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Effects of the order of addition of reagents and alkali on modification of wheat starches

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ABSTRACT

The objective of this research was to determine if adding reactive reagents to wheat starch granules before addition of alkali (the TRF method) would produce products that are different than those obtained with the conventional procedure (adding alkali before addition of reagent). Laboratory-isolated (LI) and commercial (C) normal (NWS) and waxy (WWS) wheat starches were each reacted with 6 reagents (acetic-adipic mixed anhydride (AAMA), phosphoryl chloride ($POCl_3$), sodium trimetaphosphate (STMP), acetic anhydride (AA), succinic anhydride (SA), octenylsuccinic anhydride (OSA)). Data obtained were similar to those previously obtained with maize starches (Sui, Huber, & BeMiller, 2013). Almost no starch polymer molecule modification occurred when the TRF method and AAMA or AA were used; less than a third as much reaction when SA was the reagent used, and about the same amount of reaction when $POCl_3$, STMP, or OSA were the reagents used (for different reasons).

1. Introduction

Sui et al. (2013) studied the effects of adding reagents to slurries of maize starches before adjusting the pH with alkali (the treatment-with-reagent-first (TRF) method) to determine whether allowing quite-reactive reagents that are likely to react with the first ionized starch hydroxyl groups encountered to penetrate more deeply into and throughout granules before adjusting the pH to an alkaline value might result in more efficient reactions or in modified starches with the substituent group more evenly distributed throughout granules and, therefore, with different properties. Results of the research revealed that almost no starch polymer derivatization occurred when the TRF method and acetic-adipic mixed anhydride (AAMA), acetic anhydride (AA), or phosphoryl chloride ($POCl_3$) were the reagents used, less than half as much reaction (as compared to the reaction done using the standard/conventional method [adjustment of pH with alkali before adding the reagent]) when succinic acid anhydride (SA) was the reagent used, and about the same amount of reaction when the two methods were used for reactions with sodium trimetaphosphate (STMP) and octenylsuccinic anhydride (OSA). It was concluded that (1) when the TRF method was used, most AAMA, AA, SA, and $POCl_3$ that reacted with starch granules reacted with external or channel surface protein molecules of non-swollen granules; (2) in the case of reaction with STMP, there was essentially no difference in reaction efficiency when the order of addition of catalyst and reagent was reversed because no reaction (even with water) occurred until, at least, the pH was adjusted and probably not until dried granules (impregnated with reagent and catalyst) were heated; (3) in the case of reaction with OSA, it was postulated that there was little difference in the properties of the products made using the two methods because, even with non-swollen granules, reagent molecules were driven into the structured internal water by a negative change in free energy and bypassed surface protein. The objectives of the research reported here were to do the same experiments for the same reason with wheat starches and to compare the results with those for maize starches to determine if the two starches behaved in the same way. During data analysis of this research, data for modification of maize starches with $POCl_3$ was reinterpreted.

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2. Materials and methods

2.1. Materials

Grain of waxy (IDO 630) and wild-type (Jubilee) soft wheat lines obtained from the University of Idaho Aberdeen Research and Extension Center (Aberdeen, ID, USA) was milled to straight-grade flour on a Quadramat Senior mill (Brabender, Hackensack, NJ, USA) (Approved Method 26-31, AACC, 2000), and starch was isolated from the obtained flours via the adapted protein-digestion scheme outlined by Kim and Huber (2008) and classified so that they contained 99.8% A-type granules. Commercial normal wheat starch (Midsol 50) was a gift of MGP Ingredients (Atchison, KS, USA) (99.4% A-type granules). Acetic anhydride, succinic anhydride, 2-octenylsuccinic anhydride, phosphoryl chloride, adipic acid, sodium trimetaphosphate, and thermolysin (from *Baccillus thermoproteolyticus*, p1512) were purchased from Sigma-Aldrich Corp. (St. Louis, MO, USA).

2.2. Methods

Starches were incubated with thermolysin to remove surface protein, reacted with acetic-adipic mixed anhydride (AAMA), phosphoryl chloride ($POCl_3$), sodium trimetaphosphate (STMP), acetic anhydride (AA), succinic anhydride (SA), and octenylsuccinic anhydride (OSA) both by standard/conventional methods and by TRF methods, analyzed to determine pasting and paste characteristics using a Rapid ViscoAnalyzer (RVA), analyzed to determine thermal properties of gelatinization and melting properties of retrograded amylopectin complexes in gels stored 7 days at 4 °C by differential scanning calorimetry (DSC), and analyzed to determine degrees of substitution as described by Sui et al. (2013). Surface protein was removed from granules by incubation with thermolysin (Sigma-Aldrich Corp., St. Louis, MO, USA) as described by Han and BeMiller (2008).

