The graft polymerization of acrylonitrile onto starch is easily carried out in water with ceric ammonium nitrate (CAN) initiation and can produce a graft copolymer that is composed of about 50% by weight of poly(acrylonitrile) (PAN). Saponification of starch–g–PAN in aqueous alkali converts the nitrile substituents of PAN to a mixture of alkali metal carboxylate and carboxamide and affords a polymer that exists in water as a highly swollen but largely insoluble gel. \(^3\) Isolation of saponified (hydrolyzed) starch–g–PAN (HSPAN) by methods such as alcohol precipitation, drum drying, or air drying to a film gives dry HSPAN that will absorb from several hundred to over a thousand times its weight of deionized water within a few minutes. These remarkable absorbency properties have suggested a number of end-use applications for HSPAN. In the agricultural area, seeds are now being coated with HSPAN powder to hold water at the seed surface and thus enhance the germination process. \(^4\) Also, plant roots are being dipped into HSPAN–water gel before transplanting to help prevent transplant shock. Another important area of application is in disposable soft goods, which are designed to absorb body fluids. \(^5\)

On a per-pound basis, the CAN initiator is the most expensive reagent in the polymerization process. \(^2\) It was, therefore, of interest to examine the influence of the molar ratio of corn starch:CAN on both the structure of starch–g–PAN and on the properties (absorbency and water solubility) of HSPAN, with the goal of minimizing the amount of CAN used to initiate graft polymerization. Ceric-initiated graft polymerizations onto other varieties of corn starch, such as acid-modified, waxy, and high-amylose, also were investigated. Finally, after examining the preparation of starch–g–PAN by incremental addition of CAN, we showed that HSPAN with higher absorbency could be prepared by this procedure. Smith \(^6\) has also prepared HSPAN by a stepwise grafting procedure; however, his conditions were different than those used in this study.

**RESULTS AND DISCUSSION**

In the first series of reactions (Table 1), the molar ratio of corn starch:CAN was varied between 10 glucopyranosyl units (anhydroglucose units or AGU) per Ce\(^{+++}\) and 1000 AGU per Ce\(^{+++}\). With granular starch (nos. 1–8), it is apparent that ceric ion concentrations ranging from 1 mol/10 AGU to 1 mol/500 AGU all yield starch–g–PAN with about the same % add-on. The amount of ceric ion used had little effect on \(M_r\) in the 50–200 AGU per Ce\(^{+++}\) range (nos. 2, 3, and 5); however, at 10 and 500 AGU per Ce\(^{+++}\) (nos. 1 and 6), graft molecular weights were lower and higher, respectively. Addition of \(t\)-amyl mercaptan to the polymerization mixture as a chain transfer agent lowered the PAN molecular weight by over a factor of 3 (no. 4). Lowering the amount of CAN initiator to 1000 AGU per Ce\(^{+++}\) produced starch–g–PAN with only 8% add-on and gave relatively low molecular weight PAN grafts (no. 7); however, by doubling the concentrations of starch and monomer in water (no. 8), a 33% add-on was achieved at this starch:ceric ion ratio.

Reactions run with gelatinized corn starch (Table 1) afforded starch–g–PAN with 55–56% add-on when 50, 100, and 200 AGU per Ce\(^{+++}\) were used (nos. 9–11). A 40% add-on was obtained at 500 AGU per Ce\(^{+++}\). As expected, \(^2\) graft polymerizations onto gelatinized starch gave higher graft molecular weights than did polymerizations run with granular starch.

Although gelatinized starch yielded HSPAN polymers with higher water absorbencies than the corresponding granular starch-based products, it is apparent from Table I that, within each series of products, water absorbencies are not overly sensitive to the amount of CAN used to initiate polymerizations. For example, granular starch products 1 and 5 gave about the same absorbency, even though the amount of ceric ion used varied by a factor of 20. A similar comment can be made about gelatinized starch products 9 and 11, although variations in ceric ion were not as large. Reactions 6 and 12, which were run with 500 AGU per Ce\(^{+++}\), gave saponified polymers with higher water absorbencies than those prepared with larger amounts of CAN.

