Reactive Extrusion vs. Batch Preparation of Starch-g-Polyacrylonitrile

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SYNOPSIS

Acrylonitrile (AN) was graft polymerized onto unmodified cornstarch by a continuous reactive extrusion process and, for comparison, by a typical batch reaction process. The effect of AN/starch weight ratios, level of ceric ammonium nitrate (CAN) initiator, starch in water concentration, reaction temperature, reaction time, and extruder screw speed in the reactive extrusion process was studied. Add-on, reaction efficiency, grafting frequency, weight average molecular weight (MW) and MW distribution of polyacrylonitrile (PAN), and water absorbency of the saponified copolymers were determined. Processing times in the twin-screw extruder (ZSK) were 2–3 min, and total reaction time was about 7 min before reaction of the extruded material was terminated, compared to a reaction time of 2 h used in the typical batch procedure. The continuous reactive extrusion process was found to be a rapid and efficient means of preparing St-g-PAN with high add-on (% PAN of the grafted product). For example, 42% add-on was achieved within the 7-min reaction period using an AN/starch weight ratio of 1.0 (3.5% CAN, starch weight basis), as compared to 38–49% for the 2-h batch process (0.75–1.5 AN/starch ratio). Percentages of homopolymer of the copolymers were low for both extrusion and batch processes. Grafting frequencies were substantially higher while MWs were significantly lower for grafts from the extrusion process. Water absorbency of the saponified St-g-PAN products was somewhat greater for the products prepared by the batch process.

INTRODUCTION

Reactive extrusion has been defined as the concurrent reaction and extrusion processing of polymers in an extruder.[1] Most reactive extrusion work has been carried out on thermoplastic systems. The purpose of the present work was to graft polymerize acrylonitrile (AN) onto starch in aqueous media by reactive extrusion, using ceric ammonium nitrate (CAN) initiation to produce starch-g-polyacrylonitrile (St-g-PAN) copolymers.

In 1958, graft polymerization of AN onto poly(vinyl alcohol) by ceric ion initiation led to an expansion of research on graft polymerization of various vinyl monomers onto cellulose and starch.[2] In effort to expand the market for starch-based products, considerable research on the preparation, characterization, and evaluation of starch graft copolymers was conducted by researchers at the U.S. Department of Agriculture, National Center for Agricultural Utilization Research. Parts of this work were carried out in conjunction with the Stanford Research Institute[3,4] and General Mills.[5,6] Research at the National Center resulted in the commercial development of high capacity water absorbent products from saponified St-g-PAN (Super Slurper).[7] Numerous reviews on graft polymerization of monomers onto starch have been published.[8-12] Among the variety of monomers investigated, AN is highly reactive, and reaction products containing about 60% (PAN) chains can be obtained. The high reactivity of AN, and the value of saponified St-g-PAN as an absorbent, led to the choice of AN as the monomer for the present study. St-g-PAN copolymers were prepared by a typical batch process as well as by reactive extrusion.

In a typical batch process, starch at 5% concentration in water is first gelatinized at 95°C, with stirring for 1 h, and then cooled is to room temperature. Subsequently, graft polymerization is carried out for approximately 2 h at 25–30°C with 1 mol of CAN initiator per 100 anhydroglucose units AGU.[11] In the present reactive extrusion process, concentration of starch in water was 35% and maximum reaction temperature investigated was about 80°C. Average residence times in the extruder were about 2–3 min, and the time required to complete the first wash of the extrudate was about 4–5 min, resulting in a reaction time of about 7 min. In the preparation of St–g–PAN by a typical batch process, at least 30 min are required for the graft polymerization to proceed to equilibrium.[13,14] However, at least 2 h have been typically used. In the present work, the efficiency of converting the monomer to synthetic polymer, add-on, grafting frequency, and other characteristics of the products prepared by both processes were compared. Water absorbency of the saponified grafts was also determined.[15]

