Harnessing of novel tailored modified pregelled starch derived products in sizing of cotton textiles

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Received: 8th November, 2010 ; Accepted: 18th November, 2010

ABSTRACT

Background: Several researches and developmental work efforts were made in this manuscript to synthesize what is called tailored polymeric materials with new characteristics based on pregelled starch through a number of processes which, in turns entailed several chemical treatments. This was done by subjecting the pregelled starch as a starting substrate to acid hydrolysis to obtain pregelled starch having different molecular sizes. The latter were carbamoylethylated using acrylamide and sodium hydroxide at different duration, then grafted with different monomers using potassium permanganate / citric acid redox system for initiating grafting. Furthermore, harnessing of the newly tailored pregelled starch derived products as sizing agent of cotton textiles was studied systematically. Results: It is shown from the data that, (a) the extent of carbamoylethylatation expressed as N% increases by increasing the extent of hydrolysis and duration; (b) the graft yield expressed as m.mol monomer/100 g sample of different monomers onto carbamoylethylated pregelled starch and carbamoylethylated hydrolyzed pregelled starches increases by increasing the extent of carbamoylethylatation and degree of hydrolysis and follows the order: MAam> MAN > MAA, and (c) cotton fabrics sized with graffed carbamoylethylated hydrolyzed pregelled starch acquire higher mechanical properties i.e. tensile strength, elongation at break, and abrasion resistance values than hydrolyzed pregelled starches, carbamoylethylated pregelled starch and carbamoylethylated hydrolyzed pregelled starches. Conclusions: Using the above tailored modified pregelled starch derived products in sizing of cotton textiles contributed to reinforcement the cotton textile after sizing to over come the forced loss in fabrics/yarns during weaving process.

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INTRODUCTION

Starch is probably the most abundant and low cost natural polymer commercially available after cellulose. So, its derivatives are of interest for food and non-food applications e.g. in paper, pharmaceuticals as well as textiles. However, the uses of starch are often limited by unfavorable characteristics, such as relatively high molecular weight, low solubility in water, the tendency of retrogradation etc., depending upon the application [1]. To extend their application, functional groups can be introduced into starches by a number of physical or chemical modifications in order to provide starches with improved or specific properties. Modified starches generally have markedly altered physicochemical properties, compared to their native starches, depending on the degree of substitution and the type of functional groups introduced [1]. Specifically, starch ethers, i.e. cyanomethylated [2], carbamated [3], carboxymethylated [4], hydroxypropylated [5], allylated [6], and methallylated starches [7], comprises a wide range of industrial products of different degree of substitution and useful physicochemical properties. For example, the introduction of hydroxypropylated group or carbamates groups in maize starch weakens the bond strength between the starch molecules and thereby increases the swelling power and the solubility of the starch granule upon heating [3,8].

Based on the above, considerable research and technical work has been reported so far, that chemical modification of starch or modified starch via vinyl graft copolymerization constitute the most important fascinating field for improve the starch properties, thereby enlarging the range of its utilization [9-14]. Starch graft copolymers could be achieved primarily by free radical initiation processes [9,11,13,14]. Emphasis was placed on high-energy ionization [15-17], or ceric ion [19,18] and redox system [19-22].

The aim of this paper is undertaken with a view of tailoring a novel polymeric materials based on pregelled starch as starting substrate. For this purpose, the latter is first subjected to acid hydrolysis to control the molecular size of pregel starch. Starches having different molecular sizes are then carboxomethylated followed by grafting using different monomers namely methacrylamide (MAam), methacrylonitrile (MAN) and methacrylic acid (MAA). In this way carboxomethylated groups as well as the chain molecules of synthetic vinyl polymer modify the molecular structure of pregelled starch through controlling its molecular size and substituting some of the starch hydroxyls. Finally, harnessing of the newly tailored polymeric starch products in sizing of cotton textiles was also studied in detail.

