

Studies on the Grafting of Acryloylated Potato Starch with Styrene

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Received 19 August 2004; accepted 18 October 2004

DOI 10.1002/app.21464

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An investigation of graft polymerization to determine the potential of a starch-bonded acryloyl group as a suitable coupling agent with vinyl monomers was carried out. In this case, potassium persulfate was used as a free-radical initiator using water as the reaction solvent for further graft polymerization. This work revealed the ability of water as a reaction medium; perhydroxyl and hydroxyl radicals were easily formed from persulfate to produce free radicals to activate the styrene monomer towards grafting

with acryloylated potato starch. The graft copolymers were characterized by FT-IR spectroscopy and further confirmed using saponification. The analysis results showed the grafted potato starch with the styryl chain afforded protection to the ester bond, which resisted the alkaline hydrolysis. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 452–459, 2005

Key words: potato starch; grafting; polymerization

INTRODUCTION

One approach to the preparation of chemically bonded natural-synthetic copolymers is through graft polymerization. Grafting has been utilized as an important technique for modifying the chemical and physical properties of a number of polymers. Some of the graft copolymers with high commercial utility are: (1) acrylonitrile-butadiene-styrene (ABS) (a graft copolymer obtained by grafting polyacrylonitrile and polystyrene onto polybutadiene); (2) alkali-treated cellulose-graft-polyacrylonitrile and starch-graft-polyacrylonitrile, which are used as superabsorbents in diapers, for example, sanitary napkins; and (3) high-impact polystyrene (i.e., polystyrene-graft-polystyrene) copolymer.^{1,2}

Athawale and Lele³ have reported that chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature. Grafting of vinyl monomers onto various natural polymers, such as cellulose, cotton, wool, jute, and gelatin, has been accomplished by using a range of free radical initiators, like azoisobutyronitrile (AIBN),^{4,5} benzoyl peroxide, and manganic pyrophosphate,⁶ or redox systems like Fenton's reagent.⁷ However, such grafting reactions were performed essentially on heterogeneous systems.⁸ This

can result in the production of nonhomogeneous products and in poor reproducibility of the syntheses.⁹

This article describes efforts to find a suitable reagent that, when reacted with potato starch, would allow possible further graft polymerization with vinyl monomers under homogeneous conditions. This was expected to assure important advantages, such as a better control of the degree of substitution, a more uniform distribution of substituents along the starch chain, and a higher conversion yield. For these reasons, acryloyl chloride was selected as a reagent for this reaction, which has been the subject of a previous investigation with cellulose.⁸ The unsaturated acyl chloride contains the important C=C double bond, which was considered to have potential for the grafting reaction with a vinyl monomer.¹⁰

To obtain the homogeneous synthesis of starch-styrene copolymers, a two-step process was employed. Firstly, starch was dissolved in DMA/LiCl solution by the water solvent exchange method;¹¹ then starch was treated with a suitable amount of acryloyl chloride, to obtain a starch derivative characterized by the presence of some pendant double bonds. Subsequently, styrene was added and grafted onto the unsaturated groups by free radical copolymerization using a suitable initiator. While it is necessary to know that the reaction of acryloyl chloride with starch indeed occurs, it is also possible that crosslinking may occur within the starch structure, mediated via the double bonds of the attached groups. To confirm the reaction of acryloyl chloride with starch, FT-IR and ¹³C-NMR analysis were employed. The method used in attempts to undertake the successful graft polymerization of

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TABLE I
Reaction Conditions for Acryloylated Potato Starch

Reaction no.	Potato starch (mol)	Acryloyl chloride (mol)	Pyridine (mol)
1	1	0.2	0.2
2	1	0.5	0.5
3	1	1.0	1.0
4	1	3.0	3.0

Reaction time: 30 min at 60 °C.

vinyl monomers onto the modified starch is reported. A comprehensive study of the grafting reaction was investigated to find optimum reaction conditions, and to reveal changes in the chemical physical properties of starch that arose from the grafting reaction.

