Preparation and Properties of Carbamoylethyl Wheat Flour[1]

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ABSTRACT

Ungelatinized, crude, and refined carbamoylethyl ethers of wheat flour (CEWF) were prepared by an alkali-catalyzed addition of acrylamide to flour. Best results were obtained from reactions run at 40° to 42°C. for 18 hr. Under these conditions yields of crude and refined CEWF's, based on the combined weights of dry flour and acrylamide, ranged from 77 to 86% and 73 to 84%, respectively. The CEWF's are stable, free-flowing, odorless, practically colorless, and exhibit shelf-life of more than 1 year without change in composition or performance. Differential infrared spectroscopy and nitrogen analyses suggest that carbamoylethyl groups were introduced into both the starch and gluten components of wheat flour during carbamoylethylation. Amylograph studies show that carbamoylethylation decreases the gelatinization temperature range and greatly improves the pasting characteristics of flour. Heat-gelatinized aqueous pastes of refined CEWF's (2% by weight) exhibit excellent clarity and film-forming properties and have Brookfield viscosities ranging from 375 to 715 cP. at 25°C. and 30 r.p.m. Addition of hypochlorite-treated CEWF at a 2% level to unbleached kraft furnishes gave handsheets exhibiting wet-tensile strength about 16-fold that of the control.

Recent studies (1) have shown that hypochlorite-treated carbamoylethyl corn starch (CES), when employed as wet-end additives in papermaking, impart a 10- to 16-fold increase in wet-tensile strength and substantial increases in folding endurance, and dry-tensile and bursting strengths of the paper. An investigation was initiated to determine whether products having properties similar to those of CES could be obtained from wheat flour, and whether any economic or technical advantage might be realized. We now have prepared carbamoylethyl wheat flour (CEWF) by an alkali-catalyzed addition of acrylamide to flour. Carbamoylethyl ethers of both corn starch and wheat flour prepared with the same amounts of acrylamide under the same reaction conditions were evaluated as wet-end additives in papermaking. Addition of hypochlorite-treated CEWF and CES at a 2% level to unbleached kraft furnishes gave handsheets exhibiting wet-tensile strength as high as 3,340 and 3,350 meters, respectively. These preliminary results indicate that the performance of CEWF as a wet-strength agent for paper is comparable to that of CES. Carbamoylethylation lowers the gelatinization temperature and improves the pasting characteristics of flour. This paper presents the preparation and properties of CEWF.

MATERIALS AND METHODS

The commercial hard red winter wheat flour used (Gloria Baker's Flour, Beardstown Mills) was unbleached, not malted, and contained 12 to 14% moisture

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and 13.9% protein [2.44% nitrogen (N)]. Purified gluten contained 6.6% moisture, 17.3% N, and 0.5% starch. Commercial acrylamide, sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), sodium hypochlorite (NaOCl) solution (Clorox) having 5.08% (by weight) sodium hypochloride (5.5% available chlorine), hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) were used. α-Amylase was a bacterial preparation obtained from K and K Laboratories, Plainview, N.Y. A Western unbleached softwood kraft pulp having a Canadian Standard Freeness of 570 cc. was used.

Brookfield Viscosity

A Brookfield Synchro-Lectric viscometer, Model LVF, with four speeds (6, 12, 30, and 60 r.p.m.), was used to determine the viscosity of 2% (by weight on a moisture-ash-free basis) aqueous dispersions of CEWF at 25°C. and 30 r.p.m. All dispersions were prepared by heating stirred, aqueous slurries of the products in a closed system on a steam-bath at 90+°C. for 30 min.

Pasting Characteristics

A Brabender Amylograph, Model No. 209, with a cup speed of 75 r.p.m. and a uniform heating rate of 1.5°C. rise in temperature per min. and the same cooling rate, was used to determine the pasting characteristics of 4% (by weight on a moisture-ash-free basis) aqueous dispersions of CEWF's.

Paste Clarity (Transparency)

A Coleman Junior Model 6A spectrophotometer was used to measure clarity of the aqueous pastes of CEWF's as percentage transmission of light at 650 nm., based on 100% transmission for distilled water.