EXPERIMENTAL

Materials

Pregelled starch was kindly supplied by Cairo Company for Starch and Glucose, Cairo Egypt. Methacrylonitrile and methacrylic acid stabilized with 0.01% hydroquinone were freshly distilled at 75°C and pressure 13.33 kPa (100 mm Hg). They were stored at -10°C until used. Methacrylamide, sodium hydroxide, phosphoric acid, citric acid, dimethylformamide, sodium carbonate, potassium permanganate and ethanol were of pure grade chemicals (Aldrich, St. Louis, USA).

Preparation of hydrolyzed pregelled starch

Three levels of hydrolyzed pregelled starches namely H$_1$ - H$_2$ - H$_3$ - pregelled starch having different degree of hydrolysis (expressed as copper number and apparent viscosity) have been prepared using different concentrations (0.5, 0.75, and 1 N) of phosphoric acid at 55°C for (30, 45 and 60 min.) using a material to liquor ratio of 1:7.5. After the desired duration the reaction was precipitated in 250 ml ethyl alcohol and neutralized with a dilute sodium carbonate solution till pH 7, then washed and dried in an electric oven at 60°C for 2 h. The main characteristics of the pregelled starch and hydrolyzed pregelled starches are given in TABLE 1.

Chemical modifications

(1) Synthesis of carbamoylmethylated pregelled starch and hydrolyzed pregelled starches

Pregelled starch (5 g) before and after hydrolysis was mixed well with (2.5 g) acrylamide in a 100 ml stoppered bottle. The freshly prepared catalyst NaOH (2.5 ml) of concentration 0.25 N and 10 ml cyclohexane was added to complete the total volume to 12.5
ml. The reaction mixture was stirred very well and allowed to proceed at 35°C at different duration (5-30 min.) in a thermostatic water bath. After the desired reaction time, the mixture was poured over 500 ml of ethanol for precipitation, and then washed several times with ethanol: water mixture (80:20) for 10 min. for each wash on magnetic stirrer at room temperature. It was found experimentally that 3-5 times washing with the latter mixture is quite enough to remove all the contaminants (unreacted substances). This was evidenced by measuring the nitrogen % after washing for each sample till constant nitrogen %, (three times measurements for each sample as well as their standard deviations were obtained). Finally, washed with pure ethanol and air-dried.

(2) Graft polymerization procedure

Unless otherwise indicated, grafting reaction was carried out under oxygen free nitrogen atmosphere via purging nitrogen gas into the reaction mixture. The aqueous solution of KMnO₄ of known concentration (0.1N) was placed in a glass-stoppered flask. The latter was kept in a thermostatic water bath for 15 min at 50°C. The pregelled starch or carbamoylthlated pregelled starches (5g) was introduced into the flask and the monomer (50% based on weight of starch) was immediately added, followed by 20 m.eq. / L citric acid. The total volume was then adjusted so as to give a total volume of 50 ml and the flask contents were stoppered and shaken immediately and occasionally during the course of reaction. Grafting was carried out for 1hr. At the end of the reaction, the flask contents were poured over 500 ml ethyl alcohol. At this end, a precipitate was formed which consisted of starch graft copolymer and the homopolymer. The latter can be removed in case of poly methacrylamide and poly methacrylic acid by washing with 400 ml water –ethanol mixture (30:70) several times (for 15 min. each) at room temperature, filtered and finally dried in an electric oven at 60°C for 2h. It was found experimentally that washing five times with a mixture of water/ ethanol (30:70, v/v) is quite enough for complete homopolymer removal in physical mixtures of starch/poly (methacrylamide), starch poly (methacrylic acid) by tracing the nitrogen and carboxyl content of these mixtures after each wash until constant value. On the other hand, poly (methacrylonitrile) was removed by Soxhlet extraction using dimethylformamide (DMF) for 24 h at 30°C.

