

The Effects of Chemical Modification on the Pasting Characteristics of a High-Protein Oat Flour (Hinoat)¹

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ABSTRACT

The effects of chemical modification on the pasting properties of a high-protein (Hinoat) and medium-protein (Rodney) oat flour were studied. Both acetylation and hydroxyalkylation resulted in a shift to lower gelatinization temperatures and higher viscosities than were exhibited by the parent flours. Oxidation by hypochlorite resulted in products having pastes more stable to shear and of a smoother consistency. These derivatives were resistant to retrogradation but were opaque and buff-colored. The carbamoylethyl ether of Hinoat flour had a lower peak viscosity than the corresponding wheat flour derivative, but a similar setback viscosity. Again the oat pastes were buff-colored and opaque. These results are discussed from the viewpoint of potential low-cost food and industrial applications.

The pasting characteristics of cereal and root starches have been well documented and discussed in several articles and texts (1-4). Much has also been written on the effects of chemical modification upon the pasting characteristics of such starches (5-7). The industrial preparation and uses of selected modified starches have been comprehensively reviewed by Whistler and Paschall (8).

Recently, considerable attention has been given to the chemical modification of cereal flours, particularly wheat and yellow corn, as a means of providing low-cost, wet-end additives for the paper industries. Of particular interest have been the carbamoyl ether and cationic aminoethyl ether derivatives of wheat and corn flour (9,10). These additives, besides being low in cost, as compared to the highly purified corn starch derivatives, provide equal or better binding strengths to the pulp.

In the food industry, starches have been modified to provide shear stability, retortability, resistance to retrogradation, and tolerance toward freezing and thawing. Examples of such derivatives are acetyl, carboxymethyl, and hydroxyethyl ethers and oxidized starches (11).

In this Institute, work is being conducted on oats as part of an overall program involving utilization of Canadian agricultural raw materials. There is at present a high degree of interest in North America in some new and recently licensed high-protein oat varieties, e.g. Hinoat and Dall. The protein content of dehulled groats of these varieties is in the range 22 to 26%, thereby making them potentially attractive as high-protein foods with or without further concentration or isolation. Recently Wu and Stringfellow (12) at the USDA Northern Regional Laboratory have succeeded in preparing ultrahigh protein fractions from oats by air-classification. This report presents information on the effect of oxidation, varied esterification, and etherification of high-protein oat flour from the variety OA-123-33 (Hinoat), upon the subsequent pasting characteristics of their aqueous slurries.

MATERIALS AND METHODS

Oat flours were prepared from cleaned, dehulled groats of varieties Hinoat (OA-123-33) and commercial Rodney. Groats were milled in a small laboratory

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impact mill, and sieved through a 60-mesh U.S. Bureau of Standards screen. This fraction passing the 60-mesh screen is hereafter known as "oat flour" for the purposes of this study. All modifying reagents used in the subsequent reactions were food grade approved.

Pasting of Flours

All flours, modified and unmodified, were pasted as 5% w./w. slurries using a Brabender ViscoAmylograph, equipped with a strain-gauge transducer and amplifier-recorder system as described by Voisey and Nunes (13). This modification replaces the cartridge and flat-bed recorder originally supplied with the Amylograph.

A bowl speed of 75 r.p.m. and a heating and cooling rate of 1.5°C. per min. were employed as operating conditions for pasting evaluations.

Preparation of Acetyl Oat Flours, and Oat and Wheat Starches

Forty grams flour or starch was slurried in 400 ml. water to make a fluid suspension at 25°C. Acetylation was carried out by the dropwise addition of acetic anhydride (10.2 g.) while simultaneously maintaining the pH of the suspension within the range 8.0 to 8.5 using 3% NaOH solution. When all the anhydride had been added, the pH was adjusted to 4.5 with 0.5N HCl and the slurry filtered, washed free of acid, and the wet cake dried by removing water with 200 ml. 95% EtOH followed by air-drying. Products were also prepared by

