

Graft Polymerization of Cationic Methacrylate, Acrylamide, and Acrylonitrile Monomers onto Starch by Reactive Extrusion

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ABSTRACT

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Starch graft copolymers were prepared from cationic methacrylate (CM), acrylamide (AAM), and acrylonitrile (AN) monomers by continuous twin-screw extrusion processing. The monomers were reacted separately with cornstarch under various conditions in the extruder with ceric ammonium nitrate (CAN) as the initiator. The purpose of the study was to determine the feasibility of grafting substantial levels of monomer onto the starch within brief reaction periods of 3-7 min. Effects of temperature, monomer-starch weight ratio, starch concentration, CAN addition level, screw speed, and other variables in the extrusion process were studied. For comparison, starch graft copolymers from these monomers were prepared by typical 2-hr batch processes at relatively low material concentration, temperature, and shear stress conditions. In extrusion processing,

starch graft polyacrylonitrile (St-g-PAN) copolymer products with high conversion of monomer to polymer (74-78%) and high synthetic polymer add-on (42-44% of product weight) were achieved within a reaction period of 7 min. Under similar extrusion conditions, add-on was 16-19% and conversion was 19-23% for AAM. Maximum add-on was only 6.7% for the CM monomer. AAM also was reacted with waxy maize to give 18-23% add-on. The waxy maize copolymers were more water soluble than the cornstarch copolymers. Results suggest that the continuous extrusion process could be particularly promising as a viable means of rapidly and efficiently producing St-g-PAN copolymers that are useful after saponification as commercial water-absorbent materials.

Reactive extrusion is a relatively new area of study involving the chemical preparation and modification of synthetic polymers in extruders by continuous processing. Examples of materials processed by reactive extrusion include styrene plus acrylonitrile prepolymer (free-radical copolymerization), polyol plus diisocyanate and diamine (polyaddition), and polyamide plus maleic anhydride adduct (grafting) (Eise 1986, Frund 1986). Twin-screw extruders are particularly advantageous for carrying out these and other types of polymerization reactions (Sneller 1985, Eise 1986). However, the principles and practices of continuous twin-screw reactive extrusion have not yet been significantly applied to biopolymers such as starch and cellulose. Nevertheless, twin-screw extruders have been used extensively to investigate the modification of starch by heat, shear, and pressure with and without the use of acids, bases, or enzymes (Mercier et al 1979, El-Dash 1981, Hakulin et al 1983, Mielcarek 1987).

Recently, a continuous process was reported for the conversion of unmodified starch to glycol and glycerol glucosides in a Readco twin-screw processor (READ Corp., York, PA) (Carr and Cunningham 1989) and in a ZSK 30, corotating, intermeshing, twin-screw extruder (Werner & Pfleiderer, Ramsey, NJ) (Carr 1991). In the ZSK 30 extruder, starch was converted to mono- and dimeric glucosides in nearly quantitative yield at high production rates within brief residence times of 1-1.5 min. Now the feasibility of graft-polymerizing various types of monomers onto starch by continuous reactive extrusion is being investigated. In present work, a cationic methacrylate (CM) monomer, acrylamide (AAM), and acrylonitrile (AN) each were reacted with cornstarch using ceric ammonium nitrate (CAN) as the initiator for graft polymerization. AAM also was reacted with waxy maize starch. The major objective was to determine whether substantial quantities of the monomers could be graft-polymerized onto starch within brief reaction periods of about 3-7 min. Starch graft copoly-

mers from these monomers also were prepared by typical 2-hr laboratory batch processes for comparative purposes. Starch graft copolymers prepared from these monomers have been found useful as flocculating agents, retention aids, thickening agents, and absorbents (Fanta and Doane 1986). In this study, only water solubility and water absorbency of the grafts were examined. Alkali treatment of starch graft polyacrylonitrile (St-g-PAN) yields a water-absorbent product that is commercially available and commonly referred to as Super Slurper. The development of a more efficient and continuous process for preparation of this copolymer could lower the product cost substantially and open up new markets for its use.

MATERIALS AND METHODS

Materials

Materials included 1) unmodified cornstarch, powdered, food grade, and Waxy-Maize 7351 (A. E. Staley Manufacturing Co., Decatur, IL); 2) methyl chloride quaternary salt of dimethylaminoethyl methacrylate, MADQUAT Q6, a cationic methacrylate monomer (Norsolac, Inc., Sedalia, MO); 3) acrylamide, 97% (Aldrich Chemical Co., Milwaukee, WI); 4) acrylonitrile, 99+% (Aldrich); 5) ceric ammonium nitrate, 99+% (Aldrich); 6) nitric acid, 69-71% (Reagent A.C.S., Fisher Scientific, Fair Lawn, NJ); and 7) distilled water.