(3) Proof of grafting

This was done via measuring the nitrogen and carboxyl contents by well-known standard methods of grafted products three times for each samples, as well as their statistical data (expressed as standard deviation). In other word, both the nitrogen and carboxyl contents in addition to standard deviation for each sample were taken as an evidence of grafting onto pregelled starch as a carbohydrate polymer that is free from nitrogen and carboxyl groups when it used as a starting substrate.

(4) Analysis

Copper number was estimated by a micro Briady method as modified by Heyes[23]. Nitrogen content was estimated by Kjeldahal method[24] and carboxyl content was traced according to a reported method[25].

(5) Characterization

Apparent viscosity (m.pa.s) was measured by using co-axial rotary viscometer (Haake RV20) with the rate of shear 516 cm⁻¹ at 90°C.

(6) Sizing of cotton fabrics

Cotton fabrics (kindly supplied by Misr company for Spinning and weaving, El-Mehala El-Kobra) were padded through two dips and two nips in the cooked modified pregelled starch (7.5 %) at 90°C to a wet pick-up of Ca 85% and dried in an electric oven at 100°C for 5 min. The sized cotton fabrics were finally kept at ambient conditions for at least 48 h before used.

(7) Testin

Tensile strength (T.S) and Elongation at break (%) were measured according to ASTM procedure D-2256-66T. Abrasion resistance was determined using the K-Zweigle abrader tester (Zweigle, Reutlingen, Germany).

(8) N.B.

Both tensile strength, elongation at break and abrasion resistance were measured five times for each sample in addition to their standard deviation.
RESULTS AND DISCUSSION

It is well known that the molecular structure of the polymer determines its properties and utilization. In addition, the molecular structure is governed by the molecular size of the polymer backbone and substituents present there on. So, pregelled starch as a starting substrate was hydrolyzed to obtain pregelled starch having different molecular sizes then substitute some of the starch hydroxyls by carbamoyl methylated groups along with either poly methacrylamide, poly methacrylonitrile and poly methacrylic acid chain molecules using potassium permanganate / citric acid redox system as initiators. This was done for tailoring novel polymeric materials via structural modification of pregelled starch molecules.

For simplicity, the results obtained are presented and discussed under the following headings:
1) Acid hydrolysis of pregelled starch
2) Carbamoyl methylated of native and hydrolyzed pregelled starches.
3) The combined effect of hydrolysis and carbamoyl methylation on grafting of pregelled starch using different vinyl monomers.
4) Harnessing of the newly tailored pregelled starch polymeric derived products in sizing of cotton textile.

Acid hydrolysis of pregelled starch

Pregelled starch as a starting substrate was subjected to phosphoric acid hydrolysis. The treatment was carried out using different concentration of acid and duration at 55°C. Details of the condition used are given in the text. This was done to tailor three levels of hydrolyzed pregelled starch having different degree of hydrolysis expressed as copper number and apparent viscosity as an indicator for estimating the lowering in the molecular size of the parent substrate.

It was seen that there is an inverse relationship between copper number and apparent viscosity which were taken as a measure for the degree of hydrolysis for the aforementioned substrate I, II, III and IV. This can be explained with respect to glucosidic bond session of pregelled starch molecules which will create more and more aldehydic groups, thereby significantly enhancing the copper number and decreasing the apparent viscosity.

Carbamoyl methylated of starch and hydrolyzed starches

Carbamoyl methylated pregelled starch based on native pregelled and hydrolyzed pregelled starches were affected via their reaction with acrylamide in presence of NaOH as a basic catalyst. Thus, we are dealing with a system containing pregelled starch, acrylamide and the catalyst. In such a system the following main reactions are expected to occur:

\[ \text{St}-\text{OH} + \text{H}_2\text{C}==\text{C}==\text{CONH}_2 \xrightarrow{+ \text{NaOH}} \text{St}--\text{O}==\text{C}==\text{CONH}_2 \]

