Graft Polymerization of Acrylic Acid onto Starch Using Potassium Permanganate Acid (Redox System)

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SYNOPSIS

Graft polymerization of acrylic acid (AA) onto rice starch using potassium permanganate/ acid redox system as initiator was investigated. When starch was reacted with $KMnO_4$ solution, MnO_2 was deposited onto starch. The dependence of MnO_2 amount deposited was directly related to $KMnO_4$ concentration. Subjecting the MnO_2-containing starch to a solution consisting of monomer (AA) and acid (citric, tartaric, oxalic and hydrochloric acid) formed poly(AA)–starch graft copolymers. The graft yield, expressed as meq COOH/ 100 g starch, was measured by the amount of MnO_2 deposited, AA concentration, material-to-liquor ratio, kind and concentration of acid, as well as temperature and duration. Finally, the newly prepared poly(AA)–starch graft copolymers were applied to cotton textiles to determine their suitability as sizing agents. The highest graft yield was obtained with citric acid and the least with hydrochloric acid, with tartaric and oxalic acid in between. The graft yield increased by increasing the concentration of acid to a certain concentration beyond which grafting leveled off. A similar trend was observed when the magnitude of grafting was related to the amount of MnO_2 deposited. The graft yield increased by increasing the polymerization temperature from 30° to 50°C. Increasing the temperature to 60°C is accompanied by decreased grafting. On the other hand, fabric samples sized with poly(AA)– starch graft copolymers acquire higher tensile strength, elongation at break, and abrasion resistance than that sized with native rice starch, i.e., poly(AA)–starch graft copolymers serve as good sizing agents for cotton textiles. A tentative mechanism for grafting rice starch with AA using the $KMnO_4$/acid redox system was elucidated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Chemical modification of starch via vinyl graft copolymerization constitutes a powerful means of improving the starch properties thereby enlarging the range of its utilization.[1-6] Starch graft copolymers could be achieved primarily by free radical initiated processes.[1,3,5,7] Emphasis was placed on high energy ionization radiation,[2,5,6,8] ceric ion,[3,5,9] and redox system.[3,4,10,11] Previous studies[12,13] have also disclosed that $KMnO_4$ is an oxidizing agent which in the presence of vinyl monomers induces graft polymerization onto rice starch.

This work presents a detailed study on some of the major factors which affect graft polymerization of acrylic acid onto rice starch using $KMnO_4$ along with an acid as initiator. The work was further extended to study the suitability of the prepared poly(AA)–starch graft copolymers as sizing agents for cotton textiles.

EXPERIMENTAL

Materials

Egyptian rice starch was kindly supplied by Misr Company for Starch and Yeast, Alexandria. Acrylic acid (AA) stabilized with 0.01% hydroquinone was freshly distilled at 75°C and pressure of 100 mm Hg; it was stored at 10°C until used. Potassium permanganate, citric, tartaric, oxalic, and hydrochloric acids were of reagent grade.

Treatment of Starch with Potassium Permanganate

Starch sample (10 g) was immersed for 25 min at 25°C in 100 ml KMnO$_4$ solution (0.01–0.2 N) in a conical flask with continuous shaking to ensure the homogeniety of MnO$_2$ deposition all over the sample surface. After the sample was treated, it was filtered and washed several times with distilled water to remove excess KMnO$_4$ solution. It was then squeezed between two filter papers before being introduced into the polymerization solution.

Graft Polymerization Procedure

The graft polymerization reaction was carried out as follows: The sample treated with permanganate was introduced into a reaction flask into which a solution consisting of a specific concentration of acid (5–100 meq/L) and AA was placed. A material-to-liquor ratio of 1 : 5 was used. The flask content was kept in a thermostatic water bath at different temperatures (30–60°C) for different reaction times (5–180 min). Nitrogen gas was purged into the reaction mixture to avoid the presence of oxygen and the flask content was shaken immediately and occasionally during the reaction. After the desired reaction time, the flask content was poured over 500 mL ethyl alcohol where a precipitate was formed. This precipitate consists of a mixture of poly(AA)-grafted starch and the poly(acrylic acid) (homopolymer). It was washed with ethyl alcohol for 15 min at room temperature and filtered. It was found that 4–6 times washing with a mixture of ethanol and water (80 : 20) was quite enough to remove the homopolymer. The carboxyl content of the grafted starch was determined according to a reported method.[14]

Determination of MnO$_2$ Quantity onto Starch

The amount of MnO$_2$ deposited onto starch was determined by adding 10 mL 0.1 N oxalic acid and 10 ml 2 N sulfuric acid to the starch treated with permanganate in a conical flask. The mixture was gently heated to about 60°C and then titrated against a KMnO$_4$ solution of 0.01 N.