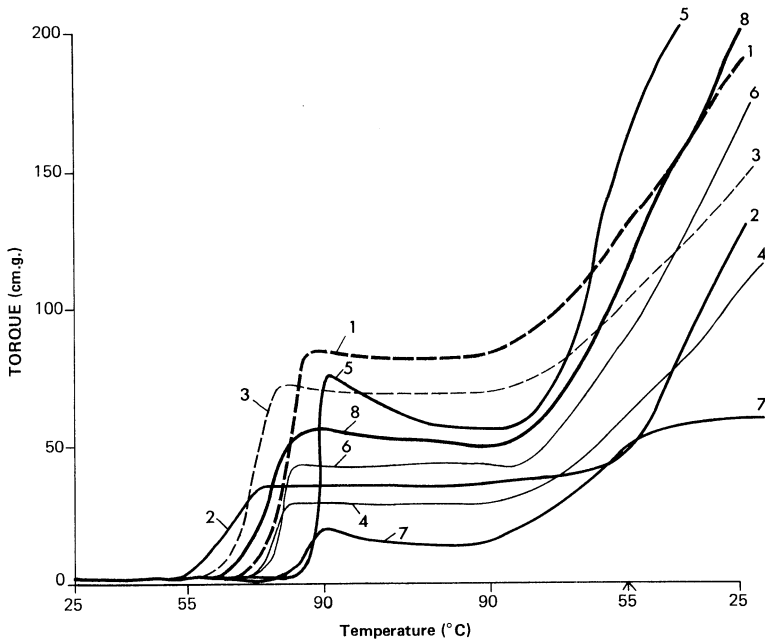


Fig. 1. The effect of acetylation on the pasting characteristics of various oat flours and starches. 1) Rodney (XI); 2) Rodney (X2); 3) Hinoat (XI); 4) Hinoat (X2); 5) Hinoat starch; 6) Hinoat starch (XI); 7) Hinoat flour; 8) wheat starch (XI).

using twice as much anhydride. Acetylated flours were thus designated as x1 and x2. The amount of acetic anhydride added was such that the maximum degree of substitution could not exceed 0.07.

Hydroxyethyl and Hydroxypropyl Flours and Starches

Forty grams flour or starch was slurried in 100 to 150 ml. water contained in a stoppered bottle at a temperature below 40°C. Approximately 15 g. NaCl was added (to prevent gelatinization of the starch component during the reaction) followed by 2 g. of a 30% NaOH solution added dropwise with vigorous stirring. The slurry was cooled to 2°C. and ethylene oxide (EO) or propylene oxide (PO) added such that 1.5 g. and 2.0 g. weight gain was achieved for EO and PO, respectively. The reaction was conducted by shaking for 24 hr. at 40°C. for EO and 48 hr. at 40°C. for PO. The reaction product was isolated by acidifying the slurry with N HCl to pH 5.0 followed by filtration, thorough washing with distilled water and soaking in ethanol (200 ml.) prior to drying in air at room temperature. The amounts of EO and PO added were such that the degree of substitution could not exceed 0.1.

Oxidation of Oat Flours

Mild Oxidation using Hypochlorite (6% available Cl_2). An aqueous fluid suspension (5%) of oat flour was adjusted to pH 9.0 with 2% NaOH solution

