

## Friction properties of chemically modified starch<sup>‡</sup>

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### ABSTRACT

Starches of varying chemical structures were esterified with anhydrides, formulated into dry film lubricants with the addition of canola oil, and its friction properties investigated. In the absence of canola, chemically modified starch displayed a very high coefficient of friction (COF). Addition of canola resulted in a sharp decrease in COF, which decreased with increasing [canola] until it attained a minimum and constant value that was independent of the further increase in [canola]. This observation was attributed to the adsorption of the canola oil onto starch due to H-bonding between the ester groups of the canola triglycerides and the free hydroxyl groups of starch. Analysis of the [canola] vs COF data using the Langmuir adsorption model showed stronger adsorption of canola to modified starch with a lower degree of substitution (DS). This was attributed to the availability of more free hydroxyl group adsorption sites on starches with lower DS than those with higher DS. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS: biobased dry film lubricant; boundary friction; canola oil; free energy of adsorption; starch

### INTRODUCTION

Starch is one of the most abundant farm-based raw materials [1]. It is obtained from a variety of cereal crops including corn, potato, rice, wheat and barley. Because of a large surplus over the demand for starch-bearing crops, there has been an extensive effort at developing new uses for starch [2]. Non-food applications of starch that are currently being investigated include biodegradable polymers [3], composites [4], elastomers [5] and lubricants [6].

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‡Names are necessary to report factually on available data; however, the United States Department of Agriculture (USDA) neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

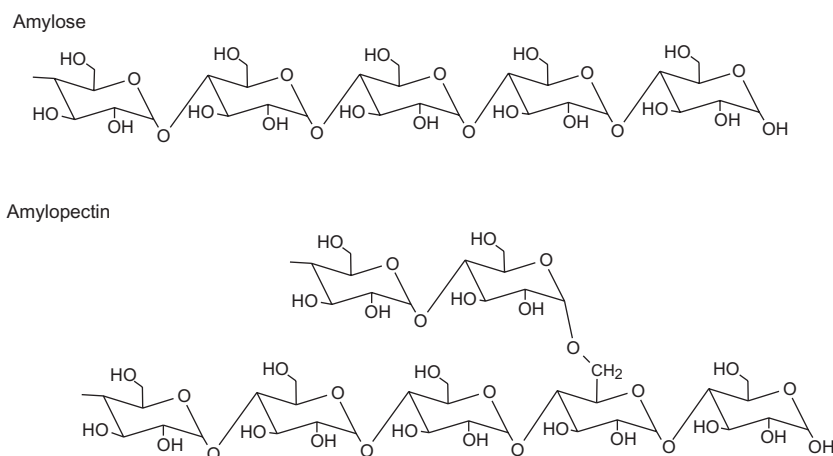


Figure 1. Structures of amylose and amylopectin starch molecules.

Starch is a biopolymer comprising glucose units connected at the 1 and 4 positions. Depending on how the glucose units are arranged in the starch biopolymer molecule, two types of starch structures are known. In amylose starch, each glucose unit is connected to two other glucose units on each side, resulting in a linear molecule. In amylopectin starch, some of the glucose units are connected to three glucose units, resulting in a branched structure. Schematics depicting amylose and amylopectin starch molecules are shown in Figure 1. The molecular weight of a starch biopolymer is dependent on its structure. The estimated molecular weight of a linear starch biopolymer amylose is in the range of  $0.5\text{--}2.0 \times 10^6$  [7]. The molecular weight of amylopectin is several orders of magnitude higher than that of amylose starch [1, 8].

The structure of a starch macromolecule in most crops is a mixture of 20–30% amylose and 70–80% amylopectin [1]. A special variety of corn called waxy corn comprises only amylopectin, or a branched structure with a very high molecular weight. There is also a special variety of corn called Cerestar® (formerly Amylomaize®) (Cerestar Co., Hammond, IN, USA) that contains an unusually high, 70%+, linear amylose starch macromolecule [9]. It should be noted that the molecular structure (linear vs branched) and molecular weight of starch molecules in a crop have a significant influence on its processability for various applications.

Starch in its native state is highly crystalline due to a strong intramolecular H-bonding between the hydroxyl groups of its glucose units [1]. As a result, starch is insoluble in water at room temperature. However, starch is soluble in solvents that are capable of disrupting the intramolecular H-bonding in favour of an intermolecular H-bonding [1]. These include some ionic liquids, concentrated aqueous solution of guanidine hydrochloride, 0.5 N aqueous NaOH, dimethyl sulfoxide (DMSO) and DMSO–water mixed solvent. Unfortunately, these solvents are not suitable for many applications in which solubility in a benign, safe and environmentally friendly solvent such as water is desired. One such application is in lubrication, where water is the most preferred solvent. Water-soluble starch can be used as the base to formulate and apply dry film lubricants. Formulation of starch-based lubricants requires solubilizing starch and various lubricant ingredients in water. Application of the dry film lubricant formulation also requires dissolving the formulation in a suitable solvent, preferably water.