The amount of MnO$_2$ deposited

$$= \frac{V.0.01.100}{W} \text{ meq/100 g sample}$$

where V is the volume of KMnO$_4$ equivalent to the MnO$_2$ in the sample and W is the weight of the sample used.

Sizing Procedure

Cotton fabrics were padded through two dips and two nips in the cooked modified starch (10%) at 90°C to a wet pickup of Ca 80% and dried in an electric oven at 100°C for 3 min. The fabric samples were finally kept at ambient conditions for at least 48 h before used.

Testing

Tensile Strength and Elongation at Break

These were determined according to ASTM procedure D-2296-66T.

Abrasion Resistance

This was determined using the K-Zweigle abrader.

RESULTS AND DISCUSSION

Effect of Potassium Permanganate Concentration on the Amount of MnO$_2$ Deposited

Starch was treated with different concentrations (0.01–0.15 N) of KMnO$_4$ solution as described in the Experimental section. The starch samples treated with KMnO$_4$ were monitored for MnO$_2$ deposited over them.

Table I shows the relation between the amount of MnO$_2$ deposited onto starch and the KMnO$_4$ concentration. The data shows that the MnO$_2$ deposit increases by increasing the KMnO$_4$ concentration up to 0.1 N. Above this concentration no marked increase was observed and the amount of MnO$_2$ deposited is almost the same over a range of KMnO$_4$

Table I Effect of Potassium Permanganate Concentration on the Amount of MnO$_2$ Deposited onto Starch

KMnO$_4$ Concentration (N)	Amount of MnO$_2$ Deposited (meq/100 g Sample)
0.01	0.550
0.03	2.560
0.05	5.575
0.07	7.400
0.08	8.250
0.10	8.525
0.13	8.525
0.15	8.525

Reaction conditions: starch, 10 g; time of treatment 25 min; treatment temperature, 25°C; material-to-liquor ratio, 1 : 10.
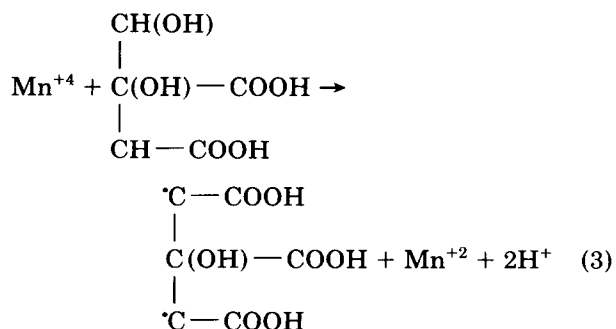
concentration of 0.1–0.15 N. It is logical to assume that MnO_2 particles are deposited uniformly all over the starch molecules and are located at certain sites, most probably at the hydroxyl group of starch molecules. Once the accessible hydroxyl groups are occupied by MnO_2 particles, extra deposition of MnO_2 will be difficult and, if deposited, the particles will be easily removed during washing. This would explain why the amount of MnO_2 deposited onto starch molecules remains constant at higher concentration than when 0.1 N of $KMnO_4$ is used.
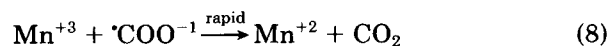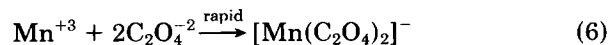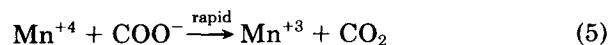
Tentative Mechanism of Grafting