Equipment

The extruder was a ZSK 30 twin-screw extruder with a 15-hp DC drive and screw speeds from 50 to 500 rpm. The processing section consisted of 14 barrel sections (each 90 mm long) consisting of seven zones, one barrel spacer (30 mm long), and an end plate (30 mm long), coupled by four tie-rods. Barrel bore and screw diameters are 30.85 and 30.70 mm, respectively. The length-diameter ratio (43:1) is the processing length (1,320 mm) divided by the screw diameter. Each barrel section (BS), except the first, had an electric heater (500 W). Barrel temperature thermocouples were located at BS 3, 5, 7, 9, 11, 12, and 14. Thermocouples for measuring material temperature were located at BS 11 and at the die head (zone 8, last zone). The die head was equipped with a 2,000-W heater and a pressure transducer. Chilled water was circulated through the extruder barrel jackets, which were equipped with solenoid valves and return line check valves to help regulate barrel temperatures within close tolerances of the settings.

The twin screw was composed of various types of 68 individual slip-on mixing screws arranged in a configuration previously reported (Carr and Cunningham 1989). A twin-screw volumetric feeder (model T20, K-TRON Corp., Pitman, NJ) was used to

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feed starch into the extruder. Liquids were fed into the extruder through drilled thermocouple plugs by reciprocating positive displacement pumps (models EK-3 and FC-3/V, American LEWA, Inc., Holliston, MA). A remote control panel was used for instrumentation, process control, and monitoring (temperature, torque, pressure, power consumption, screw speed, and feed rate).

Reactive Extrusion Process

Procedures A, B, and C are shown in Figure 1. In all procedures, starch (10% moisture) was fed into BS 1 (75.6 g/min, dry basis). In procedure A, aqueous solutions of CAN and HNO₃ were fed into BS 2, and aqueous CM monomer solutions were fed into BS 3 to obtain various weight ratios of monomer-starch, CAN addition levels (dry starch basis), and concentrations of starch in water. In procedure B, aqueous solutions of AAm were fed into BS 2, and the CAN-HNO₃ solutions were fed into BS 3. The concentration of starch in water was 35% before addition of CAN-HNO₃ solution and 25% after its addition. In procedure C, AN without water was fed into BS 3 and CAN-HNO₃ solutions were fed into BS 5 to give a starch in water concentration of 35%. In all procedures, the chemical concentrations and feed rates were varied.

In procedures A and B, the HNO₃ molarity of the reactive system varied from 0 to 0.03. In procedure C, the HNO₃ molarity of the CAN solution was 0.02, which was the same as the HNO₃ molarity of the reactive system because the CAN-HNO₃ solution contained all of the water in the reactive system. Screw speed was 400 rpm, except in procedure B with AAm (200 vs. 400 rpm). In all procedures, the die head and extruded material were completely housed in and connected to an exhaust system to prevent volatiles from entering the room. Samples were readily collected at the die head within the housed system.

In procedure A (see Fig. 1) starch was fed into the extruder at a rate of 84 g/min (75.6 g/min, dry basis), while starch in water concentrations, monomer-starch weight ratios, and CAN addition levels were varied as shown in Table I. In runs 1-4, the barrel temperature was 70°C in all eight zones. In runs 5-9, temperatures were 70 in zone 1 (Z1), 90 (Z2), 100 (Z3-5), 90 (Z6), and 70°C (Z7-8). Total reaction time for unaged extrudate samples included the average residence time of material in the extruder (2-3 min), sample collection time (1 min), and time required to complete the first sample wash (3-4 min). Portions of crude unwashed extrudate were allowed to stand at room temperature for 1-6 hr.

Procedures for procedure B were similar to those described for the CM monomer (Table II), except that the AAm solutions were incorporated into the starch before the CAN-HNO₃ solutions. However, the order of addition was not important because these chemicals were fed into the extruder so close to one another (see Fig. 1).

In procedure C, the starch, AN solution, and CAN solution were fed into BS 1, 3, and 5, respectively. Barrel temperature was 70°C in all eight zones, and total reaction time was about 7 min as previously described.