Accomplishing both of these goals, that is, formulation and application, will require disrupting the crystalline structure of starch and enhancing its solubility in water.

Currently, the most widely practiced method for solubilizing starch in water is by cooking it with steam under high pressure and temperature [10]. This procedure successfully disrupts the crystalline structure and produces water-soluble starch that can be used to formulate various products. An extension of this process called Fantesk™, a slurry of starch with the appropriate oil phase, is processed with high temperature and high-pressure steam to produce the final product directly [10]. This procedure has been used to produce water-soluble starch with encapsulated ingredients for use in various applications [11].

Another method of solubilizing starch in water is through chemical modification [12]. This is usually carried out by reacting granular starch in aqueous suspension with anhydrides or other reagents that can react with the hydroxyl groups of starch. However, these granular starch reactions usually result in heterogeneous substitution, retention of much of the native starch crystallinity, low degree of substitution (DS) and low water solubility. This problem has been overcome through microwave heating under homogeneous conditions [13]. This has resulted in the melting of crystalline domains and in chemical modifications with a higher and more uniform substitution. Chemical modification reduces the number of hydroxyl groups available to participate in the intramolecular H-bonding required for the formation of the helical crystalline structure in native starch. The net effect will be the disruption of the crystalline structure and the improved water solubility of the starch.

In the work described here, various types of starches were chemically modified, formulated into dry film lubricants, and their friction properties investigated. Starches with varying amylose content were chemically modified using anhydrides of varying chemistries. These modified starches, with varying DS of their hydroxyl groups, were dissolved in water, and their friction properties studied with and without the incorporation of canola oil.

Dry film lubricants are those that are applied on sheet metal surfaces for the purpose of protecting it from damage, corrosion, rust and stain during transportation and/or storage [14]. Another important purpose of dry film lubricants is to provide lubricity during the metalworking process in the fabrication of a pre-lubricated sheet metal into various products. Successful application of dry film lubricants in metalworking provides a number of benefits including clean and environmentally friendly work area, low health risk to workers due to the absence of vapours and mist since no sprayed lubricant is used, and significant cost savings due to the elimination of the costs associated with maintaining and operating a liquid lubricant system.

## EXPERIMENTAL

### *Materials*

Unless otherwise stated, all materials were obtained from commercial sources and used as supplied. Normal cornstarch (pure food grade), and waxy maize starch (7350) were purchased from Tate & Lyle (Decatur, IL, USA). High (70%)-amylose starch (Hylon 7) was purchased from National Starch (Bridgewater, NJ, USA). Starches were vacuum dried overnight at 110 °C before using. Glacial acetic acid, acetic anhydride (AA) (99+%), octenylsuccinic anhydride (OSA, 97%) and dodecylsuccinic anhydride (DDSA, 95%) were purchased from Aldrich Chemical Co (Wilwaukee, WI, USA). Canola

oil was obtained from Cedar Vale Natural Health (Cedar Vale, KS, USA). Sucrose was obtained from Fleming Companies, Inc. (Oklahoma City, OK, USA). Isopropanol and hexane (both 99.9%) were obtained from Fisher Scientific (Fair Lawn, NJ, USA) and used as supplied. Deionized water was used to prepare solid lubricant formulations. Type 304 stainless steel plates,  $0.076 \times 30.48 \times 30.48$  cm, were obtained from McMaster Carr Supply Co. (Elmhurst, IL, USA) and cut into  $7.6 \times 15.2$  cm specimens for use in friction experiments. Grade 100, 440-C stainless steel balls were obtained from Altek Co. (Torrington, CT, USA) and had the following specifications: diameter,  $15.88 \pm 0.02$  mm; sphericity, 0.0254 mm; hardness, 57–67 c. The steel balls and flat sheets were cleaned by consecutive 5-minute sonications in isopropanol and hexane solvents prior to use in friction experiments.

