8] with minor modifications. A small amount of wax was loaded on the glass microscopy slides and heated in an oven at 5 °C above the melting temperature of waxes for 30 minutes. A preheated cover slide was then slipped over the molten wax to produce a thin film. The prepared slides were cooled at room temperature for one hour and then analyzed with a Differential Interference Contrast (DIC) microscope (Olympus BX53, Olympus Corporation, MA, USA) at 0, 25 and 50 °C using the CellSens Dimension software (Olympus Corporation, MA, USA). The crystal images were taken at 100× magnification.

Determination of relative crystallinity using DSC

The melting profile of these coating materials was determined by using a differential scanning calorimeter (Discovery DSC, TA Instruments, New Castle, DE, USA). The temperature program started with a 1-min equilibration at 25 °C, following by 8 min conditioning at 0, 25 or 50 °C, and then heating to 110 °C at 10 °C/min and a 2-min hold at 110 °C. The heat of fusion measured by DSC is used to characterize the crystallinity as reported by Yao and Wang [11]. The degree of crystallinity (%) of various waxes relative to paraffin wax at 25 °C was estimated by the following equation:

$$RC \text{ (relative crystallinity, \%)} = 100 \times \Delta HS / \Delta HB$$

where ΔHS is the heat of fusion of the tested wax and ΔHB is the heat of fusion of paraffin wax conditioned at 25 °C.

Results and Discussion

3.1 Effect of normal force, sliding velocity and environment temperature on coefficient of friction

The measurements were conducted directly on wax samples instead of cardboard samples coated with the waxes. This is because that the tested waxes are designed for bulk coating in which the wax forms a thick layer on the cardboard surface, and testing on the wax samples and coated cardboard samples would make negligible difference. Moreover, testing directly on the wax samples help us understand the effect of these boundary conditions on the material itself. Table 1a shows the coefficient of friction of different waxes under various normal loads. It can be seen that only paraffin's μ was significantly affected by normal load. The μ of paraffin decreased when the normal load was increased from 5 to 10 N, and further increase of normal load to 15 N did not lead to further decrease in μ (Table 1a). The decrease in μ of paraffin is probably due to the formation of a paraffin film at the interface which can serve as a solid lubricant with the increased normal load. A paraffin layer was also observed on the stainless-steel balls which may have changed the surfaces in contact and resulted in a reduced μ . As 10 N already resulted a transfer film and a coating on the stainless-steel balls, no further significant decrease in μ was observed by further increasing normal load to 15 N. Zhou et al. [12] also observed similar phenomenon when evaluating tribological properties of polyurethane modified polyamide-based composites. As the applied load increases, the friction heat increased quickly and a stable transfer film which would act as a solid lubricant can be produced by the melting material, thus reduced the friction coefficient [12]. FHSO and HCO which are harder than paraffin generated powder during sliding and did not form the transfer film, thus no significant variation in μ was observed. EGMD and Estercoat are harder than paraffin but softer than FHSO and HCO, and the wear-off material of EGMD and Estercoat generated during sliding was not powdery. However, a smooth transfer film was probably also not formed. Therefore, no significant changes in μ (Table 1a) for these two materials. Beeswax's μ was not significantly affect by the increased normal load either. It is the softest material compared to the other five, and the stainless-steel balls were already fully coated with the wax at a low normal load (5 N). With no significant change on the surfaces in contact, no further formation of the transfer film, the μ was not significantly affected with increased normal load. Comparing the different materials, beeswax had the highest μ . EGMD, Estercoat and paraffin behaved similarly; and FHSO and HCO had lower μ than the other four materials at all three normal load levels (Table 1a). In addition to the transfer film formation ability, the different μ of different materials may also be attributed by their physical properties such as hardness. By Bowden's friction theory [13], the friction coefficient may be expressed in terms of $\mu = \text{Ar}/N$ (where Ar is the real contact area, which is directly proportional to the friction force, s is the shear strength, and N is the applied load). Higher hardness may lead to lower degree of deformation of the material at the contact point, and thus smaller real contact area between the material and the stainless-steel balls. Consequently, at the same applied load, materials with higher hardness would have lower friction coefficient.