Infrared Spectra

Infrared spectra were measured with a Perkin-Elmer Model 137 spectrophotometer. Differential spectra were recorded for KBr discs containing either CEWF or carbamoylethyl gluten in the sample beam with discs containing equal amounts of the corresponding parent materials in the reference beam.

Starch Determination

Determinations for starch were made according to Shasha (2).

Typical Preparation of Ungelatinized CEWF

Wheat flour (162 g., dry basis) was added to a saturated aqueous solution of Na_2SO_4 (234 ml.); and following the development of a uniform slurry, acrylamide (30 g.) was added portionwise. Five minutes after the addition of acrylamide, 17.5 g. of a 24% (by weight) aqueous solution of NaOH was added dropwise. Stirring was continuous throughout. The mixture was heated in a closed system in a thermostated water-bath at 40° to 42°C. for 18 hr. The mixture was diluted with distilled water to a total volume of 1,200 to 1,300 ml. and the pH was adjusted to 6.8 with 1N HCl. The crude product was isolated by centrifuging at 1,400 r.p.m. for 10 min. and decanting the supernatant. If the crude product was desired, the centrifugate was partially dehydrated by blending with absolute methanol (300 to 400 ml.) in a Waring Blendor, collected by suction filtration, and vacuum-dried over H_2SO_4. The refined product was obtained by washing the crude material three times with 400-ml. portions of distilled water in a Waring Blendor and isolating the product by centrifuging as described above after each washing. The water-washed product was partially dehydrated by blending with absolute ethanol (400 to 500 ml.), collected, dried over H_2SO_4, and ground to pass a 40-mesh screen.

Attempted Isolation of the Gluten Fraction from CEWF

Centrifugation of a freshly prepared reaction mixture of CEWF at 3,200 r.p.m. for 30 min. resulted in the formation of two layers of material. The top layer consisted of a mixture of starch and gluten, but the bottom layer was predominantly starch. Further purification of the top layer was attempted by suspending it in water and centrifuging at high speed in a clinical centrifuge for 3 to 5 min. The supernatant was siphoned off and the washing procedure repeated seven times. The crude gluten mixture contained 31% starch. This material was suspended in water and treated with 1 ml. of α-amylase solution (10 mg. α-amylase per 5 ml. water) and digested at 50°C. for 48 hr. with continuous agitation. The digested material was dialyzed against distilled water (water changed every 24 hr.). After 96 hr., an infrared spectrum obtained from a portion of the material in the dialysis tubing indicated that a considerable amount of starch was still present. Further work on this impure fraction was impractical.

Carbamoylethylation of Gluten

Purified gluten (2 g., dry basis) was slurried in 50 ml. of distilled water. Acrylamide (0.4 g.) was added to the mixture, followed by the dropwise addition of 0.2 g. of aqueous NaOH (24% by weight). Stirring was continuous throughout. The reaction mixture was heated in a closed system at 40° to 42°C. for 18 hr. in a thermostated water-bath. The pH of the reaction mixture was adjusted to 6.8 with 1N HCl. The reaction mixture was added portionwise to an excess of stirred absolute ethanol and the precipitate was allowed to settle. Product was collected and vacuum dried over H_2SO_4. Yield was 1.8 g.; percent N, 17.8.

CEWF Paste Preparation and Hypochlorite Treatment

Aqueous pastes of CEWF were prepared on a weight basis. The aqueous slurries were stirred and heated at 90+°C. for 30 min. in a vented system and allowed to cool to room temperature before use. A typical hypochlorite treatment of CEWF pastes is as follows: 14.4 g. of a 1% aqueous CEWF paste was acidified to pH 2 with 6N H_2SO_4, and 0.4 ml. of sodium hypochlorite (Clorox) was added. A flocculent, crosslinked product formed, and the mixture was added to the pulp furnish (7.2 g., o.d.) without further treatment.

Preparation and Physical Testing of Handsheets

Handsheets were prepared and tested as previously described (1).