#### *Preparation of Starch Esters*

Starch esters were prepared following the procedure described before [13]. In a typical procedure, 70 g dry starch, 70 g acetic acid, 7–35 g acetic anhydride, 0–7 g OSA or 0–8.8 g DDSA were added to a 270 ml Teflon vessel. A magnetic stir bar was added, and the mixture was stirred for 5 minutes. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a Milestone Microwave Labstation 1600 (Milestone Inc., Shelton, CT, USA) from 25–150 °C for over 3.5 minutes, then from 150–160 °C for over 1.5–2.5 minutes. After opening the reactor, the contents were placed in a Waring blender (Obtained from Dynamics Co., New Hartford, CT, USA) with 400 ml ethanol and blended until the precipitate was broken into fine particles (~1 minute). The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a Buchner funnel, and the starch ester was dried in a forced-air oven overnight at 50 °C and then in a vacuum oven overnight at 80 °C. DS values were estimated using  $^1\text{H}$  NMR as explained before [15]. Water solubilities were determined by stirring a 0.5 g sample in 30 ml water at room temperature, centrifuging at 3000 rpm for 10 minutes, and drying and weighing the supernatant.

#### *Preparation of Dry Film Lubricant*

In a typical procedure, 70 ml of 5% (w/w) sucrose solution in deionized water was prepared in a Waring blender. Chemically modified starch, 5.5 g, was then slowly added to the sucrose solution, and the mixture was blended at high speed for 5 minutes. The blender was then set at low speed, and the required quantity of canola oil was added drop-wise. After all the oil was added, the mixture was blended at high speed for 5 minutes. Sucrose is necessary to improve the adhesion of the starch film on the sheet metal surface, and was found to have minor effect on the measured coefficient of friction (COF) [6].

#### *Application of Dry Film Lubricant*

The dry film lubricant formulation was transferred to the siphon cup of a Badger Model 400 detail/touch-up siphon-feed spray gun (Badger Air-Brush Co., Franklin Park, IL, USA). Two pre-cleaned and pre-weighed steel plates ( $7.6 \times 15.2$  cm) were placed adjacent to each other on a stand in a fume hood. The spray gun was adjusted to operate in fine-spray mode and at 30 psi. The spray gun was held approximately 10 cm above the steel plates, and the lubricant sprayed by moving the spray gun vertically in a W pattern. After each application, the plates were dried with a hot-air dryer gun (Master Appliance Corp., Racine, WI, USA) and weighed. The process was repeated until a lubricant film of 0.15–0.20 mg was deposited on each plate.

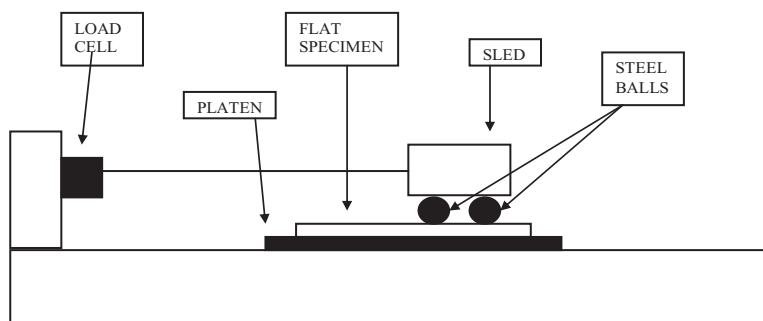


Figure 2. Schematic of a ball-on-flat tribometer.

### *Friction Test Instrument*

Friction was measured using a ball-on-flat tribometer. In the ball-on-flat tribometer, a flat sheet metal coated with the appropriate lubricant and secured onto a platen is pulled from under a sled of a specified weight and connected to a load cell. The sled contacts the flat sheet with three balls installed at its bottom. The load cell measures the friction force resisting the movement of the sled. The COF is obtained by dividing the measured friction force by the weight of the sled. A schematic of a ball-on-flat friction tester is shown in Figure 2.

The ball-on-flat tribometer used in this work was constructed by combining the SP-2000 slip/peel tester from Imass, Inc. (Accord, MA, USA), with a model 9793A test weight sled from Altek Co. The test weight sled provides the normal load and comprises slots at its bottom for securing the three steel balls. The SP-2000 has the following main features: a 2 kg load cell for measuring the friction force; a platen for securing the flat sheet metal sample and capable of travelling at a range of speeds; and an inbuilt microprocessor system for setting up test parameters, acquiring data, statistically analysing and displaying results on an on-board and on an external monitor, printing results on an external printer, transferring data to a PC for storage, and/or further data manipulations.

### *Friction Test Procedure*

Latex gloves were used to handle the test specimen, and great care was taken to prevent contamination of the test specimen surface. A typical test procedure was as follows. The sheet metal with a coated solid lubricant was secured on the platen. The sled with the selected weight was then placed on top, contacting the sheet metal with its three clean steel balls. The string from the load cell was then connected to the sled, and the platen moved to remove the slack from the string. The start button was then pushed, causing the platen to move at the selected speed and the load cell to measure the resulting friction force. The measured friction force is automatically recorded by the microprocessor at a maximum rate of 3906 samples/s. At the end of the test period, the platen stops automatically, and a summary of the results is displayed on the on-board screen, while at the same time a time vs friction force plot is displayed on the external monitor. At the end of each measurement, the instrument automatically displays the average of the friction force values in gf. The platen is then brought to the start position, and the sled removed for inspection. After inspection, the three balls are either cleaned for

reuse or replaced with a new set of clean balls. The sled is then put back onto a fresh surface of the same sheet metal for a repeat test. At the end of the second test, the friction force statistics for each test and for both tests is automatically printed on the external printer.