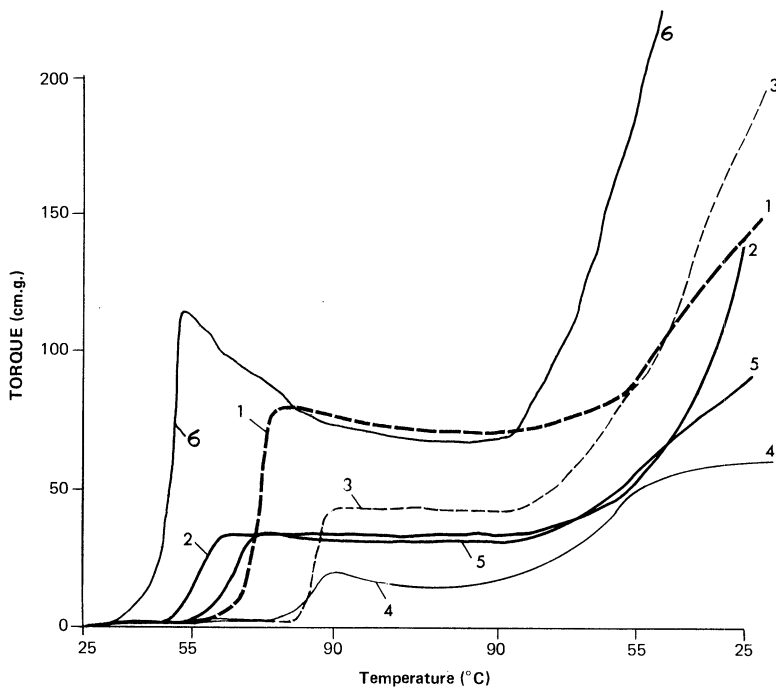


Fig. 2. The effect of hydroxyalkylation on the pasting properties of Hinoat oat flour and starches. 1) hydroxyethyl oat flour; 2) hydroxypropyl wheat flour; 3) hydroxypropyl oat flour; 4) oat flour; 5) hydroxyethyl oat starch; and 6) hydroxyethyl wheat starch.

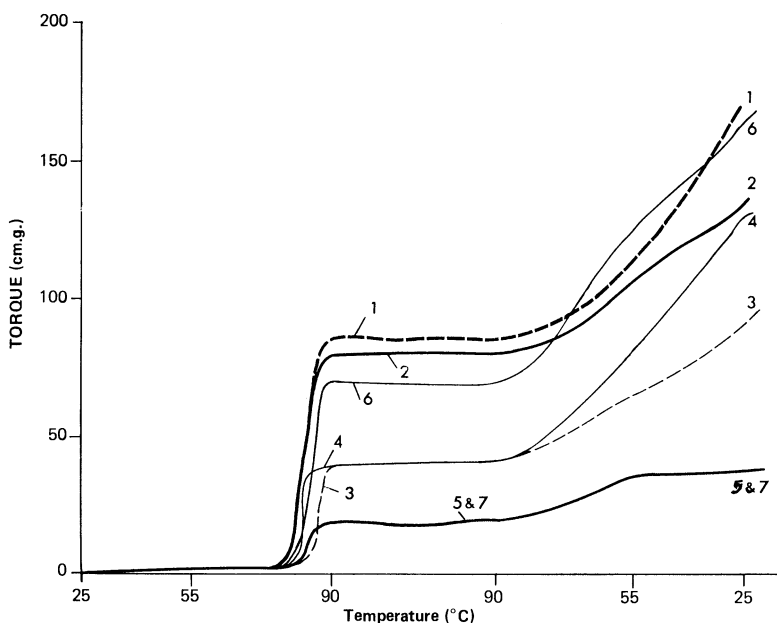


Fig. 3. The effect of oxidation on the pasting properties of oat flours. 1) Rodney ($1 \times \text{OCl}^-$); 2) Rodney ($2 \times \text{OCl}^-$); 3) Hinoat ($1 \times \text{OCl}^-$); 4) Hinoat ($2 \times \text{OCl}^-$); 5) Hinoat (aqueous NaClO_2 /acetic acid), 6) Hinoat (NaClO_2 /acetic acid in 70% MeOH); and 7) Hinoat flour.

under moderate agitation. Sodium hypochlorite solution equivalent to 10% of the weight of flour was slowly added over a period of 4 hr. while maintaining the pH at 9.0 by the concurrent addition of 0.5N HCl. Following this addition the pH was adjusted to 6.5 with 0.5N HCl. The product was isolated by filtration, water-washing (containing a small amount of NaHSO_3 to destroy excess Cl_2), soaking in ethanol (200 ml.), and final drying in a stream of cool air.

Products were also prepared by using twice as much hypochlorite as is described above. Oxidized products were designated as $1 \times \text{OCl}^-$ and $2 \times \text{OCl}^-$.

Oxidation with Sodium Chlorite in Dilute Acetic Acid. Oat flour (50 g.) was reacted for 4 hr. with mild agitation at 50°C . with 500 ml. of a 0.5% solution of sodium chlorite (NaClO_2) in 1) water adjusted to pH 4.5 with glacial acetic acid, and 2) 70% aqueous methanol similarly adjusted to pH 4.5. Products were isolated by 1) copious water washes plus an alcohol (200 ml.) exchange, and 2) washing in 400 ml. each of 70% methanol, 95% methanol, and absolute alcohol, followed by air-drying.