* The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.
TABLE I

<table>
<thead>
<tr>
<th>Starch granule state</th>
<th>Number of AGU&lt;sup&gt;b&lt;/sup&gt; per Ce&lt;sup&gt;4+&lt;/sup&gt;</th>
<th>% of total product</th>
<th>Wt% PAN</th>
<th>$M_v$ of PAN&lt;sup&gt;d&lt;/sup&gt; (g H&lt;sub&gt;2&lt;/sub&gt;O/g)</th>
<th>Absorbency (g H&lt;sub&gt;2&lt;/sub&gt;O/g)</th>
<th>Solubility in H&lt;sub&gt;2&lt;/sub&gt;O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Granular</td>
<td>10</td>
<td>99</td>
<td>53</td>
<td>47,000</td>
<td>200</td>
<td>45</td>
</tr>
<tr>
<td>2 Granular</td>
<td>50</td>
<td>96</td>
<td>54</td>
<td>62,000</td>
<td>150</td>
<td>22</td>
</tr>
<tr>
<td>3 Granular</td>
<td>100</td>
<td>98</td>
<td>47</td>
<td>70,000</td>
<td>160</td>
<td>15</td>
</tr>
<tr>
<td>4 Granular&lt;sup&gt;e&lt;/sup&gt;</td>
<td>100</td>
<td>93</td>
<td>53</td>
<td>21,000</td>
<td>150</td>
<td>39</td>
</tr>
<tr>
<td>5 Granular</td>
<td>200</td>
<td>97</td>
<td>51</td>
<td>70,000</td>
<td>190</td>
<td>24</td>
</tr>
<tr>
<td>6 Granular</td>
<td>500</td>
<td>97</td>
<td>48</td>
<td>97,000</td>
<td>270</td>
<td>34</td>
</tr>
<tr>
<td>7 Granular</td>
<td>1000</td>
<td>100</td>
<td>8</td>
<td>26,000</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8 Granular&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1000</td>
<td>99</td>
<td>33</td>
<td>100,000</td>
<td>330</td>
<td>40</td>
</tr>
<tr>
<td>9 Gelatinized</td>
<td>50</td>
<td>95</td>
<td>56</td>
<td>460,000</td>
<td>730</td>
<td>19</td>
</tr>
<tr>
<td>10 Gelatinized</td>
<td>100</td>
<td>91</td>
<td>55</td>
<td>400,000</td>
<td>1,100</td>
<td>28</td>
</tr>
<tr>
<td>11 Gelatinized</td>
<td>200</td>
<td>94</td>
<td>56</td>
<td>580,000</td>
<td>920</td>
<td>20</td>
</tr>
<tr>
<td>12 Gelatinized</td>
<td>500</td>
<td>79</td>
<td>40</td>
<td>590,000</td>
<td>1,500</td>
<td>49</td>
</tr>
</tbody>
</table>

<sup>a</sup> Polymerizations were run with 10 g corn starch, 200 mL water, and 15 g acrylonitrile (except where indicated).

<sup>b</sup> Anhydroglucose units.

<sup>c</sup> After extraction with dimethylformamide to remove ungrafted poly(acrylonitrile) (PAN).

<sup>d</sup> Calculated from intrinsic viscosity in dimethylformamide.

<sup>e</sup> t-Amyl mercaptan (0.15 g) added with the acrylonitrile.

<sup>f</sup> This reaction used 20 g starch and 30 g acrylonitrile in 200 mL of water.

The amount of CAN used to initiate graft polymerization had a greater effect on water solubility of HSPAN than it did on water absorbency, and relatively high water solubilities were observed at both 10 and 500 AGU per Ce<sup>4+</sup>. Reactions 3 and 4 make an interesting comparison, since the only difference in these two runs is the incorporation of t-amyl mercaptan in no. 4 as a chain transfer agent for growing PAN grafts. Although water absorbencies are about the same, the solubility of HSPAN in water is greater in no. 4 by over a factor of 2.

Graft polymerizations were next carried out with waxy corn starch, high-amylose corn starch, and acid-modified corn starch to determine the effect of these starch varieties on HSPAN properties using varying amounts of CAN initiator (Table II). It is apparent from Table II that waxy corn starch requires more CAN to initiate graft polymerization than do the other varieties of corn starch, particularly when it is gelatinized. With 100 AGU per Ce<sup>4+</sup>, granular and gelatinized waxy corn starch gave starch-<i>g</i>-PAN with only 40% and 14% add-on, respectively. Doubling the amount of Ce<sup>4+</sup> with respect to starch increased % add-on values to 51% and 53%. High-amylose and acid-modified corn starches afforded graft copolymers with 49-54% add-on at 100 AGU per Ce<sup>4+</sup>. As observed with normal corn starch (Table I), the starch varieties in Table II also gave higher molecular weight PAN grafts when gelatinized before graft polymerization.