Extrudate Sample Handling and Analysis

Each sample of the extruded material (extrudate) was collected for 1 min in a Waring Blender container and immediately removed to a fume hood. With constant stirring, sufficient water was added as needed to obtain a flowable mixture, and then methanol was gradually admixed until the product precipitated. The mixture was filtered using Whatman No. 54 filter paper. The precipitate on the filter was washed with methanol in a blender, filtered, and dried overnight under vacuum at 60°C. The reaction was quenched by the first wash, which required about 3-4 min. Nitrogen contents of the dried products were determined by Kjeldahl analysis. Percentages of monomer converted to polymer and add-on were calculated from the nitrogen contents of the vacuum-dried products.

Batch Processes

Batch polymerization reactions were carried out in a 2-L resin kettle by procedures similar to those of Fanta and co-workers (1987). Aqueous slurries of starch at various concentrations (e.g., 20 g of starch per 200-400 ml of H₂O) were stirred for 1 hr

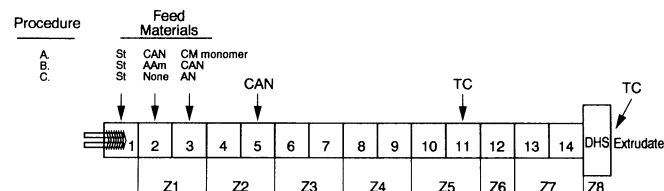


Fig. 1. Reactive extrusion process. St = Starch; CAN = ceric ammonium nitrate (aqueous solution); AAm = acrylamide; CM = cationic methacrylate monomer (see Materials and Methods); AN = acrylonitrile; TC = thermocouple; DHS = die head assembly; Z = zone. CM and AAm were added as aqueous solutions.

TABLE I
Extrusion and Batch Preparation of Starch Graft Copolymers from Cationic Methacrylate Monomer

Run Type and Number	Extrusion Conditions					
	Starch Concentration (%) ^a	Monomer-Starch Weight Ratio	Ceric Ammonium Nitrate (%) ^b	Reaction Time (hr)	Add-On (%) ^c	Monomer Conversion (%) ^d
Extrusion (70°C) ^e						
1	10	0.10	1.0	0.12	<0.1	<0.1
2	35	0.30	1.0	1.0	1.6	5.5
3	35	0.30	5.0	1.0	2.1	7.1
4	47	0.30	5.0	1.0	3.6	12.3
Extrusion (70-100°C) ^f						
5	10	0.10	5.0	0.12	0.9	9.0
6	10	0.10	5.0	16.0	5.5	58.0
7	35	0.10	5.0	2.5	3.7	38.5
8	10	0.80	5.0	1.0	6.7	8.9
Batch (25°C) ^g						
9	4.1	1.0	3.0	2.0	6.1	8.6
10	11.3	0.8	4.4	4.0	6.1	10.3

^a(Dry starch weight) ÷ (starch weight with 10% moisture + weight of water added) × 100.

^bPercentage of dry starch weight.

^cTotal synthetic polymer as percentage of the starch graft copolymer weight, dry basis.

^dPercentage of monomer that was converted to synthetic polymer.

^eAll barrel zones were 70°C.

^fBarrel zones were increased from 70 (zone 1) to 100 (zones 3-5) to 70°C (zones 7,8). See Materials and Methods.

^gStarch was gelatinized at 95°C and then cooled to 25°C to run the reaction.

TABLE II
Extrusion and Batch Preparation of Starch Graft Copolymers from Acrylamide (AAM)

Preparation Method	Extrusion Conditions						Conversion (%) ^c	Add-On (%) ^d
	Starch Concentration (%) ^a	AAM-Starch Weight Ratio	Ceric Ammonium Nitrate (%) ^b	HNO ₃ Molarity	Reaction Temperature (°C)	Reaction Time (hr)		
Batch	9.5	1.0	4.4	0.02	50	2.0	64	39
Extrusion	35/25 ^e	1.0	4.4	0.02	70	0.12	19	16
Extrusion	35/25 ^e	1.0	4.4	0.02	70	16.0	35	26

^a(Dry starch weight) ÷ (starch weight with 10% moisture + weight of water added) × 100.

^bPercentage of dry starch weight.

^cPercentage of monomer that was converted to synthetic polymer.

^dTotal synthetic polymer as percentage of the starch graft copolymer weight, dry basis.

^ePercentages before and after addition of ceric ammonium nitrate-HNO₃ solution.

at 95°C to gelatinize the starch and then cooled to 25°C with continuous stirring and nitrogen purging throughout the procedure. Under continuous stirring and nitrogen atmosphere, monomer and CAN-HNO₃ solutions (1.5 ml of 1M HNO₃ per 100 ml of H₂O) were sequentially added to the starch dispersion to give various monomer-starch weight ratios and CAN addition levels. The reactions were carried out for two or more hours, generally at 25–30°C but also at 50°C for the CM monomer. After the reaction period, methanol (100 ml) was added to the mixture and pH was adjusted to about 7 with NaOH in methanol solution. After precipitation of the material in methanol, the precipitate was filtered on Whatman No. 54 filter paper, washed twice more in methanol, and dried under vacuum at 60°C.