All friction experiments were conducted at room temperature, using a 1500 gf load sled at a speed of 2.54 mm/s for a total test time of 24 seconds. Two sheet metal specimens were prepared for each solid lubricant sample, and duplicate tests were conducted on each specimen. The COF for a solid lubricant sample was obtained by dividing the average friction force of the four measurements by the sled weight.

## RESULTS AND DISCUSSION

### *Chemically Modified Starches*

A schematic of the esterification reaction for the chemical modification of the starches is shown in Figure 3. A list of the chemically modified starches synthesized and investigated in this work is given in Table I. A total of five chemically modified starches were synthesized and investigated, of which three were based on waxy maize starch. As mentioned earlier, waxy maize is almost exclusively composed of amylopectin, that is, starch with a highly branched structure. The three chemically modified waxy maize starches differ from each other in the type of chemicals used in their preparation. One of the three was modified using only acetic anhydride, resulting in an acetate structure. The other two were modified using two anhydrides, one of which was AA and the second was either OSA or

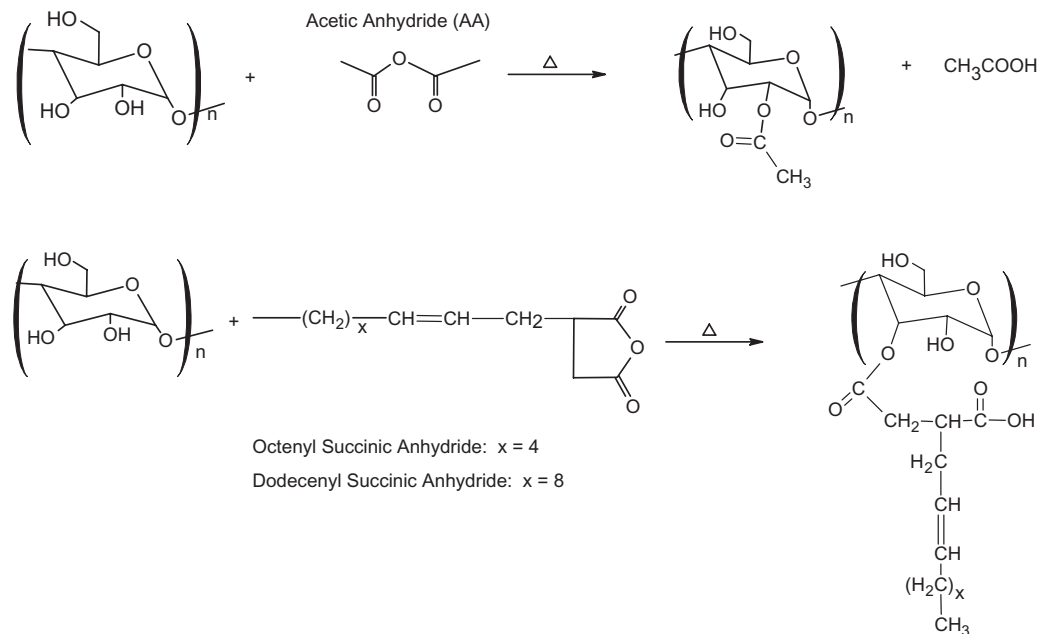


Figure 3. Esterification reactions between the glucose units of starch and anhydrides.

Table I. Chemically modified starches prepared in this work.

| Nomenclature | Starch            | Amylose<br>(%) | Degree of substitution* |       |       | Water<br>solubility†<br>(%) | Intrinsic<br>viscosity†<br>(ml/g) |
|--------------|-------------------|----------------|-------------------------|-------|-------|-----------------------------|-----------------------------------|
|              |                   |                | Acetate                 | OSA   | DDSA  |                             |                                   |
| WaxAc        | Waxy maize        | 1              | 1.12                    |       |       | 92                          | 17                                |
| WaxAcOct     | Waxy maize        | 1              | 0.36                    | 0.046 |       | 91                          | 18                                |
| WaxAcDod     | Waxy maize        | 1              | 0.31                    |       | 0.022 | 91 (0)                      | 18 (178)                          |
| NormAc       | Normal corn       | 27             | 0.95                    |       |       | 86 (0)                      | 55 (160)                          |
| HiAmylAc     | High-amylose corn | 70             | 0.89                    |       |       | 87 (0)                      | 40 (120)                          |

\* OSA = octenyl succinate, DDSA = dodecyl succinate.