(1)

\[ \text{St}--\text{O}==\text{C}==\text{C}==\text{CONH}_2 + \text{H}_2\text{O} + \text{NaOH} \xrightarrow{+ \text{NaOH}} \text{St}--\text{O}==\text{C}==\text{COONa} + \text{NH}_3 \]

(2)

Figure 1 declares the extent of carbamoyl methylation, expressed as m.mol carbamoyl methyl group/100g sample. The data signify that the extent of carbamoyl methylation of pregelled starch increases as the time of the carbamoyl methylation reaction increases. The same holds true for hydrolyzed pregelled starches. It is also seen that the extent of carbamoyl methylation for the hydrolyzed pregelled starches is higher than that of native pregelled starch and the higher the extent of hydrolysis, the higher the extent of carbamoyl methylation. This can be explained in the manner of acid hydrolysis increases the susceptibility of pregelled starch towards carbamoyl methylation, which decreases the molecular size of pregelled starch as evidenced by the tabular data of apparent viscosity in TABLE 1, thereby increasing the surface area of pregelled starch without adversely affecting the starch hydroxyls that would certainly lead to increase carbamoyl methylation reaction.

Combined effect of hydrolysis and carbamoyl methylation of pregelled starch on grafting

Figures 2, 3 and 4 show the effect of structural changes in the molecules of pregelled starch brought about by changing the extent of carbamoyl methylation (m.mol /100g sample) onto the graft yield (m.mole monomer/100g sample) using methacrylamide, methacrylonitrile and methacrylic acid as monomers and potassium permanganate / citric acid redox system as
The results (Figures 2-4) reflect the following main findings:

a. The graft yield obtained with hydrolyzed pregelled starches is higher than those of the native pregelled starch and the higher the extent of hydrolysis the greater the graft yields.

b. The carbamoylated starches derived from hydrolyzed pregelled starches exhibit much higher graft yields than the native and hydrolyzed pregelled starches, which indicate that the combined effect of hydrolysis and carbamoylation increases grafting.

c. The graft yield increases by increasing the carbamoylated content of pregelled starch and hydrolyzed pregelled starches within the range studied.

d. The graft yields of the three monomers used onto carbamoylated pregelled starches follows the order: MAam > MAN > MAA.

Based on the above finding, the enhancement in the...
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The graft-ability of pregelled starch by acid hydrolysis could be explained in terms of provision of larger surface area as shown before in carbamoylation. That is, the graft yields follow the order: grafted carbamoylated H\textsubscript{3}-pregelled starch > grafted carbamoylated H\textsubscript{2}-pregelled starch > grafted carbamoylated H\textsubscript{1}-pregelled starch > grafted carbamoylated pregelled starch.

As stated before, when native pregelled starch and hydrolyzed pregelled starches were carbamoylated before grafting, the susceptibility of the latter pregelled starch polymeric derived products towards grafting with the said vinyl monomers increases considerably. This reflects the role of carbamoyl groups which afford additional active sites for grafting via abstracting the labile hydrogen proton from imides groups of carbamoylated starch, and the free radical is very likely formed at the nitrogen atom of imides group; In addition to the presence of carbamoyl groups along with the pregelled starch chains open up the structure of pregelled starch which facilitate diffusion of the monomers thereby leading to increased grafting. With this in mind, the proposed interaction scheme of the vinyl monomer in question with the carbamoylated pregelled starch products in presence of initiator may be presented as follows:

**Initiation of grafting**

\[
\text{PSt-OH} + \text{R} \rightarrow \text{PSt-O} + \text{RH}
\]

\[
\text{PSt-O-C} - \text{C} - \text{C} - \text{CONH}_2 + \text{R} \rightarrow \text{PSt-O-C} - \text{C} - \text{CONH}_2 + \text{RH}
\]

\[
\text{PSt-O} + \text{H}_2\text{C} - \text{C} + \text{X} \rightarrow \text{PSt-O-C} - \text{C} - \text{C} - \text{CONH}_2 + \text{RH}
\]

\[
\text{PSt-O-C} - \text{C} - \text{C} - \text{N} + \text{CHX} \rightarrow \text{PSt-O-C} - \text{C} - \text{C} - \text{N} + \text{CHX}
\]