Saponification

Starch graft copolymer (4 g) was added to 1M NaOH (36 ml) in a stoppered Erlenmeyer flask. The mixture was heated for 10 min in a steam bath and then heated 80 min more in a forced-air oven set at 100°C. The saponified product was precipitated by addition of methanol, stirred in methanol with a Waring Blendor, and further stirred in methanol overnight with a magnetic bar. Then the product was filtered, washed with methanol, and dried under vacuum at 50°C. Nitrogen contents of the dried samples were determined by Kjeldahl analysis.

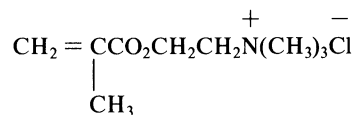
Water Absorbency of Saponified St-g-PAN Product

Twenty-five milligrams of saponified product was immersed in distilled water for 30 min. The material was gently filtered on Whatman No. 54 filter paper without vacuum or other force until excess water disappeared (30 min). Water absorbency was expressed as grams of H₂O absorbed per gram of sample.

RESULTS AND DISCUSSION

CM Monomer

The structure and nomenclature of the CM monomer are given below.



N,N,N-trimethylaminoethyl methacrylate chloride

The effect of chemical variables on monomer conversion and add-on were studied in both extrusion and batch graft polymerization reactions. Conversion is defined in this study as the weight percentage of monomer converted to synthetic polymer contained by the starch graft copolymer product. Synthetic polymer includes occluded homopolymer as well as synthetic polymer covalently bonded to starch. Add-on is defined as the weight percentage of synthetic polymer contained by the starch graft copolymer.

Table I shows that levels of add-on and/or monomer conversion were low for the CM monomer (procedure A) using a wide range

of conditions. Maximum add-on was only 6.7%, and only 8.9% of the monomer was converted to polymer using a monomer-starch ratio of 0.8 and a CAN addition level of 5% (Run 8). Monomer conversion was dramatically improved to 58% with a monomer-starch ratio of only 0.1 (Run 6). Conversion and add-on were increased by increasing the concentration of starch in water from 10 to 47%. However, the maximum add-on was low with this monomer even when the extrudates were aged for 16 hr. The results were not improved by reversing the order of monomer and CAN addition (data not shown). Due to low add-on, no attempt was made to separate homopolymer from the crude reaction products.

To determine whether substantially better results could be obtained, the CM monomer was reacted with starch by a typical batch process at the conditions shown in Table I (see Materials and Methods, Batch Processes). These data show that extents of add-on and monomer conversion were not improved over those obtained by the extrusion process. In data not shown, results were not significantly better using either ferrous ammonium sulfate-hydrogen peroxide or potassium permanganate as initiators. Thus, the primary limiting factor in the extrusion process appeared to be the inherently low polymerization reactivity of the CM monomer per se.

Other workers have grafted similar types of CM monomers onto starch by batch reaction procedures with better results. However, conversions and grafting efficiencies for such monomers have been typically low with such monomers using chemical initiation as opposed to cobalt-60 irradiation (Fanta and Doane 1986).

Acrylamide

AAM was reacted with starch by reactive extrusion with encouraging results (procedure B). Figures 2–4 show conversion and add-on data for extrusion reactions at 70°C. Starch in water concentration was 35% after addition of the aqueous AAM solution (BS 2) and 25% after addition of the aqueous (CAN-HNO₃) solution (BS 3). Figure 2 shows the effect of CAN addition levels on the extent of add-on and monomer conversion using an AAM-starch weight ratio of 1.0. These data show that the reaction rate was dramatically accelerated by increasing the CAN from 1.5 to 3.5% (dry starch basis). Add-on and conversion peaked with 5.5% CAN and then declined with 7.5% CAN. Reactions continued to significant extents when extrudates were allowed to age 16 hr before washing. Nevertheless, about 63–68% of the total add-on after aging occurred with the use of 3.5–7.5% CAN within the 7-min reaction period.