Table 1b shows the changes in μ of selected waxes with different sliding velocities. For paraffin wax, its μ first decreased when sliding velocity was increased from 1 to 5 rad/s, and then increased when sliding velocity was further increased to 10 rad/s. The decrease in μ can be explained by the same reason stated in the previous section, that a transfer film was formed to serve as a solid lubricant [12]. However, at higher sliding velocity (10 rad/s), the paraffin film may have been melted by the friction heat and transferred away. HCO had a decreasing trend in μ when sliding velocity was increased, and a significant reduction in μ was observed when sliding velocity was increased to 10 rad/s (Table 1b). HCO powders which may have lubricant effect were generated during the sliding. The HCO powder was tested in pharmaceuticals as a lubricant to prevent ingredients from clumping together and from sticking to the tablet punches or capsule filling machine [14]. With the increase in sliding speed, the friction heat may also accumulate quickly at the interface, leading to the softening and spreading of the material, which can promote the formation of a stable transfer film. The thin and stable transfer film then can act as the solid lubricant and reduces the friction coefficient of HCO at 10 rad/s [12]. For beeswax, the increased sliding velocity resulted in a significant increase in μ (Table 1b), this is likely due to the severe deformation and an increase in the real contact area with the increased sliding speed [15]. While for FHSO, EGMD and Estercoat, sliding velocity had no significant effect on their μ (Table 1b) indicating that they are less susceptible to shear. Overall, beeswax had the highest μ at all sliding velocities tested. EGMD, Estercoat, and paraffin wax again had similar frictional behavior, while FHSO and HCO had lower μ compared to the other four materials (Table 1). Physical properties of materials such as hardness again may have attributed to the friction coefficient's different responses to different sliding

velocities [13].

Table 1c shows the effect of temperature on coefficient of friction of different waxes. The μ of paraffin and beeswax increased significantly when the environmental temperature was increased to 50 °C. The elevated temperature led to softening of paraffin and beeswax (melting point both is about 62-66°C), which can subsequently cause severe deformation and larger real contact area at the contact point. Severe deformation and larger real contact area all can result in higher μ [13]. Increase temperature may also lead to faster vibration of molecules and cause a local uplifting of the surface, which could result in higher surface roughness and subsequently increase friction coefficient [16]. Low temperature did not have significant impact on paraffin, however, it reduced the coefficient of friction of beeswax (Table 1c). Beeswax was significantly hardened at freezing temperature, and the increased hardness could result in a decreased μ and less wear [13]. For FHSO and HCO, temperature (neither low nor high) had no significant effect on μ (Table 1c). HCO has a much higher melting point (86-88 °C) compared to the other five selected waxes, and it is expected that no significant changes in μ would be seen at 50 °C. Although FHSO has a lower melting point (about 66 °C), with a sharp melting profile, severe softening of FHSO may not occur when the materials is heated at a temperature lower than its melting. Thus, less significant impact of temperature on coefficient of friction was observed when heated at 50 °C. The high hardness of FHSO and HCO may also have attributed to their friction coefficients' low susceptibility to environmental temperature [17]. For EGMD and Estercoat, it was surprising to observe that both decrease and increase in temperature resulted higher μ (Table 1c). The reasons for this observation were not fully understood, and a study on the changes of the crystal structure of the EGMD and Estercoat at low temperature and high temperature was conducted and discussed in a later section to help explain this.