EXPERIMENTAL

Materials

Starch from potatoes containing 8–10% of moisture was obtained from Fluka. Acryloyl chloride (ACOCl) having purity of 96% was stored in the refrigerator and was brought to room temperature before use. Styrene was passed through a neutral alumina column to remove the polymerization inhibitor (hydroquinone) before use.^{12,13} Other chemicals used were of analytical or reagent grade.

Synthesis of acryloylated starch

The starch-styrene copolymer was synthesized by following two steps: (1) synthesis of acryloylated starch (AS); and (2) grafting of styrene onto AS.

The first step involves the water-solvent exchange method, which has been described in a previous paper.¹¹ The method is essentially as follows. Starch (6.0 g) was dissolved in water (50 mL) at 80°C for 1 h, then *N,N*-dimethylacetamide (DMA, 3 × 50 mL) was added to remove water by distillation. Lithium chloride (LiCl, 0.3 g) was added to the solution. After cooling to 60°C, a suitable amount of pyridine and acryloyl chloride (ACOCl) were added to the reaction medium, to prepare products with different DS-values. The reaction conditions are recorded in Table I. Following acryloylation, the product was precipitated with acetone and purified by dialysis in water using Visking dialysis tubing (size 12 Inf Dia 1 3/4' MWCO-12–14,000 Daltons). It was evaporated under a reduced pressure at 60°C, and further dried at 40°C overnight.

Grafting of styrene onto acryloylated starch

The method used potassium persulfate as an initiator in an aqueous solution of acryloylated starch to

achieve the grafting reaction. Details are described below.

The dried AS (0.5 g) was weighed into a 100 mL round bottom flask. Water (50 mL) was added and when the acryloylated starch was completely dissolved in water, required amounts of potassium persulfate and styrene were added to the flask with stirring. The flask and contents were placed in an oil bath set at either 60°C, 80°C, or 100°C and different reaction times. Stirring of reagents was maintained throughout the reaction.

Upon completion of the reaction, the flask contents were poured into acetone (150 mL) for precipitation, then filtered on a sintered glass crucible, washed with acetone, and dried in air. The precipitate was treated with *N,N*-dimethylformamide (DMF), toluene, or dioxane to dissolve any polystyrene homopolymer present, under reflux conditions for 2h. The mass of the residue (presumed to be starch-g-polystyrene copolymer) was recovered. From the increase of its weight with respect to both starch and acryloylated starch, the amount of grafted polystyrene was calculated. Thus, the grafting ratio (%) was calculated according to the equation:

$$\text{GR (\%)} = \frac{W_2 - W_1}{W_1} \times 100\%$$

W1 = Sample weight before grafting,

W2 = Sample weight after grafting.

Saponification reaction of grafted acryloylated starch

Further confirmation of the graft copolymer can be obtained indirectly by the acid or alkaline hydrolysis technique, in conjunction with infrared spectroscopy.² Grafted and ungrafted acryloylated starches (1.0 g) were treated with NaOH (2M, 20 mL) at 80°C for 6 h. The mixture was cooled to room temperature and neutralized with acetic acid to pH 6.5–7. The grafted product, which was filtered and washed with water, then was oven-dried overnight (100°C), and FT-IR spectroscopic analysis was performed. For the ungrafted product after hydrolysis, the liquid was placed in a separating funnel, and diethylether (3 × 100 mL) was added to the separating funnel. The two layers were separated, the ether layer was collected, and the solvent was removed under reduced pressure. The aqueous solution was poured in 3 vol. methanol (MeOH) for precipitation; the precipitate was filtered and washed with MeOH, and dried overnight (50°C). The residue was further purified using Visking dialysis tubing in water to remove the salts from neutralization. The pure, dried residue was subjected to analysis by FT-IR spectroscopy.