EXPERIMENTAL

Materials

Cornstarch (Pure Food Corn Starch Powdered, A. E. Staley Mfg. Co., code 3-832), acrylonitrile AN (99+%, Aldrich Chemical Company Inc.), and ceric ammonium nitrate (CAN) (99+%, Aldrich Chemical Company Inc.) were used as received.
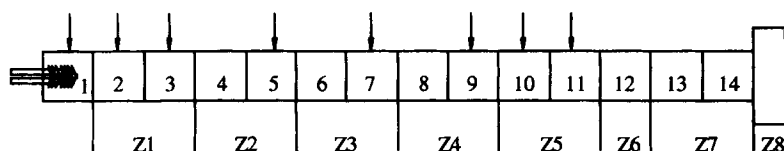
Batch Graft Polymerization

Batch polymerizations were carried out essentially by the procedure of Fanta et al.,[15] using various amounts of AN. Starch (20 g, dry basis) was stirred in 400 mL of water and was gelatinized at 95°C (45 min at 95°C, 15 min to reach 95°C) with continuous nitrogen purging in a 2-L resin kettle. The gelatinized starch was cooled to 25°C with continuous nitrogen purging above the surface of the gelatinized starch.

Then AN and an aqueous solution of CAN/HNO₃ were sequentially admixed. AN levels of addition were 30 g (Batch 1), 15 g (Batch 2), 11 g (Batch 3), and 8 g (Batch 4). The mixture was stirred for 5 min before adding the CAN solution (0.676 g CAN in 6 mL of 1N HNO₃). The reaction was carried out for 2 h at about 35°C with nitrogen purging. After 2 h, the reaction mixture was neutralized with aqueous sodium hydroxide. The product was precipitated in methanol (about 800 mL), washed with methanol twice, and dried under vacuum at 60°C.

Graft Polymerization via Reactive Extrusion

A ZSK-30 twin screw extruder with corotating, intermeshing screws of 30.7 mm in diameter (Werner & Pfleiderer Corp., Ramsey, NJ), was used as the continuous reactor for graft polymerization. Screw speed was 400 rpm and the screw configuration has been reported.[16] A diagram of the extruder barrel showing possible points of addition for starch, water, and chemicals is shown in Figure 1. Starch powder was fed from a volumetric feeder into barrel section number 1 (BS 1) at the rate of 42 and 84 g/min (38 and 76 g/min, dry basis). AN was pumped into BS 3 at rates to obtain AN/starch weight ratios of 0.5 and 1.0 (dry starch basis). CAN solution (244 and 488 g CAN in a mixture of 180 mL 1N HNO₃ and 12,000 mL H₂O) was pumped into BS 5 at the rates shown in Table I to give 35% starch in water concentration. The weight ratio of 1N HNO₃/H₂O in the CAN solution was 1.5. Fresh CAN solutions were prepared for each run. Addition levels of CAN were 3.5 and 7.0% on a starch weight basis. The percent total solids in the extruder was between 25 and 50%, depending on the percentage of monomer converted to polymer. Zone temperature settings of the extruder barrel were 50–70°C.

The extrudates were collected for 1 min in a Waring Blendor, were immediately dispersed in minimal amounts of water to obtain a paste, and then were diluted gradually, but quickly, with methanol to precipitate the products as small particles. The precipitates were filtered, and washed twice in

Figure 1 Schematic of the twin screw extruder. Numbers inside the square sections denote barrel section numbers and Z1–Z8 denote the eight separate heating/cooling zones.

Table I   Graft Polymerization Processing Conditions

Extruder (EXT) Run No.	Starch Feed Rate (g/min)	CAN[a] Solution Feed		Barrel Zone Temperature (°C)	Maximum Material Temperature (°C)
		(BS No.)[b]	(mL/min)		
1	38	5	66	70	81
2	38	5	66	50	53
3	38	5	66	50	59
4	76	3	132	70	80

[a] CAN = Ceric ammonium nitrate (3.5% starch weight basis for EXT 1, 2, 4, and 7.0% for EXT 3).
[b] BS = Barrel section.

methanol before drying the materials at 60°C under vacuum.