† Values in parentheses are for chemically unmodified starches.

DDSA. Thus, these two modified wax maize starches will have chemical structures comprising a mixture of acetates and long-chain esters. The remaining two chemically modified starches were synthesized by reacting AA with either normal cornstarch or high-amylose cornstarch, resulting in acetate chemical structures. As given in Table I, these two structures have higher amylose content and, hence, lower amylopectin on the highly branched starch than the waxy maize starch used to prepare the first three samples. Table I also shows the nomenclature that will be used henceforth to refer to these five chemically modified starches. The nomenclature is a combination of the starch variety and the anhydride used in chemical modification. As an example, the chemically modified starch obtained by treating waxy maize starch with AA is referred to as WaxAc.

These five chemically modified starches, in addition to their differences in the type of starch variety and anhydride chemistry used in their preparation, also differ in their DS, that is, the number of free hydroxyl groups that were converted to esters per glucose unit of the starch macromolecules. As shown in Table I, in spite of the big differences in the DS among the five chemically modified starches, their water solubilities remained within a narrow range of 87–92%. In contrast, the unmodified starches showed no solubility in water. Table I also shows the intrinsic viscosities of the chemically modified and unmodified starches.

### *Boundary Friction Properties*

The chemically modified starches in Table I were used to prepare dry film lubricant formulations by dissolving it in hot water, followed by blending canola oil. For each chemically modified starch, a series of formulations with increasing canola oil-to-starch ratio were prepared. The formulations were spray applied on at least two clean steel sheet metals, and its friction properties evaluated on the ball-on-flat tribometer shown in Figure 2. Each coated steel sheet was used in two friction measurements, so that there were at least four tests per formulation.

Typical data from several boundary friction measurements on the ball-on-flat tribometer are shown in Figure 4. The data in Figure 4 is an overlay of time vs friction force for the three dry film lubricant formulations prepared from WaxAcDod. These three formulations differ from each other in canola oil-to-starch ratio, which in Figure 4 is expressed in moles of canola oil (mol wt = 879 g/mol) per kilogram of chemically modified starch. Friction was measured for a maximum of 24 seconds. As shown in Figure 4, the friction force initially rises sharply and levels off to a steady-state value after

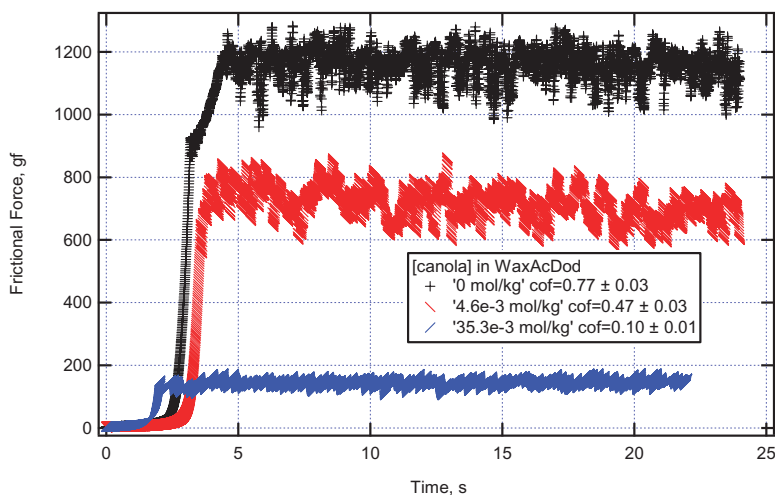


Figure 4. Friction data on the modified starch dry film lubricant measured with the ball-on-flat tribometer.

2–5 seconds. The friction force for the formulation was obtained by averaging the data in the steady-state region. The average and standard deviation values are then used to calculate the COF by dividing it by the normal load, which in this work is 1500 gf.

Figure 4 also compares the effect of the canola oil concentration on the friction properties of WaxAcDod dry film lubricants. In the absence of canola oil, a very high friction force was observed, indicating a strong interaction between the steel balls under the sled and the WaxAcDod film on the steel plates. Such a high friction is an indication that the modified starch film has a very hydrophilic surface, which is also true of the surface of the steel balls. This accounts for the strong interaction between the two surfaces, which results in a strong resistance to sliding and, hence, to the observed high friction force ( $\text{COF} = 0.77 \pm 0.03$ ). However, the addition of even a small amount of canola oil to WaxAcDod resulted in a dramatic decrease in the friction force. Thus, the addition of 4.6 mmol/kg of canola oil reduced the friction force from about 1200 gf to about 700 gf. As shown in Figure 4, further increase in the concentration of canola oil in WaxAcDod resulted in further reduction in friction force. Also, the higher concentration of canola oil resulted in reducing the variability in the friction force in the steady-state region, thereby lowering the standard deviation of the measured friction data.