TABLE II
Calculated DS-Values Based on Elemental Analysis, and Yield of Acryloyl Starch

Reaction no. ^a	Sample code	Actual elemental analysis data		Calculated DS	Yield (%)
		C (%)	H (%)		
1	AS0.2	45.8	5.9	0.2	95.5
2	AS0.5	47.6	5.8	0.5	93.1
3	AS0.8	49.0	5.6	0.8	90.3
4	AS2.0	53.1	5.0	2.0	81.5

^a Corresponding to the reaction no. in Table I.

Note: AS is abbreviation of acryloylated potato starch; the calculated DS-value is indicated by a number at the end.

Measurements

The infrared spectra of grafted and ungrafted acryloylated starch were measured as KBr pellets on a Magna-IR 750 Series II Spectrometer in the frequency range of 4000–600 cm⁻¹.

The ¹³C-NMR spectra of the acryloylated starch were collected on a Bruker 250 AC spectrometer, operating in the Fourier transform (FT) mode at 62.9 MHz using 3000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, and 0.85 s acquisition time were used. Before analysis, the samples were ground using a microdismembrator (2000 rpm for 3 min), and dried at 50°C in an oven overnight. For pure starch, the spectrum was collected in deuterated dimethylsulfoxide (DMSO-d₆) solution. For acryloylated starch, the spectrum was measured in deuterium oxide (D₂O). 50 mg of sample was dissolved in 1 mL in all cases.

RESULTS AND DISCUSSION

Characterization of acryloylated starch

The ultimate aim of using the chemical modification in this study was to create reaction sites on the starch for further possible graft polymerization with vinyl monomers. For this reason, it was necessary to know that the reaction of starch with acryloyl chloride had occurred. It was also possible that crosslinking may have occurred between the starch chains, mediated via the double bonds of the attached acryloyl groups. This would affect the properties of the modified starch for further grafting reactions. In general, three criteria have been used as evidence that the chemical modification has taken place. These are: (1) Elemental analysis; (2) Infrared spectroscopic studies; and (3) ¹³C-NMR spectra.

Elemental analysis

Evidence of the reaction of acryloyl chloride with starch was obtained by elemental analysis. Increase in the proportion of carbon and hydrogen in the product were taken to indicate introduction of the acryloyl

group. Certain assumptions are required for this to be meaningful. The product is assumed to consist solely of acryloylated starch. All by-products must be removed entirely. Degree of substitution (DS) and yield of samples were calculated. The measured and calculated results are shown in Table II.

FT-IR spectra

Evidence of the reaction of potato starch with acryloyl chloride was obtained from FT-IR spectra of the isolated products. The existence of a carbonyl absorption band can be assigned to the formation of an ester bond. Figure 1 shows the FT-IR spectra of acryloylated starches with different DS-values. Spectrum (a) represents the lowest DS = 0.2 of acryloylated starch, while spectrum (c) represents DS = 0.8. The strong O-H stretching band at 3400 cm⁻¹ decreases in intensity from spectrum (a) to (c) after the acryloylation reaction as the number of hydroxyl groups present diminishes. Also, it can be seen from Figure 1, two major changes were observed in acryloylated starch with the presence of strong carbonyl peaks C=O in the region of 1733 cm⁻¹ and the carbon double bond C=C in the region of 1635 cm⁻¹, respectively, indicating reaction. Evidence for the absence of any contaminating acryloyl chloride is gained by the lack of any absorbance in the region 1770 cm⁻¹, associated with the carbonyl stretch of the acryloylating reagent. The FT-IR spectra indicate that the esterification between acryloyl chloride and starch had occurred, and that after such acryloylation, the carbon double bond of the acryloyl group was unreacted.