Figure 3 shows the effect of HNO₃ concentration in the extrusion system (3.5% CAN, 1.0 AAM-starch ratio). Sufficient acid was added to the CAN solution to achieve a molarity of 0.01, 0.02, or 0.03, based on total water in the extruder. Data show that conversion and add-on were affected to a small extent for both aged and unaged products. For example, monomer conversion for aged products was 35% for HNO₃ molarities of 0.02 and 0.03, and 31% without acid addition. Correspondingly, add-on was 25% with acid and 24% without acid. Although the purpose of preparing CAN solutions with HNO₃ in previous batch reaction

studies was to stabilize the ceric ion complex during storage (e.g., 24 hr) and during reaction periods of 2–4 hr, HNO₃ was not required in the extrusion process when the CAN was prepared and used the same morning. However, CAN solutions without HNO₃ were not very effective when stored for 24 hr before use. Elimination of HNO₃ is desirable to reduce both starch hydrolysis and corrosive effects in the extrusion system.

Conversion and add-on for various ratios of AAm-starch are shown in Figure 4 (3.5% CAN, 0.02 HNO₃ molarity). As the AAm-starch ratio was increased from 0.25 to 1.5, the percentage of AAm converted to polymer decreased substantially from 30 to 12% for the unaged products, yet represented 2.4 times more total synthetic polymer at the 1.5 ratio than at the 0.25 ratio. In the aged product, conversion was 35% for the 0.25 ratio and 27% for the 1.5 ratio. This is because add-on increased from 8 to 29% for aged products, but from 7 to 15% for unaged products, as the ratio was increased to 1.5. The 15% add-on value for the 1.5 ratio is lower than expected, based on values of 16 and 17% in duplicate extruder runs for the 1.0 ratio.

Table II compares levels of add-on and AAm conversion obtained by the extrusion and batch processes. In the batch process, the starch in water concentration and CAN addition levels were 9.5 and 4.4%, respectively. The starch was dispersed as described previously, and the reaction then was carried out for 2 hr at 50°C. Add-on and AAm conversion were 39 and 64%, respectively, compared with 25 and 35% for the extrusion product aged 16 hr. Add-on was 16% and conversion was 19% for the unaged extrusion products.

Table III shows that add-on and conversion increased only slightly when the screw speed was decreased from 400 to 200

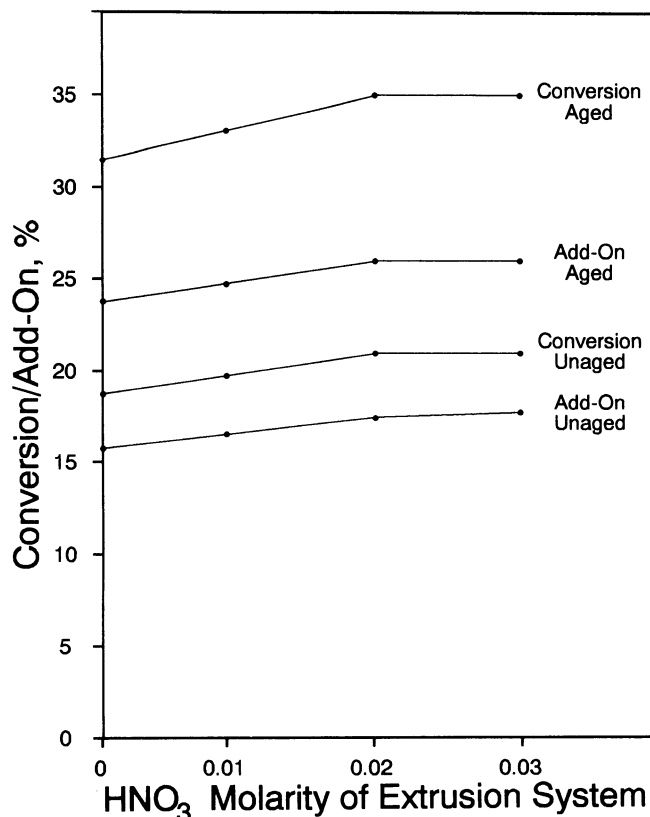


Fig. 3. Effect of HNO₃ molarity in the extrusion system on acrylamide (AAm) conversion and add-on of aged and unaged starch graft copolymers. AAm-starch weight ratio = 1.0; starch in water concentration = 25% after aqueous ceric ammonium nitrate (CAN) addition; percentage of CAN = 3.5. See Figure 1 and Materials and Methods.