Starch was turned to a brownish, dark brownish, or even black color when it was treated with $KMnO_4$ solution, depending on the concentration of the $KMnO_4$ solution used as described above. In the presence of an acid, primary radical species formation occurs as a result of the acid's action on the deposited MnO_2. Hence different primary radical species are created, depending upon the type and the nature of the acid used. In the case of tartaric acid, creation of primary free radical species occurs most probably according to the mechanisms suggested by eqs. (1) and (2):

$$Mn^{+4} + \begin{array}{c} CH(OH)-COOH \\ | \\ CH(OH)-COOH \end{array} \xrightarrow{slow}$$

$$\begin{array}{c} \cdot CH(OH) \\ | \\ CH(OH)-COOH \end{array} + Mn^{+3} + CO_2 + H^+ \quad (1)$$

$$Mn^{+4} + \begin{array}{c} \cdot CH(OH) \\ | \\ CH(OH)-COOH \end{array} \xrightarrow{fast}$$

$$\begin{array}{c} CHO \\ | \\ CH(OH)-COOH \end{array} + Mn^{+3} + H^+ \quad (2)$$
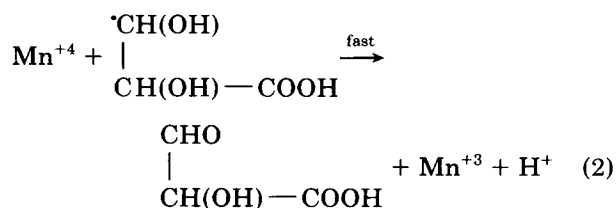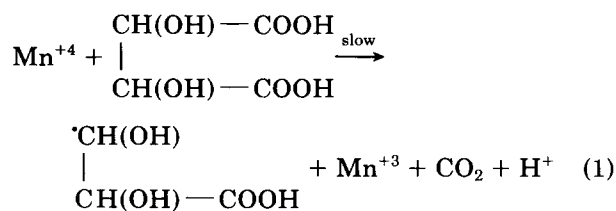
In the case of citric acid, similar mechanisms are suggested by eq. (3):

$$Mn^{+4} + \begin{array}{c} CH(OH) \\ | \\ C(OH)-COOH \\ | \\ CH-COOH \end{array} \rightarrow$$

$$\begin{array}{c} \cdot C-COOH \\ | \\ C(OH)-COOH \\ | \\ \cdot C-COOH \end{array} + Mn^{+2} + 2H^+ \quad (3)$$

whereas in the case of oxalic acid, the carboxyl radical ions constituting the primary free radical species are possibly formed as given below:[15,16]

$$Mn^{+4} + C_2O_4^{-2} \xrightarrow{measurable} Mn^{+3} + CO_2 + COO^- \quad (4)$$

$$Mn^{+4} + COO^- \xrightarrow{rapid} Mn^{+3} + CO_2 \quad (5)$$

$$Mn^{+3} + 2C_2O_4^{-2} \xrightarrow{rapid} [Mn(C_2O_4)_2]^- \quad (6)$$

$$Mn^{+3} + C_2O_4^{-2} \xrightarrow{measurable} Mn^{+2} + \cdot COO^- + CO_2 \quad (7)$$

$$Mn^{+3} + \cdot COO^{-1} \xrightarrow{rapid} Mn^{+2} + CO_2 \quad (8)$$

With respect to hydrochloric acid, it appears that the chloride ion is oxidized by MnO_2 to produce the chloride radical which acts as the primary free radical species;

$$Mn^{+4} + HCl \rightarrow \cdot Cl + Mn^{+3} + H^+ \quad (9)$$
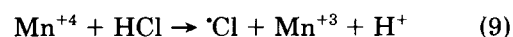
Other free radical species, namely the hydroxyl radical, may also be formed:

$$Mn^{+4} + H_2O \rightarrow Mn^{+3} + H^+ + \cdot OH \quad (10)$$
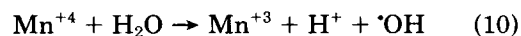
Once the free radical species ($R \cdot$) are formed, they produce starch macroradicals via direct abstraction of hydrogen atoms from starch molecules. This reaction may be represented as follows:

$$St-H + R \cdot \rightarrow St \cdot + RH \quad (11)$$
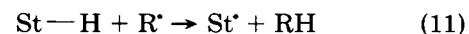
where $St-H$ represents the starch molecule.