3.2 Effect of normal force, sliding velocity and environment temperature on wear loss

The sliding caused substrate worn and wear tracks with different depth was observed. However, the weight difference of the sample before and after sliding was little and cannot accurately represent the significance of the boundary conditions on wear loss. Therefore, wear loss was characterized by precisely measuring the depth of the wear track, and Table 2a shows the surface wear loss of different coating materials under different normal loads at fixed sliding velocity of 5 rad/s. It can be seen that all the materials had increased wear loss when the normal load was increased. Others have reported similar trend although different materials were used for the evaluation [12, 18]. As the normal load increases, the friction heat produced at the contact surface is generated faster leading to a higher transient temperature, and the waxes would melt and adhere to the surface of the counterface, thus resulted in a more severe wear. Among the different materials, beeswax at all normal load levels had the most severe wear, while HCO had the least wear (Table 2a). The difference in wear of different materials under same sliding conditions is also very likely determined by their hardness. Among these materials, HCO has the highest hardness, followed by FHSO, Estercoat, EGMD, paraffin and lastly beeswax. The wear loss of these materials (from shallow to deep) seems to follow the same order of their hardness, thus the higher hardness of the material, the less wear. Others also have reported that materials with lower hardness and softening temperature can be transferred away from the friction surface more easily, resulting in more wear loss [12]. Overall, our Estercoat which has higher hardness than paraffin had less wear indicating that under similar frictional conditions, Estercoat may have better performance durability than paraffin.

Table 2b shows the wear loss of different coating materials under different sliding velocities with fixed normal load of 5N at room temperature (25 °C). It was observed that the wear loss of all the materials except that of EGMD increased as sliding velocity was increased. When sliding velocity was increased, the sliding distance was also increased as the sliding time was kept constant, and longer sliding distance theoretically leads to more wear loss. However, the wear loss of EGMD surprisingly decreased with the increased sliding velocity. The wear behavior of coatings is strongly dependent on their ability to form the transfer film at the interface [18, 19]. It is possible that EGMD has formed a transfer film which prevented further contact of the steel ball with the surface by the high shearing force under the high sliding velocity. Such film can be useful for preventing fatigue deformation and reducing plough effect for coatings [12]. Similar to the data shown in

table 1, harder material tends to be more wear resistant. Beeswax having high coefficient of friction and being the softest material had the most wear, while HCO which has high hardness and low coefficient of friction had the least wear at different sliding velocities. FHSO and Estercoat were similar at low sliding velocity, while Estercoat has better performance at high sliding velocity. This is probably due to Estercoat having better transfer film forming ability than FHSO under high shearing force. The Estercoat also outperformed paraffin at different sliding velocity, indicating that the Estercoat as a surface coating probably has better performance durability.

The effect of environmental temperature on wear was also evaluated. Samples went through sliding at fixed normal load and sliding velocity (5 N and 5 rad/s, respectively) under different temperatures, and the wear loss was quantified. Table 2c shows that the wear loss of paraffin, FHSO, and beeswax all increased when the temperature was increased. The wear loss of HCO, EGMD and Estercoat was at the lowest when at room temperature, however, increased when the temperature was either lowered or elevated. The low temperature may have negatively affected the formation of transfer film, while the high temperature could have increased the transfer away of the coating on the counterface, thus all resulted in increased wear loss [12, 18, 19]. The wear loss of paraffin, beeswax, EGMD and Estercoat all corresponded to their changes in surface coefficient of friction with temperature. Low temperature did not have significant impact on paraffin, however, it reduced the coefficient of friction of beeswax. While the elevated temperature resulted in higher surface friction coefficient of paraffin and beeswax and may have led to softening and transferring away of paraffin and beeswax at the interface [12, 18], thus more severe wear at high temperature. For EGMD and Estercoat, their surface coefficient of friction was higher at lowered and elevated temperatures than when at room temperature, which matched their wear behavior. The coefficient of friction of HCO and FHSO was not significantly affected by temperature, however, their wear loss was significantly affected. It is suspected that the different response of wear loss to temperature may relate to the crystal structure and melting profile of the different materials. Overall, the Estercoat would outperform paraffin according to their observed friction and wear behaviors.