N,N–Dimethylformamide (DMF) Extraction

Three DMF washes (21 h, 3 h, and 2 h) were carried out to extract the homopolymer from the St–*g*–PAN copolymers. Two 2.5-g portions of the products were each added to 200 mL of DMF in 250-mL centrifuge bottles and were stirred continuously with a magnetic bar at room temperature. Each mixture was centrifuged. The supernatant was decanted and concentrated by a rotovap. DMF solubles in the concentrate were precipitated by addition of methanol. The precipitate was filtered, washed with methanol, and dried. The DMF insolubles were washed with water and then dried at 60°C under vacuum.

Acid Hydrolysis of the DMF Insoluble Fraction

Two grams of DMF insolubles, prepared as described above, were refluxed in 150 mL 0.5N HCl for 1.5 h. The insoluble portion was filtered, washed with water, and dried under vacuum at 60°C. Twelve mg of each DMF insoluble fraction in 10 mL DMF was heated for 2 h at 100°C, cooled, and filtered through a 0.45 μm filter. The number average molecular weight of this sample was determined by gel permeation chromatography, using polystyrene standards and two Ultrastyragel columns of pore size 10^5 and 10^6 Å. DMF was pumped at 0.5 mL/min and the columns were kept at 70°C.

Saponification of the Graft Polymerization Product

Four grams of the original methanol-washed extrudate and 36 mL of 1N NaOH solution were mixed in an Erlenmeyer flask and were heated in a steam

bath for 10 min. The saponification was then continued for 80 min in an air circulated oven, set at 100°C. In a Waring Blendor, the saponified product was precipitated in methanol, filtered, and was further washed by stirring the precipitate in methanol overnight to obtain small particles. The particles were filtered and dried under vacuum at 60°C.

Determination of Water Absorbency

About 25 mg of the original St–*g*–PAN product was precisely weighed and immersed in distilled water for 30 min. After 30 min, the swollen product was filtered on a Whatman #54 filter paper for 30 min without use of vacuum or other force. The wet material, drained free of excess water, was removed from the filter paper and was weighed. The weight of wet sample was divided by the dry weight to obtain the absorbency values.

Kjeldahl Analysis

The nitrogen contents of the original, methanol-washed extrudate, its fractions (obtained as described above), and the saponification products were determined by Kjeldahl analysis. Percent add-on, percent of monomer converted to polymer, percent polyacrylamide as homopolymer, and ratio of carboxamide/carboxylate groups of the saponified product were calculated from their nitrogen content.

RESULTS AND DISCUSSION

Add-on and Monomer Conversion

The reaction path for ceric ion-initiated graft polymerization of AN onto starch has been previously reported.[8] Presumably, starch-free radicals are formed at carbons 2 or 3, which react with AN to initiate graft polymerization. The presence of free

Table II   Add-on for St–*g*–PAN Copolymers from Extrusion vs. Batch Processes

| Batch (B) and Extruder (EXT) Run No.	AN/Starch Weight Ratio[a]	CAN (%)[b]	Reaction Temperature Range (°C)	Monomer Converted to Polymer (%)	Add-on (%)[c]
B 1	1.50	3.5	25–30	63	49
B 2	0.75	3.5	25–30	81	38
B 3	0.55	3.5	25–30	54	23
B 4	0.40	3.5	25–30	52	17
EXT 1	1.00	3.5	70–81	74	42
EXT 2	1.00	3.5	50–53	55	35
EXT 3	1.00	7.0	50–53	78	44
EXT 4	0.50	3.5	70–80	63	27

[a] AN = Acrylonitrile.
[b] Ceric ammonium nitrate, % dry starch weight basis.
[c] Wt % of polyacrylonitrile (PAN) of St–*g*–PAN product including homopolymer.