Starch macroradicals may also be formed by direct attack of Mn^{+4} or Mn^{+3} ions on the starch molecule via abstraction of the hydrogen atom.

$$St-H + Mn^{+4} \rightarrow St \cdot + Mn^{+3} + H^+ \quad (12)$$

$$St-H + Mn^{+3} \rightarrow St \cdot + Mn^{+2} + H^+ \quad (13)$$
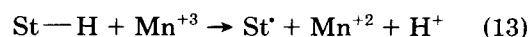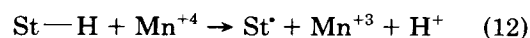
In the presence of a vinyl monomer the starch is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and starch with creaction of a free radical on the monomer, i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto starch as follows:

$$St \cdot + \begin{array}{c} H \\ | \\ CH_2=C \\ | \\ X \end{array} \rightarrow \begin{array}{c} H \\ | \\ St-CH_2-C \cdot \\ | \\ X \end{array} \quad (14)$$

$$St—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet} + nCH_2=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}} \rightarrow$$

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}—)—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet}$$

(Graft propagation)   (15)
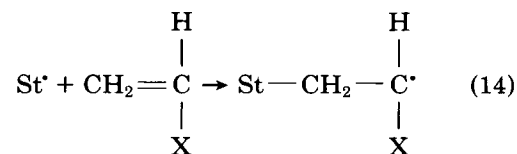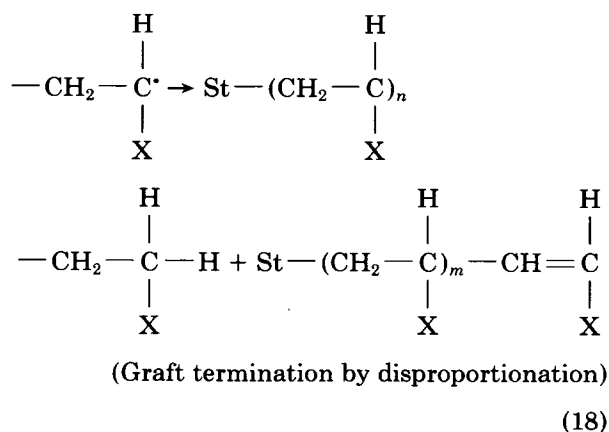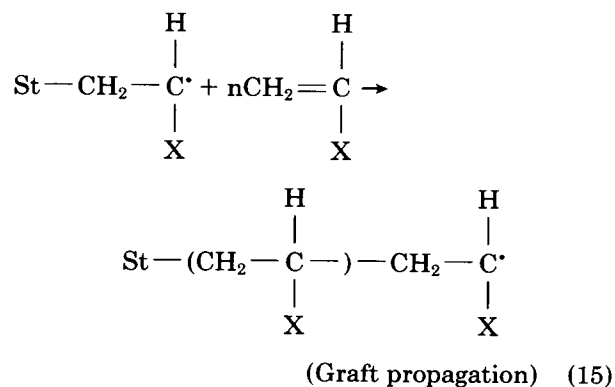
Finally, termination of the growing grafted chain may occur via reaction with the initiator, disproportionation, coupling, or chain transfer, as follows:

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_n—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet} + Initiator^{\bullet} \rightarrow$$

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_n—CH_2=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}$$

(Graft termination by initiator radical)   (16)

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_n—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet} + {}^{\bullet}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}—CH_2$$

$$—(—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}—H_2C)_n—St \rightarrow$$

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_{n+1}—(\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}—H_2C—)_{n+1}—St$$

(Graft termination by coupling or combination)

(17)

$$St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_n—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet} + St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_m$$

$$—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{}^{\bullet} \rightarrow St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_n$$

$$—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}—H + St—(CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}})_m—CH=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}$$

(Graft termination by disproportionation)