RESULTS AND DISCUSSION

Preparation of CEWF

Exploratory studies (data not shown) revealed that temperatures of 21° to 23°C., and reaction periods of 12 or 24 hr., gave CEWF's with N contents below those of the alkali flour controls. Products with higher N contents were obtained from reactions conducted at 40° to 42°C. for 18 hr., and these conditions were employed in this study. Pertinent data on several preparations of crude and refined CEWF are summarized in Table I. Yields of crude and refined CEWF's expressed as the combined weights of dry flour and acrylamide ranged from 77 to 86% and 73 to 84%, respectively. Yields previously obtained for CES are generally 10 to 15% higher than those obtained from similar reactions of wheat flour. The lower yields of CEWF can be partly explained on the basis of the loss observed with controls, as treatment of wheat flour with alkali under the same conditions used for carbamoylethylation resulted in an 8% loss of flour.

Both crude and refined CEWF's are stable, free-flowing, odorless, practically colorless, and showed no change in composition or in performance as wet-end additives over a 12-month storage period at room temperature.

Pasting Characteristics

Data from amylograph studies and Brookfield studies on the refined CEWF's in Table I are summarized in Table II. Both the gelatinization temperature range and paste temperature at maximum viscosity of CEWF decreased as carbamoylethyl content increased. However, maximum viscosity gradually peaked and then declined as the carbamoylethyl content increased. This same trend was also shown by Brookfield viscosity measurements. Variations in viscosity at 55° and 25°C. among the different CEWF's were slight. In general, paste clarity of the aqueous CEWF dispersions employed for Brookfield viscosity measurements improved as the N content increased. However, values for clarity of the pastes used in the amylograph studies were quite erratic. Crude CEWF's had lower paste viscosity, poorer clarity, but higher gelatinization temperature ranges.

Performance of CEWF in Handsheets

Comparative data on the physical properties of unbleached kraft-pulp handsheets prepared with both crude and refined CEWF and CES as the wet-end additive are

TABLE I. PREPARATIVE DATA ON CRUDE AND REFINED CEWF[a]

Product	Acrylamide g.	Ash %	Yield[b] g.	Nitrogen[b] %
Refined				
Alkali-flour control	0	0.2	148.3	2.2
CEWF-10	10	0.3	145.0	2.2
CEWF-20	20	0.6	152.2	2.7
CEWF-30	30	0.5	150.6	3.0
CEWF-40	40	0.5	156.0	3.4
CEWF-50	50	0.9	155.9	3.5
Crude				
Alkali-flour control	0	4.7	149.0	2.3
CEWF-10	10	4.9	148.8	2.3
CEWF-20	20	6.0	153.0	2.8
CEWF-30	30	5.5	153.1	3.2
CEWF-40	40	7.3	159.5	3.6
CEWF-50	50	9.6	163.8	4.0

[a] All runs were carried out on 162 g. (dry basis) wheat flour, 234 ml. of a saturated aqueous solution of Na_2SO_4, and 17.5 g. of 24% (by weight) aqueous NaOH solution, with the amounts of acrylamide reported in the table at 40° to 42°C. for 18 hr.

[b] Moisture-ash-free basis.

TABLE II. PASTING CHARACTERISTICS OF REFINED CEWF

	Amylograph[a]							Brookfield Viscosity[b]		
Product	Gelatinization temperature range °C.	Paste temperature at maximum viscosity °C.	Maximum viscosity B.U.	Viscosity at 55°C. B.U.	Setback viscosity 25°C. B.U.	Paste pH, 25°C.	Paste clarity[c], 25°C. %	cP.	Paste clarity[c], 25°C. %	Paste pH, 25°C.
Unmodified wheat flour	25–92	92	5	20	30	5.5	2	42	5	5.9
Alkali-flour control	25–92	92	20	40	80	7.9	5	14	13	8.1
CEWF-10	53–68	68	690	540	1,200	7.1	5	375	60	7.0
CEWF-20	43–62	62	805	500	1,000	7.0	37	450	77	6.9
CEWF-30	37–57	57	1,015	570	1,300	6.7	27	715	73	6.7
CEWF-40	34–55	55	950	580	1,200	6.6	42	650	83	6.7
CEWF-50	31–49	49	890	550	1,190	6.1	15	620	85	6.7

[a] 4% (by weight on a moisture-ash-free basis) aqueous pastes.