radicals has been confirmed by election spin resonance. Levels of add-on (wt % of total synthetic polymer) of the St–*g*–PAN copolymers were 27–44% for the extrusion process and 17–49% for the batch process, depending upon the various conditions that were used (Table II and Fig. 2). Add-on increased substantially as the AN/starch ratio was increased, in agreement with the batch reaction studies by others.[14] Previous batch reaction studies have also shown that the initial formation rates of PAN chains increased as temperatures were increased from 10 to 35°C.[11,13] Autoacceleration of radical polymerization as a possible mechanism for chain termination has also been previously discussed.[13] In the present work, the highest temperatures of material in the

extruder were 53°C and 81°C for the barrel temperature settings of 50°C and 70°C, respectively. In spite of the short reaction period in the extruder (2–3 min), the add-on levels were close to those obtained in the 2-h batch process (Table II). Both temperature (EXT 1 vs. EXT 2) and CAN addition level (EXT 2 vs. EXT 3) had a substantial effect on add-on. Presumably, the greater extent to which starch swelled at the higher temperature (70–81 vs. 50–53°C) contributed to the higher add-on that was obtained in EXT 1 (42%), as compared with EXT 2 (35%). Since the gelatinization temperature of the unmodified starch begins at about 65°C, the starch component of these extrudates may not have been fully gelatinized at 70–81°C within residence
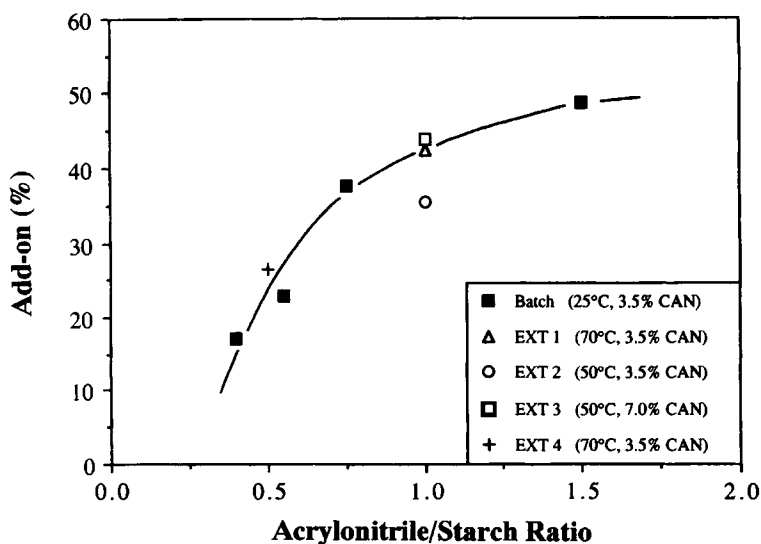
Figure 2   Effect of the acrylonitrile/starch weight ratio on add-on. Maximum temperatures of material in the extruder were 53°C and 81°C for 50°C and 70°C settings.
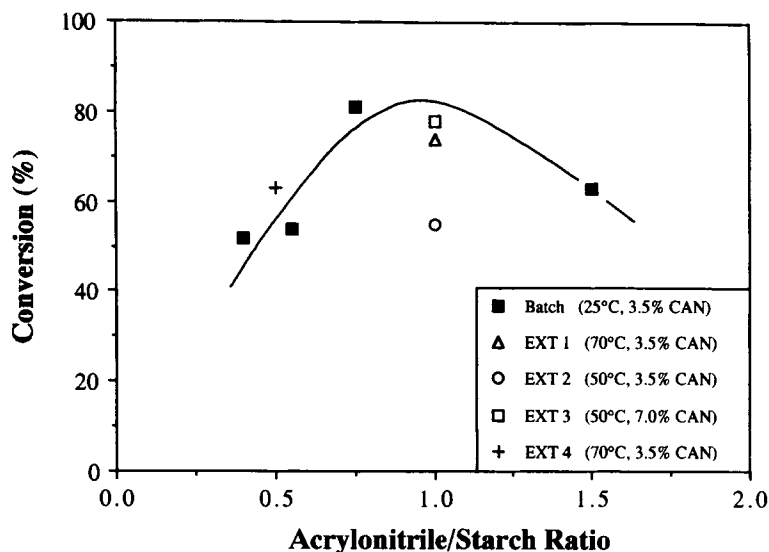
Figure 3 Effect of acrylonitrile/starch weight ratio on percentage of AN converted to polymer.