(18)
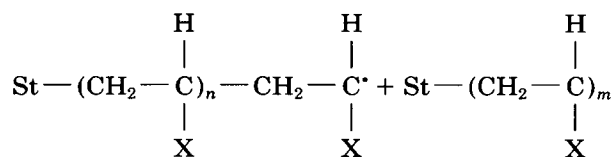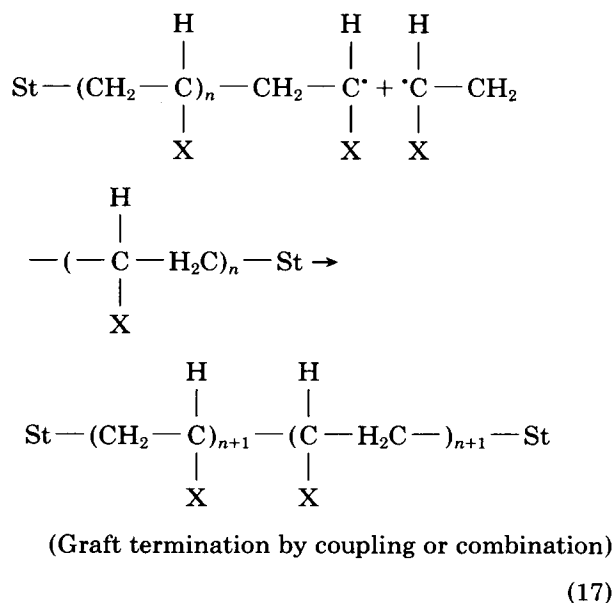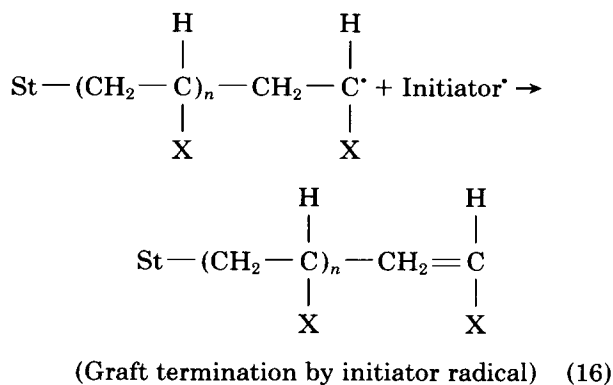
Effect of MnO₂ Deposited on the Graft Yield

Table II shows the graft yield, expressed as m.eq. —COOH/100 g starch versus the amount of MnO_2 deposited onto the starch when the latter was graft polymerized with AA in the presence of citric acid as activator. Obviously, the graft yield increases substantially as the MnO_2 deposit increases until MnO_2 concentration of 8.525 meq/100 g starch is reached, then the yield remains constant. The enhancement in grafting by increasing the amount of MnO_2 deposited up to 8.525 is due to MnO_2 and free radical species participate mainly in the creation of starch macroradicals which are capable of initiating grafting. On the other hand, the fact that the graft yield remains constant after 8.525 meq $MnO_2/100$ g starch is deposited onto the starch may be attributed to: (a) a faster termination rate between two chain radicals via bimolecular collision, and (b) a lower diffusion rate of monomer from the aqueous phase to the starch phase due to the excess amount of MnO_2 deposited.

Table II   Graft Yield (Expressed as meq —COOH/100 g Starch) of Poly (AA)–Starch Graft Copolymers Versus Amount of MnO₂ Deposited

Amount of MnO₂ Deposited (meq/100 g Starch)	Carboxyl Content; (meq/100 g Starch)
0.550	40.5
2.560	62.4
5.575	81.7
7.400	90.3
8.250	96.3
8.525	100.5
8.525	100.5
8.525	100.5

Reaction conditions: starch, 10 g; [Citric acid], 40 meq/L; polymerization time, 1 h; polymerization temperature, 60°C; AA, 2 mL; material-to-liquor ratio, 1 : 10.