With the exception of the product of reaction 6, made from gelatinized high-amylose starch, water absorbencies of HSPAN samples in Table II were all higher than those of comparable products in Table I, made with normal corn starch. The low water-absorbency value for the gelatinized high-amylose HSPAN is probably due to the higher degree of hydrogen bonding and crystallinity in high-amylose starches, hence the greater difficulty in gelatinizing the granules by heating them in water. The high water solubility of HSPAN prepared from acid-modified corn starch (no. 7) reflects the lower molecular weight of the partially depolymerized starch component.

Although the graft polymerizations in Tables I and II were carried out by adding CAN initiator in a single portion to a water dispersion of starch and monomer, portionwise addition of initiator may also be carried out, and this alternative method of addition is examined in Table III. In reaction 2, made with 400 AGU per Ce<sup>4+</sup>, CAN was added in five equal portions at 1-hr intervals; reaction 1 was made under the same conditions, except that initiator was added in one portion. These two methods produced starch-<i>g</i>-PAN with about the same % add-on; however, portionwise addition
TABLE II
Influence of Starch Variety on Graft Copolymer Composition and Properties

<table>
<thead>
<tr>
<th>No.</th>
<th>Variety</th>
<th>Granule state</th>
<th>Number of AGU(^b) per Ce(^+4)</th>
<th>% of total product</th>
<th>Wt % PAN</th>
<th>(\bar{M}_n) of PAN(^d)</th>
<th>Absorbency (g H(_2)O/g)</th>
<th>Solubility in H(_2)O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Waxy corn</td>
<td>Granular</td>
<td>100</td>
<td>86</td>
<td>40</td>
<td>96,000</td>
<td>680</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>Waxy corn</td>
<td>Granular</td>
<td>50</td>
<td>92</td>
<td>51</td>
<td>66,000</td>
<td>320</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>Waxy corn</td>
<td>Gelatinized</td>
<td>100</td>
<td>71</td>
<td>14</td>
<td>330,000</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Waxy corn</td>
<td>Gelatinized</td>
<td>50</td>
<td>75</td>
<td>53</td>
<td>500,000</td>
<td>1900</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>High amylose corn</td>
<td>Granular</td>
<td>100</td>
<td>94</td>
<td>54</td>
<td>63,000</td>
<td>280</td>
<td>37</td>
</tr>
<tr>
<td>6</td>
<td>High amylose corn</td>
<td>Gelatinized</td>
<td>100</td>
<td>93</td>
<td>54</td>
<td>230,000</td>
<td>430</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>Acid modified corn</td>
<td>Granular</td>
<td>100</td>
<td>82</td>
<td>49</td>
<td>55,000</td>
<td>590</td>
<td>59</td>
</tr>
</tbody>
</table>

\(\text{a Polymerizations were run with 10 g starch, 200 mL water, and 15 g acrylonitrile.}\)

\(\text{b Anhydroglucose units.}\)

\(\text{c After extraction with dimethylformamide to remove ungrafted poly(acrylonitrile) (PAN).}\)

\(\text{d Calculated from intrinsic viscosity in dimethylformamide.}\)

gave a higher molecular weight for grafted PAN and produced HSPAN with a significantly higher water absorbency. HSPAN with high water absorbency was also produced in reaction 3, in which CAN initiator (100 AGU per Ce\(^+4\)) was added in 10 equal portions, while one additional gram of acrylonitrile monomer was added with each portion. Reaction 4 was carried out as a double addition of monomer and initiator and was actually run as two separate grafting reactions onto the same 10 g of granular starch, each reaction employing 15 g of acrylonitrile and an initiator concentration corresponding to 200 AGU per Ce\(^+4\). Although this procedure produced starch—g—PAN with higher add-on (65%), the absorbency of the saponified polymer was not significantly higher than that of reaction no. 3 of Table I.

Scanning electron micrographs of the starch—g—PAN polymers of Table III suggest a reason for the higher HSPAN absorbencies observed with portionwise addition. Before extraction with DMF, the surfaces of grafted granules of products 1 and 2 show rough textures due to deposition of PAN [Fig. 1, (A) and (C)]. DMF extraction removed most of this surface polymer from product 1 [Fig. 1(D)]; however, product 2 retained much of this surface-deposited PAN even after repeated extraction.