times of 2–3 min. The starch was only partially swollen at 50–53°C.

The effect of starch concentration on add-on has been previously observed in batch preparations of St-g-PAN.[17] For example, at an AGU/ceric ion molar ratio of 1000:1, an add-on of 33% was reported for graft polymerization of AN onto starch at 9.1% starch concentration, compared to 8% add-on at 4.8% starch concentration, using the same AN/starch ratio. Indeed, the higher concentrations of starch, AN, and CAN, as well as the higher temperatures in the reactive extrusion process, were all beneficial in rapidly obtaining high add-on within the 7-min reaction period. The higher add-on, obtained at 7.0% vs. 3.5% CAN, is contrary to results

reported for batch graft polymerizations.[17] Apparently the CAN concentrations at the levels investigated were much more important for short reaction periods (e.g., 3–7 min vs. 1–2 h), in which the initial reaction rate is highly dependent upon CAN concentration. The effect of inhibitor in the AN (35–45 ppm hydroquinone monomethyl ether) was not studied in either extrusion or batch reactions.

Figure 3 shows that the percentages of monomer converted to polymer were similar for the extrusion and batch processes for similar AN/starch weight ratios, except for EXT 2. Apparently, the CAN addition level must be 7% at 50°C or the temperature must be 70°C at 3.5% CAN in the extruder process, as opposed to 3.5% CAN at 50°C.

Table III Compositional Characteristics of St-g-PAN Fractions from DMF Extraction

Run No.	Add-on (%)	DMF[a] Insolubles (Wt %)	DMF[a] Insolubles (PAN %)[b]	DMF Solubles (Wt %)	DMF Solubles (PAN %)	Unaccounted Wt. Loss (%)[c]	Acid Hydrolysis of DMF Insolubles (Wt %)	Acid Hydrolysis of DMF Insolubles (PAN %)
B 1	49	83	45	14	70	3	48	93
B 2	38	90	35	7	70	3	36	89
B 3	23	94	23	4	57	2	24	87
B 4	17	96	16	2	58	2	18	89
EXT 1	42	81	43	9	34	10	48	92
EXT 2	35	83	36	10	44	7	41	90
EXT 3	44	85	45	10	49	5	46	96

[a] DMF = N,N-dimethylformamide.
[b] PAN = Polyacrylonitrile.
[c] Primarily material that did not precipitate in methanol (see Experimental Section).

DMF Extraction and Acid Hydrolysis

St-*g*-PAN copolymers were treated with DMF, and the DMF insoluble material was treated with acid as described in the Experimental section. Data are shown in Table III. Copolymers that were prepared by the reactive extrusion process were 81–85% insoluble in DMF, as compared with 83–90% for copolymers prepared by the batch process. Presumably, the DMF soluble material contained homopolymer and small proportions of low molecular weight (LMW) copolymer. Starch of the DMF solubles may exist as LMW chains alone and/or as LMW backbones of the St-*g*-PAN. However, some of the LMW material may have been removed when the crude extrudates were first washed.