Type and Concentration of Acid

Table III shows the effect of type and concentration of acid on the graft yield of poly(AA)-grafted starch using MnO_2. Acids used were citric, tartaric, oxalic, and hydrochloric. It is also clear that increasing citric acid concentration up to 20 meq/L is accompanied by enhancement in the graft yield expressed as meq —COOH/100 g starch. Above this concentration, grafting decreases. On the other hand, tartaric and oxalic acids up to 40 meq/L cause a significant increase in grafting; further increase in concentration leads to a decrease in grafting. The same situation is achieved with hydrochloric acid, but the decrement in grafting above 20 meq/L HCl concentration is not observed. The graft yield obtained with the four acids used follows the order: Citric > Tartaric > Oxalic > Hydrochloric. These may be attributed to: (a) the nature and affinity of primary free radical species formed to starch, (b) the ability of these radical to react with other ingredient(s) rather than starch, and (c) the half-life time of these primary free radicals. In addition, the lowest graft yield obtained with hydrochloric acid can be explained thus: oxidation of the chloride ion (eq. [9]) by MnO_2 would lead to a decreased amount of Mn^{+4}, which is the main factor for initiating grafting.

Material-to-Liquor Ratio

Table IV shows the effect of the material-to-liquor ratio on the graft yield of poly(AA)–starch graft copolymers. Increasing the material-to-liquor ratio from 1 : 1 to 1 : 5 brings about enhancement in

Table III Effect of Type and Concentration of Acid on the Graft Yield (Expressed as meq —COOH/100 g Starch) of Poly (AA)-grafted Starch

Acid Concentration (meq/L)	Carboxyl Content, m.eq. —COOH/100 g Starch of Different Types of Acids			
	Citric	Tartaric	Oxalic	Hydrochloric
5	60.0	45.6	37.9	20.0
10	81.5	67.3	56.3	26.5
20	106.5	81.2	70.2	30.2
40	100.5	85.0	74.9	31.0
60	86.5	76.5	65.1	31.1
80	80.0	70.0	60.0	31.1
100	76.5	62.0	50.3	31.1

Reaction conditions: starch, 10 g; [MnO₂], 8.525 meq/100 g starch; AA, 2 mL; polymerization time, 1 h; polymerization temperature, 60°C; material-to-liquor ratio, 1 : 10.

Table IV Effect of Material-to-Liquor Ratio on the Graft Yield (Expressed as meq —COOH/100 g Starch), of Poly (AA)-grafted Starch

Material-to-Liquor Ratio	Carboxyl Content, (meq —COOH/100 g Starch)
1 : 1	36.9
1 : 2.5	86.7
1 : 5	106.5
1 : 7.5	103.2
1 : 10	100.5
1 : 12.5	90.2
1 : 15	80.2
1 : 20	70.0

Reaction conditions: starch, 10 g; [MnO₂], 8.525 meq/100 g starch; [Citric acid], 20 meq/L; polymerization time, 1 h; polymerization temperature, 60°C; AA, 2 mL.

grafting. Above a material-to-liquor ratio of 1 : 5, grafting decreases within the range studied. In other words, of all the liquor ratios studied, a material-to-liquor ratio of 1 : 5 constitutes the best. It is likely that at this particular ratio a good grafting environment is created through intimate association of the monomer and initiator with starch macromolecules. Once this is the case, greater availability of the monomer and initiator in the vicinity of starch macromolecules occurs, thereby leading to higher grafting. The opposite situation is encountered at higher liquor ratios. That is why lower graft yield values are seen at higher liquor ratios.

Table V Effect of Acrylic Acid Concentration on the Graft Yield (Expressed as meq —COOH/100 g Starch) of Poly (AA)-grafted Starch

Acrylic Acid Concentration (Based on Weight of Starch)	Carboxyl Content, (meq —COOH/ 100 g Starch)
10	46.5
30	86.3
50	106.5
75	113.5
100	123.9
125	130.0
150	134.5
200	138.2

Reaction conditions: starch, 10 g; [MnO₂], 8.525 meq/100 g starch; [Citric acid], 20 meq/L; polymerization time, 1 h; polymerization temperature, 60°C; material-to-liquor ratio, 1 : 5.

Acrylic Acid Concentration

Table V shows the graft yield expressed as meq —COOH/100 g starch against AA concentration using MnO_2/citric acid as initiator. It is clear that the graft yield is directly related to the acrylic acid concentration within the range studied. Increasing the AA concentration to 100% based on the weight of starch leads to higher significant enhancement in grafting than that found when higher concentration ranges of 100–200% are used. This can be explained in terms of greater availability of AA molecules in the proximity of starch.