TABLE III
Influence of Incremental Additions of Ceric Ion on Graft Copolymer Composition and Properties

<table>
<thead>
<tr>
<th>No.</th>
<th>Total number of AGU(^b) per Ce(^+4) added</th>
<th>Number of equal portions of Ce(^+4) added</th>
<th>Total acrylonitrile used (g)</th>
<th>% of total product</th>
<th>Wt % PAN</th>
<th>(\bar{M}_n) of PAN(^d)</th>
<th>Absorbency (g H(_2)O/g)</th>
<th>Solubility in H(_2)O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>1</td>
<td>15</td>
<td>96</td>
<td>49</td>
<td>67,000</td>
<td>300</td>
<td>31</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>5</td>
<td>15</td>
<td>94</td>
<td>46</td>
<td>140,000</td>
<td>450</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>10</td>
<td>24</td>
<td>87</td>
<td>57</td>
<td>—</td>
<td>530</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>2</td>
<td>30</td>
<td>85</td>
<td>65</td>
<td>160,000</td>
<td>200</td>
<td>15</td>
</tr>
</tbody>
</table>

\(\text{a Polymerizations were run with 10 g granular corn starch and 200 mL water.}\)

\(\text{b Anhydroglucose units.}\)

\(\text{c After extraction with dimethylformamide to remove ungrafted poly(acrylonitrile) (PAN).}\)

\(\text{d Calculated from intrinsic viscosity in dimethylformamide.}\)
Fig. 1. Influence of portionwise addition on appearance of starch-\textit{g}-PAN granules prepared at 400 AGU per Ce\textsuperscript{4+}. (A) Product 2, Table III, not extracted with dimethylformamide (DMF). (B) Product 2, Table III, after DMF extraction. (C) Product 1, Table III, not extracted with DMF. (D) Product 1, Table III, after DMF extraction.

[Fig. 1(B)], which indicated that this PAN was chemically bonded to starch. A similar comparison can be made between products 3 and 4 (Fig. 2), although differences are not as great. It is thus apparent that portionwise addition of initiator gives granules that are more highly grafted at the surface, probably because each small amount of added ceric ion reacts rapidly with the polysaccharide near the granule surface before it has a chance to diffuse to the granule interior. An explanation of why higher HSPAN absorbencies are realized by the grafting of higher concentrations of PAN near the starch granule surface must await further study.

**EXPERIMENTAL**

**Materials**

Pearl corn starch (Globe 3005) was from CPC International. Waxy corn starch (Amioca) and high-amylose corn starch (Amylon 7) were from National Starch and Chemical Corp. Acid-modified corn starch was Clinton 290B from Clinton Corn Processing Co. Starches contained about 12% moisture. Acrylonitrile, Eastman practical grade, was distilled at atmospheric pressure through a 14-in. Vigreux column, and a center cut was collected. CAN was Fisher Certified ACS grade.

**Graft Polymerization**

**CAN added in one portion.** A slurry of 10.0 g (dry basis) of starch in 200 mL of distilled water was stirred at 25°C for 1 h while a slow stream of nitrogen was allowed to bubble through the mixture. For graft polymerizations onto gelatinized starch, the slurry was sparged with nitrogen for 30 min at 85°C and then cooled to 25°C. Acrylonitrile (15.0 g) was added, followed after 5 min by a freshly prepared solution of CAN in 3 ml of 1N nitric acid. The resulting mixture was stirred under nitrogen
Fig. 2. Influence of portionwise addition on appearance of starch–\(g\)–PAN granules prepared at 100 AGU per Ce\(^{4+}\). (A) Product 3, Table III, not extracted with DMF. (B) Product 3, Table III, after DMF extraction. (C) Product 4, Table III, not extracted with DMF. (D) Product 4, Table III, after DMF extraction.

for 2 h at 25°C. Ethanol (200 mL) was added, and the pH was adjusted to 6–6.5 with sodium hydroxide solution. The polymer was separated by filtration, washed first with 50% ethanol–water and then with ethanol, and finally dried under vacuum at 60°C. Ungrafted PAN was removed by several extractions with DMF at room temperature, and the percentage of the original polymer which remained insoluble in DMF was determined.