3.3 Effect of temperature on crystal structure and crystallinity of different waxy materials

Figure 3 shows the crystal morphology of paraffin, beeswax, FHSO, HCO, EGMD and Estercoat at 0, 25 and 50 °C. In agreement with what was previously reported by Fei et al. [8] and Hwang et al. [20], paraffin, beeswax, EGMD and Estercoat all showed needle-like and fibrous crystal, however, their sizes and networks were different. It seemed that paraffin, EGMD and Estercoat all had dendritic crystals which are highly interconnected and formed junction points, while beeswax has much finer crystals. FHSO crystallized into more ordered and larger crystals, while HCO seems to have mixed crystal morphology (rosette, fibrous, and irregular) at 25 °C which agree with what was reported by Yang et al. [21]. As shown in Figure 3, when temperature was increased to 50 °C, the crystal type of paraffin, beeswax, EGMD and Estercoat was not significant altered, however, the crystal number and density seemed to be decreased. When the temperature was lowered from 25 to 0 °C, crystal morphology of paraffin was not significant changed, while beeswax had denser crystals, and EGMD's and Estercoat's crystal density was reduced. For FHSO, temperature did not have significant impact on their crystal structures. For HCO, observation of the crystals became difficult when temperature was lowered to 0 or increased to 50 °C. The changes in crystal structure may correlate to the changes in coefficient of friction of these materials as they significantly influence the physical properties such as hardness of waxes. It was observed that the lower crystal density would lead to higher surface coefficient of friction as paraffin, beeswax, EGMD and Estercoat all have increased friction coefficient when temperature was increased from 25 to 50 °C. The increased temperature resulted in lower crystal density and led to a softer material, which subsequently negative affected transfer film forming and increased the real contact area at the interface, thus increase the friction coefficient. For FHSO, no significant changes in crystal structure was observed with temperature changes, thus, the coefficient of friction of FHSO was quite consistent at low and high temperatures. Although the crystal structure of HCO at 0 and 50 °C was not clear for unknown reasons, it is reasonable to speculate that it was not significantly changed as its friction coefficient was not significantly affected.

Table 3 shows the enthalpy and relative crystallinity (RC) of the tested waxes. In general, the RC of the materials decreased as the temperature increased. However, RC of several materials including FHSO and HCO were not sensitive to the variation of the equilibration temperature. This is probably another reason for why their coefficient of friction was not affected by the environmental temperature (Table 1c). Paraffin, beeswax, EGMD and Estercoat all had the highest RC at 0 °C, and their RC significantly decreased when the temperature was increased from 25 to 50 °C. Correspondingly, their coefficient of friction and wear loss all significantly increased (Table 2c). Beeswax had significantly higher RC at 0 than 25 °C, and accordingly, lower coefficient of friction and wear loss was observed at 0 °C. However, EGMD and Estercoat had slightly higher RC at 0 °C compared to 25 °C, but their coefficient of friction and wear loss were actually higher at 0 °C. Factors other than the crystallinity such as surface topography at different temperature may also have played a role on the surface properties of the EGMD and Estercoat. There is very limited study on the possible physical property changes of waxes when they are conditioned under various temperature after solidification. Studies on the surface characteristics under various temperatures using laser scanning microscopy could be helpful for a better understanding of surface property variations with temperature.