Unaccounted weight loss data in Table III represents primarily the percentage of material that did not precipitate by addition of methanol to the DMF soluble material. The precipitate was collected, washed, dried, and weighed. The weight of the DMF insoluble material, plus the weight of the precipitate, was 2–3% less than the weight of the copolymers not treated with DMF for the batch process and 5–10% less for the extrusion process. The combined PAN content of the DMF soluble material (precipitated in methanol) and of the DMF insoluble material represents 90% of the add-on for the EXT 1 product and 95% or more for the other products (EXT 2, 3, and B 1–4). Nitrogen-containing DMF solubles that did not precipitate in methanol were presumably low MW materials.

The DMF insoluble material was treated with acid to remove the starch backbone as water-soluble carbohydrates. The water insoluble hydrolyzate was filtered, washed, dried, and solubilized in DMF for MW analysis, as discussed later. Table III shows that 87–96% of the water-insoluble hydrolyzate was PAN, based on nitrogen analysis.

Homopolymer and Grafting Frequency

Data in Table IV show PAN content of the DMF insolubles and of the DMF solubles (expressed as % add-on) and show the % PAN as homopolymer (ungrafted PAN). The % homopolymer of the St-*g*-PAN copolymers was calculated from the nitrogen content of the DMF solubles. These values are estimates, because some of the occluded homopolymer was probably not removed by DMF extraction, and some of the PAN in the DMF solubles was probably LMW copolymers. Based on these estimates, the percentages of homopolymer were 7–13% of the total PAN content, except for the B 1 product with 2% homopolymer. This high grafting efficiency is not unusual. For example, previous work showed that when starch (21.9 g) was heated in water (507 mL), before reaction with AN (31 g) and CAN (0.41 g) at 25°C, only 8% of the PAN was homopolymer.[8]

Table IV shows that grafting frequencies (calculated from the PAN content of DMF insolubles) were substantially higher for the St-*g*-PAN from reactive extrusion than for the batch processes. This result could be expected for starch that was not fully gelatinized.[9] In batch processes, grafting frequency was found to be more frequent at high starch dilution (0.37% vs. 4.9% starch concentration), but less frequent as temperature was increased from 30°C to 50°C.[8,18,19]

Molecular Weight (MW) and MW Distribution (MWD)

Table V shows the number average MW and MWD of the DMF insoluble material after acid hydrolysis treatment to remove the starch. The MW values were somewhat lower and had a slightly broader MWD than those from the batch process. The lower

Table IV   Distribution of Polyacrylonitrile (PAN) in St–*g*–PAN Copolymers

Run No.	% Add-on[a]		% of PAN		Grafting Frequency (PAN Grafts/10^5 AGU)[c]
	DMF Insolubles	DMF Solubles	Grafted	Ungrafted[b]	
B 1	37	10	76	20	4.76
B 2	31	5	76	13	4.35
B 3	21	2	84	10	1.35
B 4	15	1	88	7	1.27
EXT 1	35	3	84	7	7.69
EXT 2	30	4	85	13	9.09
EXT 3	38	5	85	11	9.09

[a] See Table II, footnote c.
[b] Homopolymer.
[c] Polyacrylonitrile chains per 100,000 anhydroglucose units.

Table V   Number Average Molecular Weight and Molecular Weight Distribution of St–*g*–PAN Copolymer Products

| Run No. | DMF Solubles | | Acid Hydrolysis Product of DMF Insolubles | |
	$(M_n \times 10^6)$	$(M_w/M_n)^a$	$(M_n \times 10^6)$	(M_w/M_n)
B 1	1.4	5.0	2.8	4.1
B 2	1.5	6.3	2.0	4.8
B 3	4.1	3.7	3.5	4.3
B 4	6.7	2.8	2.4	5.8
EXT 1	2.4	8.8	1.6	5.3
EXT 2	2.2	9.1	1.0	4.9
EXT 3	1.9	7.4	1.5	5.6

[a] M_n = Number average mol wt. M_w/M_n = Mol wt distribution (MWD).