Polymerization Time and Temperature

Table VI shows the graft yield, expressed as m.eq. —COOH/100 g starch, as a function of polymerization time at different temperatures. It is seen from Table VI that grafting exhibits an initial fast rate which slows down with time, then levels off. This is observed regardless of the polymerization temperature used. The extent of grafting increases by raising the temperature from 30–50°C. Increasing the temperature to 60°C is accompanied by decreased grafting.

The favorable effect of temperature (up to 50°C) on grafting could be ascribed to: (a) diffusion of AA into the starch structure, (b) the swellability of starch, (c) mobility of AA molecules and their collision with starch macroradicals for initiating of grafting, and (d) propagation of the graft. On the other hand, the lower grafting observed at 60°C is perhaps due to the faster termination rate and greater amount of homopolymer formation at higher temperatures.

It may be further noted that the levelling off of grafting is perhaps a direct consequence of the depletion in initiator and monomer concentration as the reaction proceeds. It is likely that, during the course of grafting, starch undergoes modification (i.e., the ratio between the amylose, an essentially linear polymer, and amylopectin, a highly branched polymer, is changed because some of the hydroxyl groups of starch macromolecules are occupied by AA molecules as well as the higher viscosity of the grafted starch) and the modified starch derived therefrom is not as amenable to grafting as the unmodified starch, a point which may be taken into consideration when explaining the levelling off of grafting after a certain time.

Sizing of Cotton Textiles

Trials were made to apply the newly prepared poly(AA)–starch graft copolymers having different carboxyl contents, expressed as meq —COOH/100 g starch, as well as native rice starch to light cotton fabric to determine their suitability for the sizing of cotton textiles.

Table VII shows the major mechanical properties (i.e., tensile strength, elongation at break, and abrasion resistance) of cotton fabrics sized with native rice starch and poly(AA)–starch graft copolymers. Table VII also gives the carboxyl content of poly(AA)–starch graft copolymers.

The results shown in Table VII reveal a number of interesting features:

- Fabric samples sized with native rice starch exhibit higher tensile strength and abrasion resistance but lower elongation at break than unsized cotton fabric.
- Fabric samples sized with poly(AA)–starch graft copolymers acquire tensile strength, elongation at break, and abrasion resistance which exceeds that of fabric sized with native rice starch.
- Fabric samples sized with poly(AA)–starch graft copolymers having different carboxyl contents ranging from 20 to 138.5 meq —COOH/100 g starch showed higher tensile strength and abrasion resistance by increasing the carboxyl contents within the range studied; on the other hand, elongation at break was approximately unchanged.

Table VI   Effect of Polymerization Time and Temperature on the Graft Yield (Expressed as meq—COOH/100 g Starch) of Poly (AA)-grafted Starch

Polymerization Time (min)	Carboxyl Content, (meq C—OOH/100 g Starch) at Different Temperatures (°C)			
	30	40	50	60
5	36.9	63.1	65.5	60.0
10	40.2	73.2	78.2	70.3
15	46.3	80.2	84.3	76.3
30	53.2	92.9	98.5	88.5
60	64.9	111.2	118.9	106.5
120	66.0	113.1	119.9	109.1
180	67.5	113.8	121.0	111.2

Reaction conditions: starch, 10 g; [MnO_2], 8.525 meq/100 g starch; [Critic acid], 20 meq/L; AA, 2 mL; material-to-liquor ratio, 1 : 5.

Table VII   Tensile Strength, Elongation at Break and Abrasion Resistance of Light Cotton Fabric Sized with Native Rice Starch as Well as Poly (AA)-grafted Starch having Different Carboxyl Contents

Fabric Sample	Carboxyl Content (meq/100 g Starch)	Physicomechanical Properties		
		Tensile Strength (kg)	Elongation at Break (%)	Abrasion Resistance (cycles)
Unsized	—	48.0	10.0	880
Sized with native rice starch	—	49.5	9.1	886
Sized with poly (AA)-grafted starch	20.0	50.0	9.6	894
	46.5	51.0	9.8	900
	86.3	52.0	9.9	908
	113.5	53.0	9.7	912
	130.0	53.5	9.6	918
	138.5	53.5	9.6	918

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