Conclusions

Surface friction coefficient of waxes is shown to be significantly influenced by normal load, sliding velocity and environmental temperature. The wear loss of these waxes also varies significantly with different sliding conditions. The transfer film forming ability and hardness of these materials significantly affect their friction and wear behaviors. Paraffin wax was susceptible to both normal load and sliding velocity. Larger normal load resulted in lower friction coefficient while higher sliding velocity led to higher friction coefficient of paraffin. FHSO, HCO, beeswax, EGMD and Estercoat were less sensitive to normal load and sliding velocity, and their friction coefficient were almost consistent. Higher environmental temperature decreased crystal density and crystallinity of paraffin, beeswax, EGMD and Estercoat, and subsequently increased their friction coefficient. Increased normal load, sliding velocity and environmental temperature, in general, resulted more severe wear of all the tested materials. Overall, the soybean oil-based Estercoat is confirmed to have friction and wear properties comparable or better than paraffin under tested conditions and can be a good ecofriendly substitute of paraffin. The information provided in this study can also be used as a reference for correctly designing systems for coating, conveying, packaging operations, transporting and storing of papers and paperboards coated with these materials.

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Figures and Tables



Figure 1. The three-ball on plate setup for tribological property measurements (TA instrument).

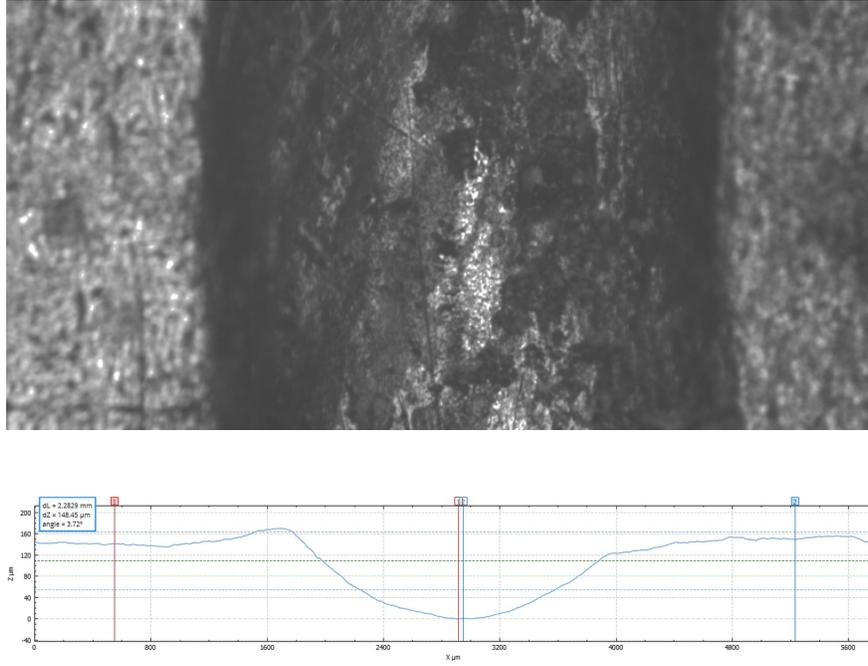
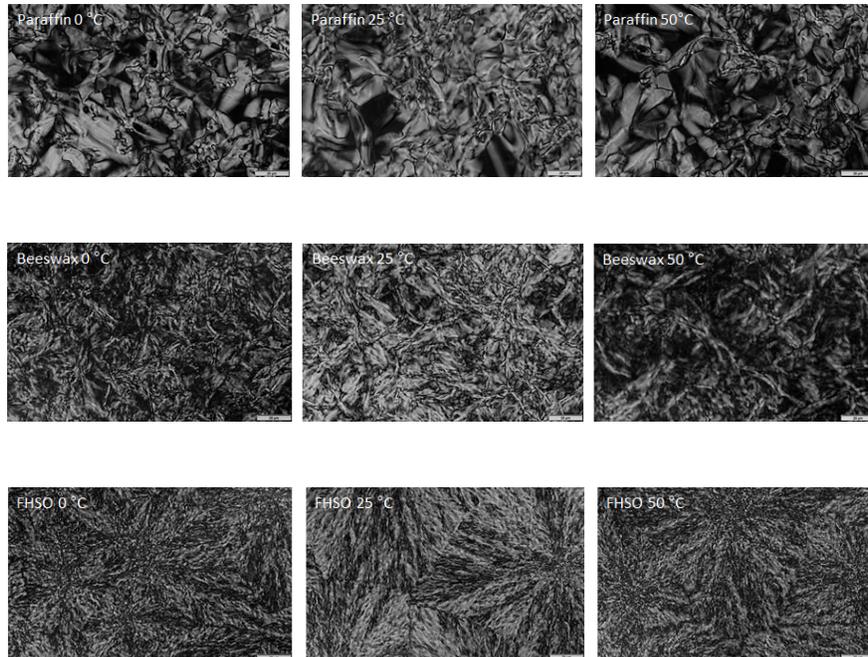