The effect of canola oil concentration on COF in chemically modified starch is illustrated in Figure 5. In Figure 5, the concentration of canola oil is expressed in moles of canola oil per litre (mole/L or M) of starch. This is accomplished by multiplying the concentration of canola oil expressed in moles/kg (such as that shown in Figure 4) by 1.4 kg/L, the density of starch [1]. As will be discussed in the next section, such conversion allows for a proper analysis of the friction data.

The data in Figure 5 shows that the COF of the dry film lubricant reduces sharply with increasing concentration of canola oil. However, this reduction in COF occurs until a canola concentration of about 30 mM, where the COF approached about 0.1. Further increase in the concentration of canola oil above 30 mM resulted in a very little further reduction of the COF. Thus, a 2.5-fold increase in



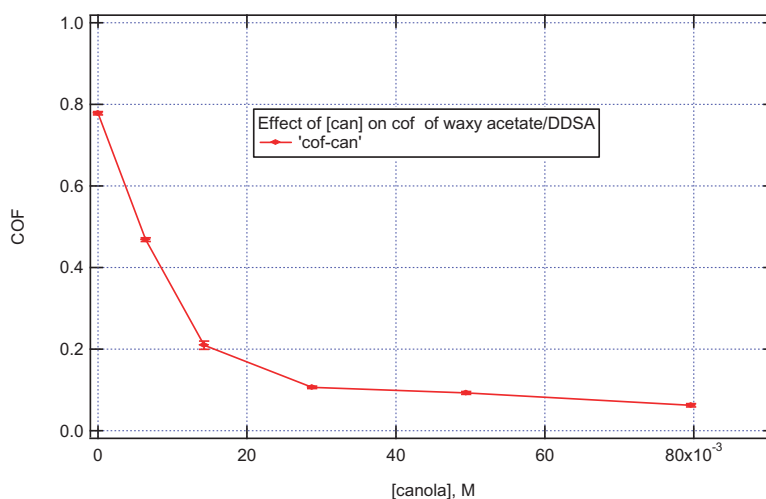


Figure 5. Effect of [canola] on the boundary friction of chemically modified starch.

canola oil concentration beyond 30 mM resulted in a less than 0.05 reduction in COF. Similar results were observed in all the dry film lubricants formulated with the chemically modified starches listed in Table I.

Based on the previous observations, the canola oil concentration–COF data shown in Figure 5 can be divided into three regions: (i) a low-concentration region, where the COF displays a sharp reduction with increasing canola oil concentration; (ii) an intermediate-concentration region, where the COF shows a gradual decrease with increasing canola oil concentration; and (iii) a high-concentration region, where the COF is constant and independent of canola oil concentration.

#### *Starch–Oil Interaction*

The data in Figure 5, where the COF of the chemically modified starch first reduces dramatically with increasing canola oil concentration and then levels off to a steady-state constant value at a relatively low canola concentration, can be explained if one assumes specific interactions between the starch and the oil molecules. The interaction being considered here is a H-bonding between the free hydroxyl groups of the glucose units of the starch macromolecule and the ester linkage in the triglyceride canola oil.

As mentioned before, starch in its native state is highly crystalline due to the intramolecular H-bonding between the free hydroxyl groups of its glucose units [1]. This means that the free hydroxyl groups are not available to participate in intermolecular H-bonding with other molecules, such as with the ester groups in triglycerides. However, the chemical modification of the starch disrupts the intramolecular H-bonding by the free hydroxyl groups and makes them available for intermolecular H-bonding. The availability of the free hydroxyl groups for intermolecular H-bonding also causes the starch surface to become highly polar and hydrophilic, and can explain the observed high water solubility and high COF of these chemically modified starches.

The reduction in COF when canola oil was blended into the chemically modified starch can be attributed to the reduction in the polarity of the starch film due to the adsorption of triglyceride molecules onto the free hydroxyl groups via H-bonding. As shown in Figure 5, as more and more canola oil was added to the formulation, the COF continued to decrease, indicating the progressive decrease in the number of free hydroxyl groups not participating in intermolecular H-bonding and, hence, the progressive decrease in the polarity of the starch.