**Propagation of grafting**

\[
\text{St-O-C} - \text{C} - \text{C} - \text{N} + \text{CHX} \rightarrow \text{PSt-O-C} - \text{C} - \text{C} - \text{N} + \text{CHX}
\]

where PSt-OH and PSt-O-CH\textsubscript{2}-CH\textsubscript{2}-CO-NH\textsubscript{2} is the pregelled starch and carbamoylated pregelled starch respectively, while R represents the free radical formed from the redox system.

The above postulation is in deed in full agreement with previous report (26) dealt with grafting onto carbamoylated cellulose. On the other hand, the order of graft-ability of the three monomers in ques-
TABLE 1: Main characteristics of pregelled starch and hydrolyzed pregelled starches as well as their statistical data

<table>
<thead>
<tr>
<th>Substrate no</th>
<th>Hydrolyzed pregelled starches</th>
<th>Copper number</th>
<th>Apparent Viscosity* (m.pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.003 ± 0.024</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>0.082 ± 0.042</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>1.614 ± 0.086</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>1.926 ± 0.068</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>

Where; Substrate I: native pregelled starch (NPS). Substrate II-IV: hydrolyzed pregelled starches to different extent (H₁-, H₂- and H₃- pregelled starch). ± Values are the standard deviations of copper number samples measured three times for each sample. *The condition of the pastes for viscosity measurements was 7.5%. Detail of the conditions used is given in the experimental part.

Application in sizing of cotton textiles

The work presented in this section aims at harnessing the newly tailored polymeric pregelled starch derived products in sizing of cotton textiles. This is done to find out the suitability of the latter polymeric materials as sizing agent of cotton textiles.

TABLE 2 represents the major mechanical properties i.e. tensile strength, elongation at break and abrasion resistance of cotton fabrics sized with native pregelled starch, hydrolyzed pregelled starches, carboxamylethylated pregelled starches and poly (MAA)- pregelled starch graft copolymers derived from native pregelled and hydrolyzed pregelled starches to different levels (H₁-, H₂- and H₃- starch) before and after carboxamylethylataion. Also, the physico-chemical characteristics of these pregelled starch derived products such as copper number, nitrogen content, carboxyl content and apparent viscosity are given in TABLE 2.

For simplicity, the results will be given under the following headings:

Tensile strength

a. Tensile strength of cotton fabrics sized with native pregelled starch and hydrolyzed pregelled starches derived thereof amounts to 23.5, 24.5, 24.0 and 22.5 Kg for native pregelled starch, H₁- pregelled starch, H₂- pregelled starch and H₃- pregelled starch respectively. This is against a tensile strength of 21.0 Kg for unsized fabric. It follows the order: H₁- pregelled starch > H₂- pregelled starch > native pregelled starch > H₃- pregelled starch.

b. Tensile strength of cotton fabrics sized with carboxamylethylated pregelled starch products derived from native pregelled starch, H₁- pregelled starch, H₂- pregelled starch and H₃- pregelled starch respectively. It follows the order: Carboxamyletlated H₁- Pregelled starch > Carboxamyletlated H₂- pregelled starch > Carboxamyletlated native Pregelled starch > Carboxamyletlated H₃- Pregelled starch.

c. Tensile strength of cotton fabrics sized with poly (AA)- pregelled starch graft copolymers amounts to 25.5, 27.5, 26.5 and 25.5 Kg for grafted native pregelled starch, grafted H₁- pregelled starch, grafted H₂- pregelled starch and grafted H₃- pregelled starch respectively. It follows the order: grafted H₁- pregelled starch > grafted H₂- pregelled starch > grafted native pregelled starch > grafted H₃- pregelled starch.