Carbamoylethyl Oat Flour and Wheat Flour

Carbamoylethyl oat and wheat flours were prepared as described by Smith et al. (9) for wheat flour.

Slurries were repeatedly diluted to 1,500 ml. with water, neutralized, filtered, or centrifuged. Finally, products were isolated by blending in 200 ml. alcohol, crumbling the filtered cake, and air-drying.

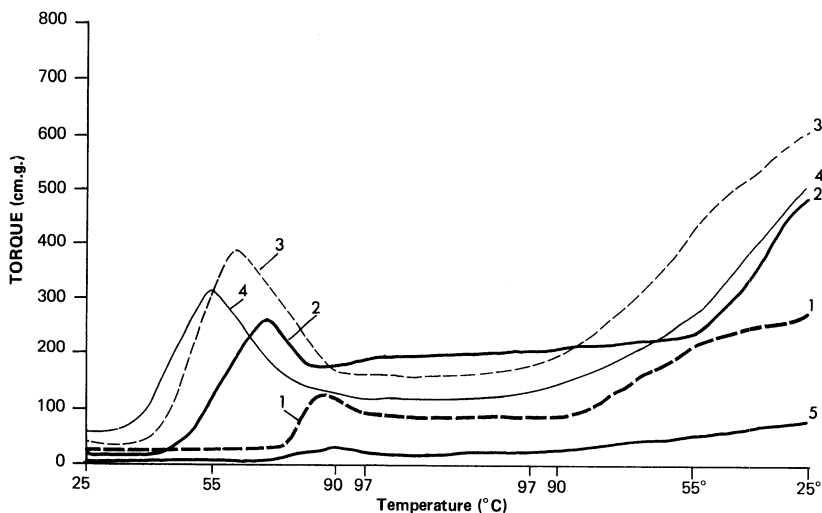


Fig. 4. Pasting curves for various carbamoylethyl oat flours. 1) Hinoat-10; 2) Hinoat-20; 3) Hinoat-30; 4) Hinoat-40; 5) Hinoat flour. Numerical designation (-10, etc.) indicates the amount of acrylamide present during reaction.

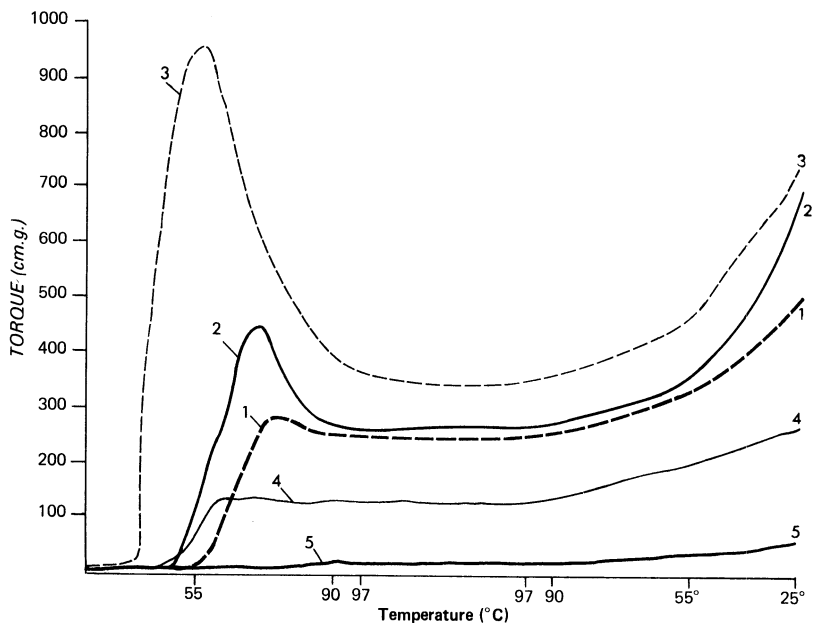


Fig. 5. Pasting curves of carbamoylethyl wheat flour. 1) Wheat-10; 2) wheat-20; 3) wheat-30; 4) wheat-40; 5) wheat flour. Numerical designation (-10, etc.) indicates the amount of acrylamide present during reaction.