However, it is clear from Figure 5 that the reduction in COF continues only up to a certain concentration of canola oil, beyond which the COF becomes constant and independent of the concentration of canola oil. A possible explanation for this observation is that there is a limited number of adsorption sites (free hydroxyl groups) for the triglyceride molecules to adsorb onto. Once all the adsorption sites are filled, the addition of more canola oil will not result in the additional adsorption of triglyceride molecules and, hence, no change in measured COF, as was observed in Figure 5. Such phenomenon can be expressed as an equilibrium process between the occupied ( $S_o$ ) and unoccupied ( $S_u$ ) starch sites as follows:



$$K_o = \frac{[S_o]}{[O_b][S_u]} \quad (2)$$

where  $[O_b]$  is the concentration of oil not adsorbed on a starch site (M) and  $K_o$  is the equilibrium constant ( $M^{-1}$ ).

In equation (2),  $[S_o]$  and  $[S_u]$  can be expressed in terms of fractional surface coverage,  $\theta$ , defined as follows:

$$\theta = \frac{[S_o]}{[S_t]} \quad (3)$$

where  $[S_t] = [S_o] + [S_u]$ .

Substitution of equation (3) in equation (2) leads to

$$\frac{1}{\theta} = 1 + \left( \frac{1}{\{K_o [O_b]\}} \right) \quad (4)$$

Equation (4) is called the Langmuir adsorption model [16–18]. It predicts that a plot of  $[O_b]^{-1}$  vs  $\theta^{-1}$  will give a straight line with an intercept of 1.0 and a slope of  $K_o^{-1}$ .  $K_o$  obtained from such a plot can be used to estimate the free energy of adsorption,  $\Delta G_{ads}$ , in Kcal/mol, of canola oil on the chemically modified starch as follows:

$$\Delta G_{ads} = -RT [\ln(K_o)] \quad (5)$$

where  $R = 1.987 \text{ cal}^\circ\text{K}^{-1}\text{mol}^{-1}$  is the universal gas constant and  $T$  is the absolute temperature in  $^\circ\text{K}$ .

Equations (4) and (5) can be used to analyse boundary friction data such as that shown in Figure 5 [19–21]. This is possible because the fractional surface coverage,  $\theta$ , can be estimated from boundary friction data using the following relationship [19–21]:

$$f_o = f_s (1 - \theta) + f_m \theta \quad (6)$$

where  $f_s$  and  $f_o$  are the COF of chemically modified starch without and with added canola oil, respectively, and  $f_m$  is the minimum COF of chemically modified starch with added oil ( $f_m$  is also referred to as the COF at full surface coverage).

Figure 6 shows the analysis of the data in Figure 5 using the Langmuir model [equation (5)]. As can be seen in Figure 6, plots of  $[\text{canola}]^{-1}$  vs  $\theta^{-1}$  gave a straight line with a slope of  $0.8 \pm 0.1$ , which is in the range predicted by the model. From the slope,  $K_o$  was obtained and used to calculate  $\Delta G_{\text{ads}}$  using equation (6). Table II is a summary of the  $\Delta G_{\text{ads}}$  of canola oil on the chemically modified starches investigated in this work. Also shown in Table II is the DS of the free hydroxyl groups by the anhydrides. The data indicate that both starch structure and DS affect the adsorption of canola. Thus, canola adsorbs stronger on chemically modified starches with lower DS and higher composition of amylose. The effect of DS is consistent with the expectation that starches with lower DS will have more free hydroxyl groups and, hence, more adsorption sites than those with high DS. This explanation is supported by the data in Table III, which compares  $\Delta G_{\text{ads}}$  from this work with that of soybean oil on

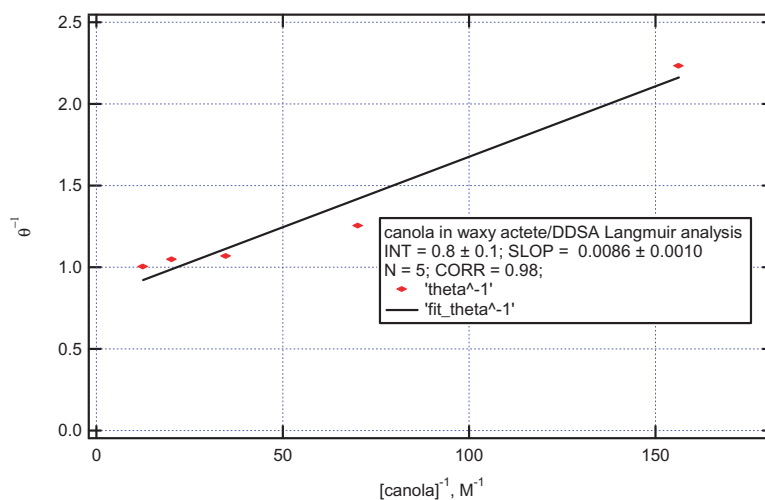


Figure 6. Langmuir analysis of the boundary friction data of chemically modified starch formulated with canola oil.