¹³C-NMR spectra

In addition to FT-IR studies, potato starch and acryloylated starch were analyzed by ¹³C-NMR spectroscopy, and the spectra are shown in Figure 2. In the spectrum of unmodified potato starch, spectrum (a), C-1, C-4, and C-6 have chemical shifts at 99.5, 78.2, and 59.9 ppm, respectively, while C-2, C-3, and C-5 have chemical shifts in the region 71.5–72.7 ppm. The ¹³C-

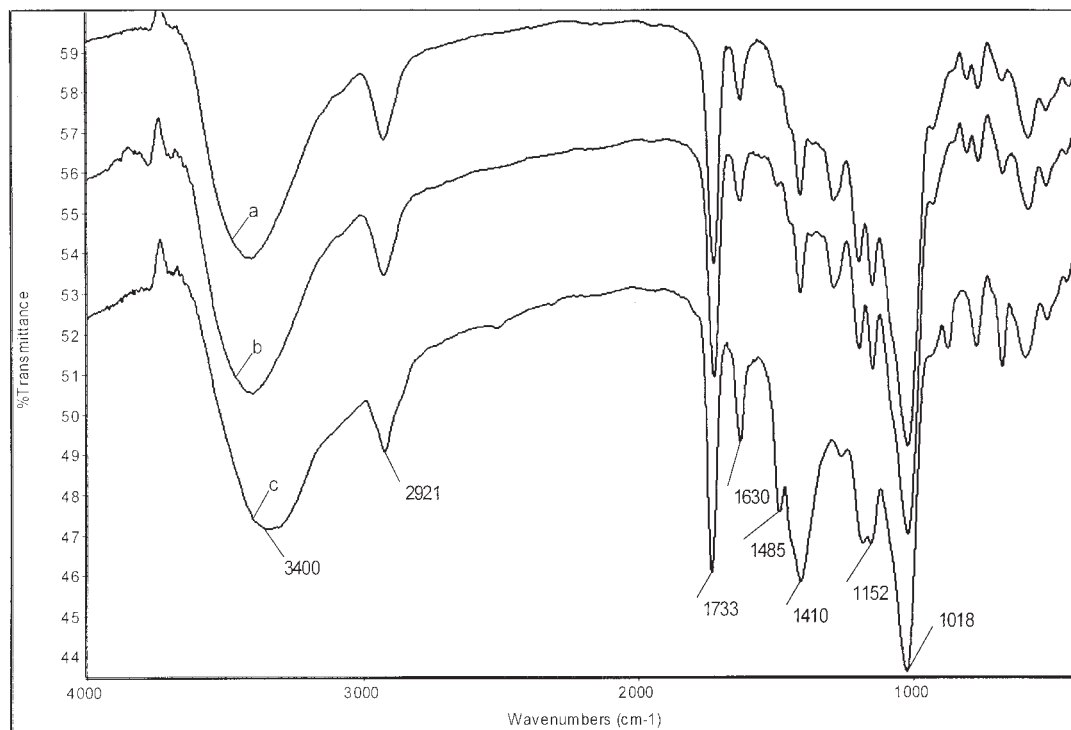


Figure 1 FT-IR spectra of acryloylated starches of different DS-values: (a) DS, 0.2; (b) DS, 0.5; and (c) DS, 0.8.

NMR spectrum of acryloylated starch (b) revealed a new peak at 170.2, due to the carbonyl group (C=O), and peaks at 147.5 and 130.9 ppm due to the carbon

double bond (C=C). They are assigned as C-7, C-8, and C-9 on the acryloyl moiety, respectively.¹⁰ From the NMR spectra, it can be seen that after acryloylation, a carbon double bond (C=C) was observed, and this group was potentially available for further reaction.