Figure 2. Typical wear track (top) and the profile (bottom) measured by laser microscope



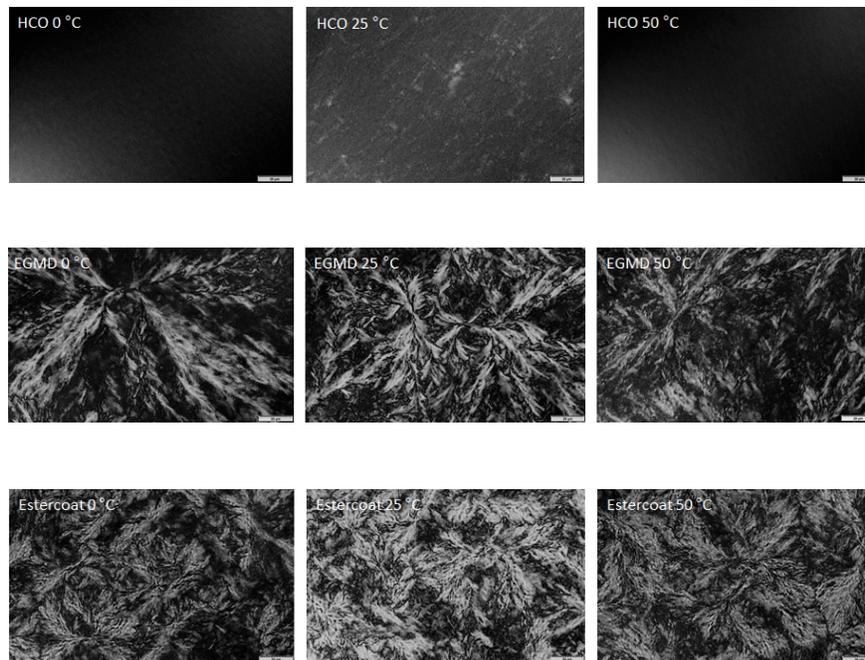


Figure 3. Crystal structures of paraffin, beeswax, fully hydrogenated soybean oil (FHSO), hydrogenated castor oil (HCO), ethylene glycol mono- and diester (EGMD) and Estercoat under 0, 25 and 50 °C

Table 1. Summary of coefficient of friction of different waxy materials under (a) different normal load, (b) different sliding velocity and (c) different environmental temperature.

c.

Paraffin
FHSO
HCO
Beeswax
EGMD
Estercoat

b.

Paraffin
FHSO
HCO
Beeswax
EGMD
Estercoat

c. Environmental Temperature (°C) Environmental Temperature (°C) Environmental Temperature (°C) 0 25 50 Paraffin 13

Table 2. Summary of wear loss of different waxy materials under (a) different normal load, (b) different sliding velocity and (c) different environmental temperature.

c.

Paraffin
 FHSO
 HCO
 Beeswax
 EGMD
 Estercoat
 b.