Portionwise addition of CAN. For the reaction run with five portions of CAN totaling 400 AGU per Ce\(^{4+}\), a slurry of 10.0 g (dry basis) of corn starch, 200 mL of distilled water, and 3 mL of 1N nitric acid was stirred for 1 h while sparging with nitrogen. Acrylonitrile (15.0 g) was added, followed after 5 min by 0.6 mL of a solution of 0.0845 g of CAN in 3 mL of 1N nitric acid. The mixture was stirred for 1 h at 25°C and the remaining CAN solution was then added in 0.6 mL portions, allowing a 1-h reaction between each addition. After the last addition, the mixture was stirred for 1 h, and the product was isolated by filtration and washed with water. The pH of the product was adjusted to 7, and the polymer was washed with water and with ethanol and dried under vacuum at 60°C.

For the reaction run with 10 portions of CAN totaling 100 AGU per Ce\(^{4+}\), a slurry of starch, water, and 1N nitric acid was prepared as described above. Acrylonitrile (15.0 g) was added, followed after 5 min by 0.3 mL of a solution of 0.338 g of CAN in 3 mL of 1N nitric acid. The mixture was stirred for 45 min at 25°C and the remaining CAN solution was then added in 0.3-mL portions, allowing a 45-min reaction between each addition. One g of acrylonitrile was added along with each of the nine successive additions of CAN. After the last addition, the mixture was stirred for 45 min, 200 mL of ethanol was added, and the pH adjusted to 6.5. The polymer was separated by filtration, washed, and dried.

For the reaction run with two portions of CAN totaling 100 AGU per Ce\(^{4+}\), a slurry of 10.0 g (dry basis) of granular starch in 200 mL of water was prepared. Acrylonitrile (15.0 g) was added, followed after 5 min by 1.5 mL of a solution of 0.338 g of CAN in 3 mL of 1N nitric acid, and the mixture was
stirred at 25°C for 1 hr. Another 15.0 g of acrylonitrile was then added, followed after 5 min by the remaining 1.5 mL of CAN solution. The reaction mixture was stirred for 2 h and then worked up as described above.

Removal of Starch from Starch-g-PAN

Starch was removed from a 2.00-g portion of DMF-extracted starch-g-PAN by heating the graft copolymer under reflux for 1.5 h in 150 mL of 0.5N hydrochloric acid. The polymer was separated by filtration, washed with water and with ethanol, and dried under vacuum at 60°C. Infrared analysis showed PAN with less than 5% residual carbohydrate. The wt % PAN in starch-g-PAN was calculated from weight loss on acid hydrolysis. The molecular weight of the isolated PAN was then calculated from the intrinsic viscosity in DMF at 25°C.9

Saponification of Starch-g-PAN

A suspension of 1.00 g of starch-g-PAN in 9 mL of 0.7N sodium hydroxide was heated on a steam bath for 5–10 min until the mixture assumed the typical10 red-brown color and thickened sufficiently to preclude settling on standing. The flask was loosely stoppered (to permit escape of ammonia) and placed in a 95–100°C oven for 3 h. The yellow reaction mass was stirred with 350 mL of methanol for 1 min at high speed (Waring Blendor), and the solid was separated by filtration. The solid was triturated in a mortar and pestle with fresh methanol, and the mixture was let stand for 10 min. The polymer was separated by filtration, dried overnight under vacuum at 60°C, and ground to pass 60 mesh.

Water Absorbency and Solubility of Saponified Starch-g-PAN

An accurately weighed sample of saponified starch-g-PAN (2–10 mg, depending on absorbency) was allowed to soak for 30 min in 50 mL of deionized water. Polymer gel was then separated from unabsorbed water by screening through a tared 280-mesh sieve. The polymer gel was allowed to drain for 20 min, and the sieve was then weighed to determine the weight of gel. The absorbency (g H2O/g dry polymer) was then calculated.

To determine the water solubility of saponified starch-g-PAN, about 0.5 g of polymer (accurately weighed) was added to an accurately measured quantity of water (amount used depended on absorbency). The container was covered and let stand for about 18 h with occasional stirring. The dispersion was allowed to gravity-filter through fluted Whatman 54 paper, and the resulting filtrate was filtered again through fluted Whatman 25 paper. A known weight of this final filtrate was freeze dried, and the percent water solubles was calculated from the weight of freeze dried solid.

Microscopy

Scanning electron microscopy was carried out as described previously.11 Samples were photographed at a magnification of 1000.

We thank F. L. Baker for the scanning electron micrographs.

References

NOTES


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