[b] 2% (by weight on a moisture-ash-free basis) aqueous pastes at 25°C. and 30 r.p.m.

[c] Measured at 650 nm.

presented in Table III. The data show that refined CEWF gives more strength improvement than crude CEWF. The poorer performance of crude CEWF may result from the high ash (salt) content which makes less CEWF available, on a weight basis, for imparting strength properties to paper. The data also show that hypochlorite-treated CES is a better dry-strength agent for paper than its CEWF counterpart. However, hypochlorite-treated CEWF is comparable to CES as a wet-strength agent for paper.

Characterization of CEWF and Carbamoylethyl Gluten

Attempts to separate the starch and protein fractions from CEWF by fractional precipitation and differential solubility were not successful. An attempt to isolate the gluten (protein) fraction by enzymatic removal of the starch was also unsuccessful. Thus, to determine whether the gluten fraction would be derivatized during carbamoylethylation of wheat flour, purified gluten was treated under the same reaction conditions used in the preparation of the flour derivative, except that no gelatinization inhibitor (Na_2SO_4 solution) was used. N values for unmodified gluten and carbamoylethyl gluten were 17.3 and 17.8%, respectively. Based on the N value of the modified gluten, conversion was quantitative. The N content (17.2%) of an alkali-gluten control indicated that little, if any, deamination occurred.

Both CEWF and carbamoylethyl gluten showed infrared absorption bands at 1,670 to 1,690 cm.$^{-1}$ that were identified as Amide I and characteristic for the carbonyl of primary amides, and an absorption band at 1,620 cm.$^{-1}$ that was identified as Amide II and characteristic for NH_2 deformation of primary amides (3). The Amide II band for primary amide was missing in unmodified wheat flour, indicating that the presence of this group in CEWF and carbamoylethyl gluten must result from carbamoylethylation. Differential spectroscopy of CEWF vs. unmodified wheat flour and of carbamoylethyl gluten vs. unmodified gluten also confirms that carbamoylethyl groups had been introduced.

CONCLUSION

Wheat flour reacts with acrylamide in the presence of base to give a carbamoylethylated product (CEWF). Hypochlorite-treated CEWF, when

TABLE III. COMPARATIVE DATA ON PHYSICAL PROPERTIES OF UNBLEACHED KRAFT HANDSHEETS PREPARED WITH CRUDE AND REFINED CES AND CEWF AS WET-END ADDITIVES[a]

Additive	Level of Addition[b] %	NaOCl[c]/ Additive g.	Basis Weight g./m.^{2}	Burst Factor (g./cm.^{2})/ (g./m.^{2})	Breaking Length Dry m.	Breaking Length Wet m.	Folding Endurance MIT
Untreated pulp control	0	0	61.4	43.4	6,670	240	400
Refined CES	2	0.02	61.1	78.2	11,130	3,350	2,200
Refined CEWF	2	0.02	61.8	75.2	10,510	3,340	2,090
Crude CES	2	0.02	58.6	78.7	11,750	2,990	1,590
Crude CEWF	2	0.02	62.2	72.6	10,380	2,970	1,210

[a] Both CES and CEWF were prepared from 30 g. acrylamide per 162 g. of starch or flour. All handsheets were oven-dried at 105° C. for 15 min.

[b] Based on oven-dried pulp.

[c] Added as Clorox, which contains 5.08% NaOCl.

incorporated as an additive to paper, significantly improves strength properties of paper over those of the untreated control. On the basis of current yield, the cost of CEWF would have to be about 15% below that of CES for CEWF to be competitive with CES as a wet-end additive. Yields of CEWF, and hence their competitive position, can probably be improved through further developmental work. Then, too, CEWF may have technological advantages over CES in applications yet unexplored.

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