Table II. Free energy of adsorption of canola oil on chemically modified starch.

| Chemically modified starch | Degree of substitution | $\Delta G_{\text{ads}}$ (kcal/mol) |
|----------------------------|------------------------|------------------------------------|
| WaxAc                      | 1.12                   | -2.24                              |
| NormAc                     | 0.95                   | -2.33                              |
| HiAmylAc                   | 0.89                   | -2.74                              |
| WaxAcOct                   | 0.36/0.046             | -2.41                              |
| WaxAcDod                   | 0.31/0.022             | -2.80                              |

Table III. Effect of starch treatment on the free energy of adsorption of vegetable oils on starch.

| Method* | Starch | Oil     | $\Delta G_{\text{ads}}$ (kcal/mol) | Reference |
|---------|--------|---------|------------------------------------|-----------|
| Chem    | NormAc | Canola  | -2.33                              | This work |
| Cook    | Normal | Soybean | -2.96                              | [21]      |
| Chem    | WaxAc  | Canola  | -2.24                              | This work |
| Cook    | Waxy   | Soybean | -2.91                              | [21]      |

\* Chem = chemically modified, Cook = steam-jet cooking of starch-oil slurry.

starches that were solubilized in water using a steam-jet cooking process called Fantesk<sup>TM</sup> [21]. It is clear from this comparison that the adsorption of vegetable oils on steam-jet cooked starch, which does not have any of its free hydroxyl groups converted to esters (i.e. DS = 0), is stronger than that on chemically modified starch, where some of the hydroxyl groups are converted to esters (i.e. DS > 0).

## SUMMARY AND CONCLUSION

Starch is one of the most abundantly available farm-based raw materials. It is a significant component of major commodity crops such as corn, potato, rice, wheat and barley. Starch is a high-molecular-weight biopolymer of glucose sub-units arranged linearly without branching, called amylose, or with branching, called amylopectin.

Development of new applications for starch requires that it be soluble in a suitable solvent, preferably in a benign solvent such as water. However, starch in its native state is insoluble in room temperature water. This is attributed to its highly crystalline structure as a result of a strong intramolecular H-bonding between the free hydroxyl groups of its glucose units. One method of increasing the solubility of starch in water is to chemically modify it by converting a portion of its free hydroxyl groups into esters. Such chemical modification will reduce the number of free hydroxyl groups available for intramolecular H-bonding, thereby disrupting the crystalline structure and promoting solubility in water.

In the work described here, starches with various degrees of amylose content (1–70%), were chemically modified by reacting it with anhydrides in a microwave reactor. The starches were waxy maize with 1% amylose, normal cornstarch with 27% amylose, and high-amylose cornstarch with 70% amylose. The anhydrides were AA, OSA and DDSA. Each type of starch was modified by reacting it with AA. In addition, waxy maize starch was modified by reacting it with a mixture of AA and either OSA or DDSA. The synthesis resulted in highly water-soluble modified starches of varying DS of the free hydroxyl groups.

The chemically modified starches were then dissolved in water and formulated into dry film lubricants. Dry film lubricants are those that are applied on clean sheet metal to protect it from damage, rust, corrosion and stain during transport and storage. It is also intended to provide lubricity during the metalworking operation, where the sheet metal is fabricated into various products. Each of the chemically modified starches was used to formulate several dry film lubricants differing in concentration of canola oil. The dry film lubricant formulations were then dissolved in water, spray applied on clean steel sheet metal, and its friction properties investigated.

Chemically modified starch without added canola oil displayed a very high COF. This was attributed to the high polarity of the starch surface due to the presence of free hydroxyl groups that did not react with the anhydride and also do not participate in intramolecular H-bonding. The addition of canola oil resulted in a sharp decrease of COF initially. With further addition of canola oil, the COF attained a minimum value, which remained constant and independent of canola oil concentration. The effect of canola oil on COF was attributed to the H-bonding between the ester groups of the canola oil triglyceride and the free hydroxyl groups of the starch glucose units. The H-bonding reduces the polarity of the starch surface and, hence, its COF.

The canola oil concentration vs COF data for the modified starches was analysed using the Langmuir adsorption model. The analysis showed that the free energy of adsorption,  $\Delta G_{\text{ads}}$ , of canola oil on the modified starch surface was a function of the chemical structure and DS of the starch. Thus,  $\Delta G_{\text{ads}}$  was stronger (larger negative number) on starches with higher composition of amylose and lower DS. The effect of DS was attributed to the availability of more adsorption sites for the canola oil triglycerides molecules to form H-bonding on the modified starch with lower DS than those with higher DS.

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