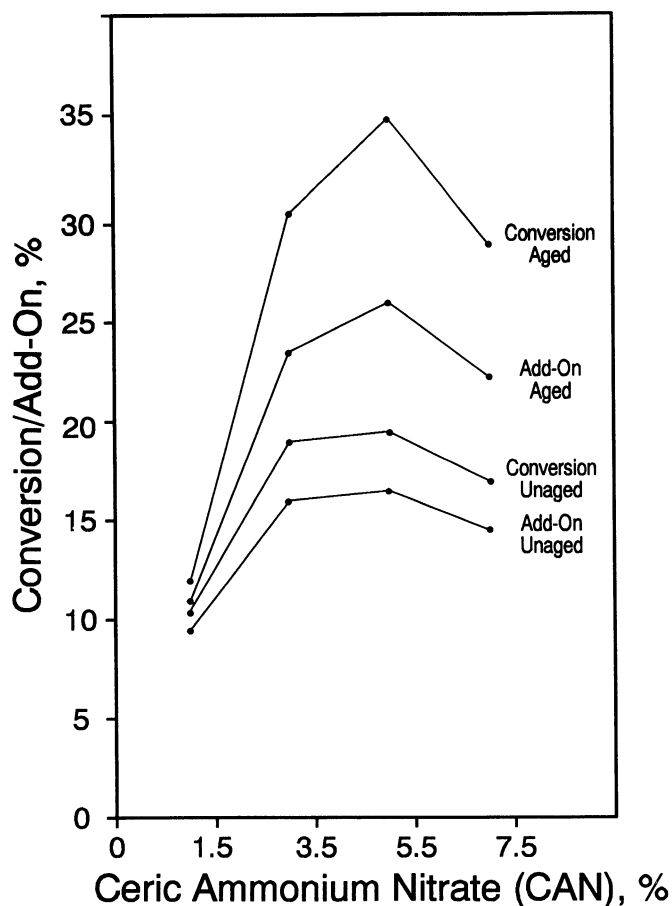


Fig. 2. Effect of ceric ammonium nitrate (CAN) addition levels in the extrusion process on acrylamide (AAm) conversion and add-on for aged and unaged starch graft copolymers. AAm-starch weight ratio = 1.0; starch in water concentration = 25% after aqueous CAN addition; HNO₃ molarity = 0.02. See Figure 1 and Materials and Methods.

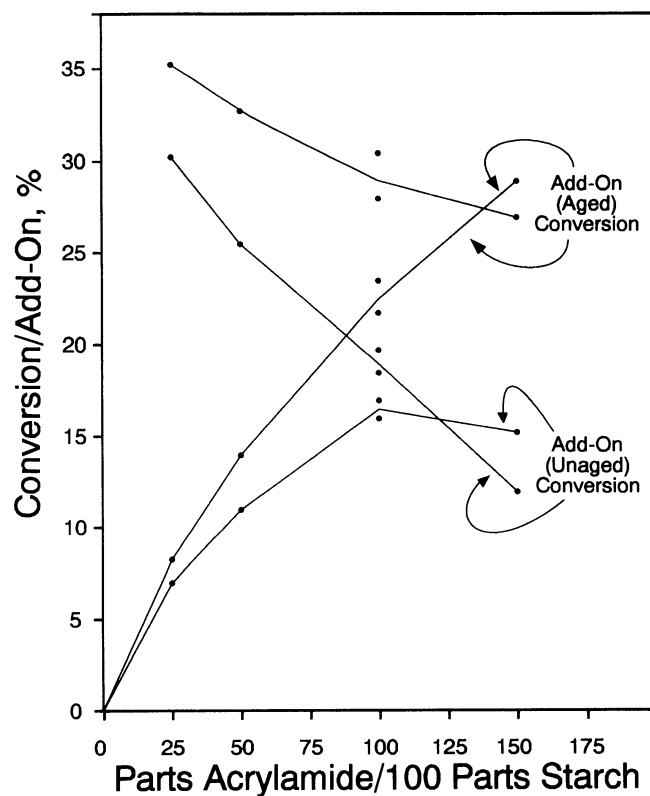


Fig. 4. Effect of acrylamide (AAm)-starch weight ratio in the extrusion process on AAm conversion and add-on for aged and unaged starch graft copolymers. HNO₃ molarity = 0.02; starch in water concentration = 25% after aqueous ceric ammonium nitrate (CAN) addition; percentage of CAN = 3.5. See Figure 1 and Materials and Methods.

rpm (1.0 AAm-starch ratio, 3.5% CAN). The average residence time of material in the barrel was about 2 min at 400 rpm compared with 3 min at 200 rpm. It may be concluded that the AAm polymerization rate was not sufficiently rapid to obtain high add-on in the extruder per se, although the effect of many variables such as screw configuration, feed rates (throughput), extent of barrel filling, die pressure, and some chemical variables has not been studied yet.