Paraffin
 FHSO
 HCO
 Beeswax
 EGMD
 Estercoat

c. Environmental Temperature (°C) Environmental Temperature (°C) Environmental Temperature (°C) 0 25 50 Paraffin 13

&

| c. | Environmental Temperature (°C) | Environmental Temperature (°C) | Environmental Temperature (°C) |
|-----------|--------------------------------|--------------------------------|--------------------------------|
| | 0 | 25 | 50 |
| Paraffin | 134.18±9.95 ^{bB} | 144.77±3.25 ^{bB} | 532.67±11.21 ^{aB} |
| FHSO | 46.89±2.33 ^{cDE} | 76.71±4.92 ^{bC} | 150.81±3.44 ^{aD} |
| HCO | 21.10±1.87 ^{bE} | 6.76±0.27 ^{cD} | 64.02±3.62 ^{aE} |
| Beeswax | 80.09±6.61 ^{cCD} | 314.81±30.96 ^{bA} | 1,100.68±59.18 ^{aA} |
| EGMD | 559.84±57.02 ^{aA} | 156.75±7.23 ^{cB} | 447.28±27.22 ^{bC} |
| Estercoat | 132.27±4.86 ^{bBC} | 90.18±3.11 ^{cC} | 426.14±6.14 ^{aC} |

&

| c. | Environmental Temperature (°C) | Environmental Temperature (°C) | Environmental Temperature (°C) |
|-----------|--------------------------------|--------------------------------|--------------------------------|
| | 0 | 25 | 50 |
| Paraffin | 134.18±9.95 ^{bB} | 144.77±3.25 ^{bB} | 532.67±11.21 ^{aB} |
| FHSO | 46.89±2.33 ^{cDE} | 76.71±4.92 ^{bC} | 150.81±3.44 ^{aD} |
| HCO | 21.10±1.87 ^{bE} | 6.76±0.27 ^{cD} | 64.02±3.62 ^{aE} |
| Beeswax | 80.09±6.61 ^{cCD} | 314.81±30.96 ^{bA} | 1,100.68±59.18 ^{aA} |
| EGMD | 559.84±57.02 ^{aA} | 156.75±7.23 ^{cB} | 447.28±27.22 ^{bC} |
| Estercoat | 132.27±4.86 ^{bBC} | 90.18±3.11 ^{cC} | 426.14±6.14 ^{aC} |

&

| c. | Environmental Temperature (°C) | Environmental Temperature (°C) | Environmental Temperature (°C) |
|----------|--------------------------------|--------------------------------|--------------------------------|
| | 0 | 25 | 50 |
| Paraffin | 134.18±9.95 ^{bB} | 144.77±3.25 ^{bB} | 532.67±11.21 ^{aB} |
| FHSO | 46.89±2.33 ^{cDE} | 76.71±4.92 ^{bC} | 150.81±3.44 ^{aD} |

| c. | Environmental Temperature (°C) | Environmental Temperature (°C) | Environmental Temperature (°C) |
|-----------|--------------------------------|--------------------------------|--------------------------------|
| HCO | 21.10±1.87 ^{bE} | 6.76±0.27 ^{cD} | 64.02±3.62 ^{aE} |
| Beeswax | 80.09±6.61 ^{cCD} | 314.81±30.96 ^{bA} | 1,100.68±59.18 ^{aA} |
| EGMD | 559.84±57.02 ^{aA} | 156.75±7.23 ^{cB} | 447.28±27.22 ^{bC} |
| Estercoat | 132.27±4.86 ^{bBC} | 90.18±3.11 ^{cC} | 426.14±6.14 ^{aC} |

| Materials | Enthalpy (J/g) | Enthalpy (J/g) |
|--|--|--|
| | 0 °C | 25 °C |
| Paraffin | 188.5±0.8 | 184.9±2.1 |
| FHSO | 179.9±3.6 | 181.9±9.6 |
| HCO | 130.0±6.1 | 128.1±8.6 |
| Beeswax | 168.5±1.7 | 164.7±5.3 |
| EGMD | 183.0±30.9 | 169.1±44.8 |
| Estercoat | 177.0±34.7 | 164.9±0.8 |
| For abbreviations, see footnote of Figure 3. | For abbreviations, see footnote of Figure 3. | For abbreviations, see footnote of Figure 3. |