MW values may be because starch was not fully gelatinized during reaction and because some starch hydrolysis occurred in the extruder. With respect to gelatinization, MW differences were not as great as those between St–*g*–PAN from granular and gelatinized starch in batch reaction.[8,18,19] Autoacceleration of the starch radical has been suggested as a possible explanation for the fact that the MW values of St–*g*–PAN is higher when prepared from gelatinized rather than granular starch.[13] Autoacceleration is a result of diffusion-controlled termination, which is influenced by the viscosity of the reaction mass. Even though temperatures for EXT 2 and EXT 3 were less than is required for full gelatinization of starch, the high viscosity of the reaction mass in the extruder, due to high solids concentration, may have increased autoacceleration. Such an effect has been reported with batch products at lower concentrations.[8,18,19] In those reports, MW values of St–*g*–PAN chains were lower at high dilution (0.37% starch in water) than at a more typical batch starch

concentration (4.4%). Because the grafting reaction media was highly acidic and temperatures were higher than normally used in batch work, starch may have been hydrolyzed to some extent. However, the higher temperatures may have increased MW of the PAN chains.[11,16]

Saponification of St–*g*–PAN

Saponification of St–*g*–PAN with NaOH or KOH produces a highly water-absorbent material.[20] The nitrile groups undergo hydrolysis to carboxamide and carboxylate groups. Complete hydrolysis to the carboxylate does not occur under conditions normally used.[8] Ratios of carboxamide/carboxylate group ranged from about 0.2 to 0.3 for the saponified extrusion and batch products with high add-on. Water absorbency of the saponified St–*g*–PAN products are shown in Table VI. Since nitrile absorption was not observed in the infrared spectra of the saponified products, it was assumed that essen-

Table VI   Water Absorbency of Saponified St–*g*–PAN Copolymers

| Run No. | Unsaponified St–*g*–PAN | | | Saponified St–*g*–PAN | |
	ANU/AGU[A] (mol ratio)	Nitrogen Content (%)	AAmU[b]/AGU (mol ratio)	Carboxamide/Carboxylate Ratio	Water Absorbency (g H_2O/g Sample)
B 1	2.9	3.6	0.52	0.22	610
B 2	1.9	2.9	0.40	0.26	410
B 3	0.9	2.0	0.26	0.40	380
B 4	0.6	1.5	0.19	0.45	210
EXT 1	2.3	3.4	0.47	0.26	290
EXT 2	1.7	3.1	0.42	0.33	270
EXT 3	2.4	3.7	0.52	0.28	32

[a] Acrylonitrile repeating units/anhydroglucose unit ratio.
[b] Acrylamide repeating unit.

tially all product nitrogen was from the acrylamide repeating units (AAmU). Although water absorbency of the saponified extrusion products was less than that of the saponified batch products with similar add-on, absorbencies of about 300 g H_2O/g polymer appeared to have been sufficient for many applications, based on our water-absorbency test of some saponified St-g-PAN products that are commercially available.

CONCLUSIONS

Starch graft polyacrylonitrile (St-g-PAN) copolymers were prepared by a continuous reactive extrusion process. For comparison, St-g-PAN products were prepared by a typical batch process. These products were characterized and evaluated for water absorbency after saponification with sodium hydroxide. This study shows that the extrusion process was a rapid and effective means of graft polymerizing high levels of acrylonitrile (AN) onto unmodified cornstarch within a total reaction period of about 7 min. For example, with 3.5% ceric ammonium nitrate (dry starch weight basis) as the initiator and an AN/starch weight ratio of 1.0, add-on was 42%, as compared with 38–49% for a typical 2-h batch reaction (0.75–1.5 AN/starch weight ratios). The effect of reaction variables on molecular weight (MW), MW distribution, grafting frequency, and percentages of grafted and ungrafted PAN (homopolymer) in the products was discussed. Water absorbency of the saponified copolymers was less for the copolymers prepared by extrusion than for those prepared by batch procedures. However, many reaction variables, which could affect water absorbency of these extrusion products, still need to be studied.

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