Attempts to separate polyacrylamide (PAAm) homopolymer from the crude reaction products were not successful. Separation of occluded PAAm may not be desirable from economic and utilization viewpoints but would be important to characterize the composition of these products.

Waxy Maize Starch vs. Cornstarch

Starch graft copolymer products that were prepared from cornstarch and AAm by the extrusion process did not disperse completely in water at room temperature. Grafts from the batch procedure dispersed to a greater extent, but neither readily nor completely. However, grafts from waxy maize and AAm dispersed essentially completely in water at room temperatures. Table IV shows that levels of AAm monomer conversion and add-on for the grafts prepared by the extrusion process were only slightly greater for waxy maize than for cornstarch (1.0 AAm-starch ratio, 3.5% CAN). The greater water solubility of the waxy maize products should not be attributed to the slightly higher level of add-on. The greater solubility may be because waxy maize, containing all highly branched amylopectin, undergoes less retrogradation than does ordinary cornstarch, which contains about 27% linear amylose.

Acrylonitrile

Table V shows results for reaction of AN with cornstarch by

TABLE III
Effect of Extruder Screw Speed on Graft Polymerization of Acrylamide (AAm) onto Starch^a

Screw Speed (rpm)	Reaction Temperature (°C)	Reaction Time (hr)	Conversion (%)	Add-On (%)
200	70 ^b	0.14 ^c	23	19
400	70 ^b	0.12 ^c	19	16
200	70/25 ^d	16.0 ^c	31	23
400	70/25 ^d	16.0 ^c	25	20

^aAAm-starch weight ratio was 1.0; ceric ammonium nitrate initiator addition level was 3.5% (dry starch weight basis).

^bAll barrel zones were 70°C. Reaction was quenched within 5 min after the material was extruded.

^cAverage residence time (RT) of the material in the barrel was about 3 min, and sample collection plus quenching time was about 4 min at 200 rpm. RT was 2 min at 400 rpm.

^dSame temperature and RT as in b and c, but samples were allowed to stand at room temperature (25°C) for 16 hr without stirring before the extrudates were washed.

the extrusion and batch processes (procedure C). Within the 7-min reaction period, levels of monomer conversion and add-on were 74 and 42%, respectively (1.0 monomer-starch ratio, 3.5% CAN). These results were similar to those obtained in a 2-hr batch reaction period using the same monomer-starch ratio and CAN addition level. However, most of the reaction in the batch process probably occurred in 20–25 min (Gugliemelli et al 1973).

The high graft polymerization reactivity of AN makes this monomer particularly attractive for developing a continuous reactive extrusion process in which an ex situ reaction period may not be required to obtain high add-on. However, considerably more study is needed. Currently, molecular weight (MW), MW distribution, grafting frequency, extent of homopolymer formation, and other characteristics of the St-g-PAN copolymer products are being studied. Water absorbency of the saponified St-g-PAN copolymers that were prepared by the batch process was greater than that of the copolymers prepared in the extrusion process. For example, the saponified extrusion product containing 42% add-on and a carboxamide-carboxylate ratio of 0.26 absorbed 290 g of distilled water per gram of saponified product, compared with 410 g/g for the saponified batch product containing 38% add-on and the same carboxamide-carboxylate ratio. Variables that may affect water absorbency of the copolymer products prepared by extrusion need further study.

CONCLUSIONS

CM, AAm, and AN monomers were graft-polymerized onto cornstarch with CAN as the initiator by a continuous twin-screw extrusion process. AAm was also graft-polymerized onto waxy maize starch. Total reaction time included material residence time in the extruder (2–3 min), collection time (1 min), and quenching time (3–4 min). Samples also were aged 16 hr. Starch graft copolymers from these monomers also were prepared by typical 2-hr batch processes.

TABLE IV
Waxy Maize Starch versus Cornstarch in Graft Polymerization of Acrylamide (AAm) onto Starch Substrates by Reactive Extrusion

Starch Substrate	Reaction Time (hr)	Conversion (%) ^a	Add-On (%) ^b	Water Soluble ^c
Waxy maize	0.12	22	18	Yes
Cornstarch	0.12	19	16	Partially
Waxy maize	16.0	30	23	Yes
Cornstarch	16.0	25	20	Partially

^aPercentage of monomer that was converted to synthetic polymer.

^bTotal synthetic polymer as percentage of the starch graft copolymer weight, dry basis.