RESULTS AND DISCUSSION

Introduction of small amounts of acetyl groups into any starch lattice 1) alters

the gelatinization range, 2) reduces the tendency of the paste to break down under constant shear, and 3) prevents retrogradation of the cooled, cooked paste. Acetylation (often coupled with minimal cross-linking) also provides a resistance to syneresis during freezing and thawing cycles.

The pasting curves for acetylated oat flours are shown in Fig. 1, and are compared with those for acetylated wheat starch, oat starch, and unmodified oat flours and oat starch. Acetylation slightly lowers the gelatinization point, increases the peak viscosity, provides shear stability, and provides a higher cooled-paste viscosity at 25°C. after cooking. Pastes allowed to stand for 12 to 18 hr. at room temperature showed no retrogradation in the case of acetylated Rodney and Hinoat oat flours, nor for acetylated oat and wheat starches. However, the derivatized oat flour paste was buff-colored and did not have as high a gloss as pastes from acetyl oat and wheat starches.

This effect is attributed to the protein in the flour. There is little marked difference in the viscosities of the oat flours at the various reference points when compared with acetyl wheat starch and acetyl oat starch. Thus, if translucence is not of major concern, oat flours could possibly replace some starches for certain applications.

Hydroxyalkyl oat flours show similar amylographic behavior to acetylated flours (Fig. 2). Pastes are smooth and creamy and show no signs of retrogradation when stored at 2°C. and 25°C. for 18 hr. It is interesting to note that both hydroxyethyl and hydroxypropyl oat flour slurries (5%) have higher viscosity profiles than the corresponding hydroxyethyl oat starch (5%) from the same variety. However, neither the hydroxyalkyl flours nor starch from oats is as highly viscous as hydroxyethyl wheat starch.

The effects of oxidation by NaOCl on oat flours are quite marked (Fig. 3). Amylograph curves are similar to those for hydroxyalkyl flours, except that the gelatinization peak temperature is not displaced to lower values. Setback viscosity is lower than some hydroxyalkyl derivatives. A very stable flat plateau exists for all samples over a 30-min. holding period at 95°C. There is, however, a marked difference in the curves for oat variety Rodney as compared with Hinoat. This difference was much smaller in the acetylated oat flours. It is unclear at present why this large difference exists. Attempts were made to oxidize oat flour under mildly acidic conditions using NaClO₂/dilute acetic acid as oxidizing agent. This agent is used in the nondegradative bleaching of high-purity wood pulps. If bleaching is carried out in a totally aqueous medium, no effect is seen, since the subsequent curve for the treated flour is identical to that of the parent flour. However, when conducted in 70% aqueous alcoholic solution, a marked change takes place. The amylograph curve of Hinoat approaches the viscosity profile for oxidized Rodney flour. It has not been possible to explain this effect. All oxidized pastes are smooth and creamy and do not exhibit retrogradation.

Though it is unsuitable for food use, the carbamoyl ethyl oat flour is included here because of the high degree of interest being shown in providing low-cost, wet-end additives and coatings for the paper industry. The oat derivatives are less viscous than those made from an all-purpose wheat flour (Figs. 4 and 5); further, cooked slurries of oat derivatives are cream/buff-colored and opaque, whereas the wheat flour derivatives are off-white and slightly translucent. Oat flour derivatives remain to be tested as wet-end additives, but may find uses in the

manufacture of some brown papers at a lower overall cost than wheat or corn flour derivatives.

It is also interesting to note that none of these derivatives gives rise to a translucent paste. As mentioned before, this is probably due to the effect of the protein on paste clarity. However, the cream-buff color of pastes made from acetyl, hydroxyalkyl, and oxidized (NaOCl) oat flours may not be objectionable, since many food applications of modified starches do not require this translucence (e.g., sauces, gravies, emulsions, salad dressings, puddings, baby food). Work is continuing in an effort to find out whether these modified flours are acceptable in some common food formulations and preparations.

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