3. Results and discussion

The objective of this research was to determine if impregnating wheat starch granules with presumed to be rapidly-reacting and, therefore, granule surface-reacting reagents before adjusting the pH by addition of alkali would produce different products than those obtained using the standard/conventional procedure (adding alkali before addition of reagent). Laboratory-isolated normal soft wheat starch (LI-NWS), commercial normal wheat starch (C-NWS), laboratory-isolated waxy soft wheat starch (LI-WWS), and the same starches protease-treated (PT) to remove surface protein were used. The starch preparations were reacted with each of three crosslinking reagents (acetic-adipic mixed anhydride (AAMA), phosphoryl chloride ($POCl_3$), or sodium trimetaphosphate (STMP)) or each of three stabilizing reagents (acetic anhydride (AA), succinic anhydride (SA), or 2-octenylsuccinic anhydride (OSA)). Products were characterized by determining DS values and by RVA and DSC analysis.

3.1. General properties of modified and unmodified wheat starches

RVA attributes of unmodified starches and those derivatized by the standard (STD) and the treatment-with-reagent-first (TRF) methods are given in Tables S1 and S2. Looking generally at the values in Table S1, it can be seen that the values for commercial wheat starch (C-NWS) differed from those of laboratory-isolated normal wheat starch (LI-NWS). There are two possible reasons for the differences: (1) The starches were of different genetic backgrounds. (2) There may have been a difference in protein content, which was concluded to play a role in modification of maize starches (Sui et al., 2013). A third potential reason, viz., that commercial wheat starch normally contains a greater ratio of A:B granules than does wheat starch isolated in the laboratory using the protease-treatment method (99% A-type vs. <80% A-type) (Bertolini, Souza, Nelson, & Huber, 2003), was eliminated from consideration by classifying the laboratory-isolated starch so that all preparations contained >99.4% A-type granules.

3.2. Properties of crosslinked wheat starches

RVA data gives some, but limited, information about degrees of crosslinking because both increases and decreases in peak, trough, and final viscosities can indicate increases in the degree of crosslinking. However, decreases to values less than those for the native (unmodified) starch, which were rarely found with the amounts of reagent used in this research, indicate a greater degree of crosslinking as compared to values greater than those for the native starch. Values for BD in Tables S1 and S2 were also converted into percent breakdown (%BD) by dividing mean values for BD by mean values for PV, and the values for SB were converted into percent setback (%SB) by dividing mean values for SB by mean values for FV to give better indicators of the degrees of change (Kim, Patel, & BeMiller, 2013). Table 1 and Figs. 1 and 2 indicate the degrees of change in values for peak viscosity (PV), %BD, %SB, and final viscosity (FV) for the various starches modified by the two methods compared to those for the unmodified (parent) starches.

Comparison of values of FV of LI-NWS and C-NWS modified by reaction with the AAMA reagent using the standard method (Table S1) revealed that they were increased substantially (1.9x and 2.0x, respectively) over the values for the parent starches, when the standard method was used, but were changed only a small amount or not at all (1.2x and 0.98x, respectively) compared to the control values when the TRF method was used (Table S2), indicating very little reaction when the TRF method was used (See also Fig. 1A). The fact that, when the TRF method was used, the values were close to 1.0 was supported by the fact that almost no measureable ester formation occurred when C-NWS and LI-NWS were reacted with the AAMA reagent using the TRF method, the titratable ester being only 0.4% and 6.2%, respectively, of the values of the products made using the standard method (Table 2).

When mean values for PV, %BD, %SB, and FV for the products of reaction with the AAMA reagent using the TRF method (Table S2) were divided by the same values for the same products made using the standard method (Table S1), the respective values for the four RVA attributes were 0.71, 2.5, 1.0, and 0.61 for LI-NWS and 0.70, 1.3, 0.59, and 0.49 for C-NWS. The corresponding values for laboratory-isolated normal maize starch (LI-NMS) and commercial normal maize starch (C-NMS) calculated from the data of Sui et al. (2013) were 0.69, 0.33, 0.61, and 0.74, respectively, and 0.87, 0.87, 0.57, and 0.65, respectively, values that are somewhat different than those for LI-NWS and C-NWS–most notably in the effect on %BD, which increased for the wheat starches and decreased for the maize starches.

Results from modification with the AAMA reagent, which also contains AA and introduces both adipyl (crosslinking) and acetyl (stabilizing) groups, are difficult to interpret. After reaction using the standard method, PV and FV increased, as they do after crosslinking. However, because the data are similar to those obtained using AA as the derivatizing reagent (Section 3.3), it appears that acetylation had a greater impact on pasting and paste behaviors than did crosslinking, as was concluded for maize starches (Sui et al., 2013).

Since there is no commercial waxy wheat starch, only LI-WWS could be used. Comparison of the mean FV value of LI-WWS modified by reaction with the AAMA reagent divided by the same values