d. The tensile strength of cotton fabrics sized with poly (AA)-grafted carboxamylethylated starches amounts to 26.0, 28.5, 28.0 and 25.0 Kg for grafted carboxamylethylated pregelled starch, grafted carboxamylethylated H₁- pregelled starch, grafted carboxamylethylated H₂- pregelled starch and grafted carboxamylethylated H₃- pregelled starch respectively.

e. Finally, the increase in tensile strength of the sized cotton fabrics follows the general order: grafted carboxamylethylated Pregelled starches > grafted pregelled starches > carboxamylethylated Pregelled starches > hydrolyzed pregelled starches > native pregelled starches.

So, the graft polymerization of methacrylic acid onto modified starches improves greatly the sizability irrespective of the backbone of starch.

Elongation at break

TABLE 2 reveals that the cotton fabrics sized with the modified pregelled starches under investigation ex-
Abrasion resistance hibit higher elongation at break than the original unsized fabrics. It follows the order: grafted carbamoylethylated pregelled starches > grafted pregelled starches > carbamoylethylated Pregelled starches > hydrolyzed pregelled starches > native pregelled starches.

Abrasion resistance

The results of TABLE 2 reveals that (a) the abrasion resistance of all sized fabrics is higher than that unsized one, (b) the abrasion resistance of fabrics sized with native pregelled starch and hydrolyzed pregelled starches \( (H^-_1, H^-_2, \text{and } H^-_3 \text{ PSt}) \) amounts to 911,952,932 and 907 cycles against 880 cycle for unsized fabric, (c) the values of abrasion resistance of carbamoyletylated pregelled starches amounts to 942, 981, 960 and 923 cycle for carbamoyletylated pregelled starch, carbamoyletylated \( H^-_1 \), carbamoyletylated \( H^-_2 \), and carbamoyletylated \( H^-_3 \) pregelled starch respectively against 880 cycles for unsized fabric (d) the abrasion resistance values of fabrics sized with poly (MAA)-grafted pregelled starches amounts to 958, 993,969 and 933 cycles for grafted native pregelled starch, grafted \( H^-_1 \), and grafted \( H^-_2 \) pregelled starch respectively and follows the order: grafted \( H^-_2 \)-pregelled starch > grafted \( H^-_1 \)-pregelled starch > grafted carbamoylethylated \( H^-_2 \)-pregelled starch > grafted carbamoylethylated \( H^-_1 \)-pregelled starch and (e) the abrasion resistance of fabrics sized with poly (AA)-grafted pregelled starches amounts to 958, 993,969 and 933 cycles for grafted native pregelled starch, grafted \( H^-_1 \), and grafted \( H^-_2 \) pregelled starch respectively and follows the order: grafted \( H^-_2 \)-pregelled starch > grafted \( H^-_1 \)-pregelled starch > grafted carbamoylethylated \( H^-_2 \)-pregelled starch > grafted carbamoylethylated \( H^-_1 \)-pregelled starch and (e) the abrasion resistance of fabrics sized with poly (MAA) – grafted carbamoyletylated pregelled starches exhibits the values of 966, 1000, 985 and 947 cycles for grafted carbamoyletylated pregelled starch, grafted carbamoyletylated \( H^-_1 \), grafted carbamoyletylated \( H^-_2 \), and grafted carbamoyletylated \( H^-_3 \)-pregelled starch respectively vis-à-vis 880 cycles for unsized fabric.

Finally, there is a direct relationship between tensile strength and abrasion resistance as shown from the tabular data given in TABLE 2.
CONCLUSIONS

- Of all hydrolyzed pregelled starches used, H\textsubscript{1}-pregelled starch is serving as a suitable sizing agent.
- All carbamoylethylated pregelled starches under investigation are suitable as sizing agent except that based on H\textsubscript{3} – pregelled starch.
- All grafted pregelled starches serve as superior sizing agent.

REFERENCES