^cWaxy maize graft was soluble at room temperature, and the cornstarch graft was mostly insoluble at 95°C (5 g of graft per 100 ml of water). A 1.0 weight ratio of AAm to starch or waxy maize and 3.5% ceric ammonium nitrate were used in the reaction.

TABLE V
Extrusion and Batch Preparation Graft Copolymers from Starch and Acrylonitrile (AN)

Starch Concentration (%) ^a	Extrusion Conditions		Reaction Time (hr)	Conversion (%) ^c	Add-On (%) ^d
	AN-Starch Weight Ratio	Ceric Ammonium Nitrate (%) ^b			
Extrusion (70°C)					
35	1.00	3.5	0.12	74	42
35	0.50	3.5	0.12	63	27
Batch (25–30°C)					
5	1.50	3.5	2	63	49
5	0.75	3.5	2	81	38

^a(Dry starch weight) ÷ (starch weight with 10% moisture + weight of water added) × 100.

^bPercentage of dry starch weight.

^cPercentage of monomer that was converted to synthetic polymer.

^dTotal synthetic polymer as percentage of the starch graft copolymer weight, dry basis.

In both the extrusion and batch processes, reactivity of the CM monomer was poor at all conditions investigated. Reactivity of AAm with cornstarch and waxy maize in the extrusion process was sufficient to obtain 16–18% add-on (weight percentage of synthetic polymer of the starch graft copolymer) using an AAm-starch weight ratio of 1.0. Add-on increased to 25–30% when the extrudates were allowed to age overnight at 25°C. AAm add-on was 39% for a 2-hr batch process.

AN was considerably more reactive than AAm in the extrusion process. With an AN-starch weight ratio of 1.0, add-on was 42% within the 7-min reaction period, without a significant increase in add-on by aging the extrudate. Conversion of monomer to synthetic polymer was correspondingly high (74%). These values were similar to those obtained in the batch process. The relatively high temperature, concentration, and shear stress conditions used in the extruder contributed to the accelerated rate at which graft polymerization occurred. Presumably, viable commercial extrusion processes for the preparation of starch graft copolymers could be developed based on results of this preliminary study. AN is a particularly suitable monomer for continuous reactive extrusion processing because of its high reactivity, and it is the monomer used in the preparation of a commercial water-absorbent starch graft product commonly known as Super Slurper.

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LITERATURE CITED

- CARR, M. E. 1991. Starch-derived glycol and glycerol glycosides prepared by reactive extrusion processing. *J. Appl. Polym. Sci.* 42:45.
- CARR, M. E., and CUNNINGHAM, R. L. 1989. Glycol glucosides from starch by continuous twin-screw extruder processing. *Cereal Chem.* 66:238.
- EISE, K. 1986. Continuous reactive processing with twin-screw extruders. *Plast. Compd.* 9:44.
- EL-DASH, A. A. 1981. Application and control of thermoplastic extrusion of cereals for food and industrial uses. Pages 165-216 in: *Cereals: A Renewable Resource*. Y. Pomeranz and L. Munck, eds. American Association of Cereal Chemists: St. Paul, MN.
- FANTA, G. F., and DOANE, W. M. 1986. Grafted starches. Pages 149-178 in: *Modified Starches: Properties and Uses*. O. B. Wurzburg, ed. CRC Press Inc.: Boca Raton, FL.
- FANTA, G. F., BURR, R. C., and DOANE, W. M. 1987. Absorbents from saponified starch-g-poly(acrylonitrile-co-2-acrylamido-2-methylpropanesulfonic acid). Some practical considerations. *Starch/Staerke* 39:322.
- FRUND, Z. N. 1986. Reactive extrusion. *Plast. Compd.* 9:24.
- GUGLIEMELLI, L. A., SWANSON, C. L., and DOANE, W. M. 1973. Kinetics of grafting acrylonitrile onto starch. *J. Polym. Sci.* 11:2451.
- HAKULIN, S., LINKO, Y.-Y., LINKO, P., SEILER, K., and SEIBEL, W. 1983. Enzymatic conversion of starch in twin-screw HTST-extruder. *Starch/Staerke* 35:411.
- MERCIER, C., CHARBONNIERE, R., GALLANT, D., and GUILBOT, A. 1979. Structural modification of various starches by extrusion cooking with a twin-screw French extruder. *Easter Sch. Agric. Sci. Univ. Nottingham Proc.* 27:153.
- MIELCAREK, D. F. 1987. Twin-screw compounding. *Chem. Eng. Prog.* 83:59.
- SNELLER, J. A. 1985. Reactive processing. New era of innovation begins in resin production. *Mod. Plast.* 62(7):56.

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