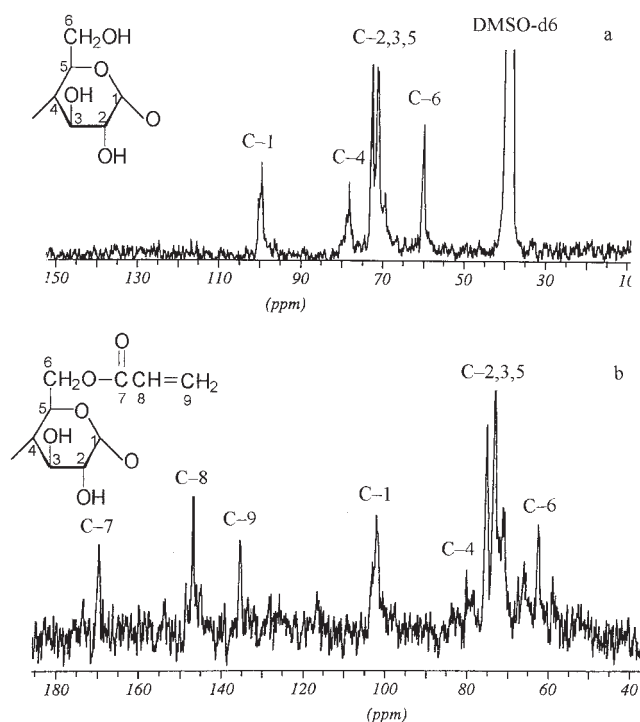


Figure 2 ¹³C-NMR spectra of potato starch (a) and acryloylated starch (b, DS = 0.8).

Grafting studies

Acryloylation of potato starch resulted in the presence of a carbon-carbon double bond in the material, which was to be used for further grafting reaction with vinyl monomers. Prior to the grafting reactions, a body of work was carried out to find the most appropriate conditions for reaction of acryloylated starch with styrene. For this purpose, the grafting reaction was performed under a variety of conditions. Factors studied include initiator concentration, monomer concentration, reaction time, and temperature, as well as the acryloylated starch concentration.

Samples 1-3 in Table III show the effect of the amount of acryloylated starch on the extent of polymerization expressed as % acryloylated starch grafted with styrene. It is clearly seen that as the amount of acryloylated starch increases from 0.5 to 1.0 g in water (50 mL), the GR (%) decreased from 90 to 25%, respectively. The likely reason was that the higher concentration of acryloylated starch and high DS resulted in inter or intramolecular double bond crosslinking be-

TABLE III
Effect of Various Factors on Graft Ratio (%)

Sample no.	AS2.0 (g)	K ₂ S ₂ O ₈ (g)	Styrene (mL)	Temperature (°C)	Time (h)	GR (%)
1	0.5	0.3	12	80	2	90
2	0.8	0.3	12	80	2	43
3	1.0	0.3	12	80	2	25
4	0.5	0.1	12	80	2	62
5	0.5	0.2	12	80	2	88
6	0.5	0.2	12	60	2	8
7	0.5	0.2	12	100	2	69
8	0.5	0.2	12	80	4	112
9	0.5	0.2	12	80	6	120
10	0.5	0.2	9	80	4	94
11	0.5	0.2	6	80	4	53
12	0.5	0.2	3	80	4	48

Reaction conducted at DS = 2.0 acryloylated starch (0.5 g) in H₂O (50 mL).

tween starch chains, thus reducing the potential for grafting with styrene.

Samples 4, 5, and 1 show the effect of K₂S₂O₈ concentration on the grafting of styrene onto acryloylated starch. It is clear that there exists a critical concentration of K₂S₂O₈ from 0.1 g up to 0.3 g, as the GR (%) increased from 62 to 90%. This can be attributed to the increasing number of free radical sites on the acryloylated starch backbone at which the monomer can be grafted. However, addition of 0.3 g of K₂S₂O₈ only gave a slightly higher GR (%) than addition of 0.2 g of K₂S₂O₈, which resulted in a slightly improved GR (%).

Samples 5, 6, and 7 show the effect of reaction temperature on the extent of grafting. It was found that a grafting reaction temperature of 60°C only afforded a low GR (8%). However, a high GR (%) occurred at 80°C; when the temperature was raised to 100°C, the GR (%) decreased, which may be due to the high temperature favoring styrene homo-polymerization, or some alternatively acryloylated starch degra-

dation at high temperature. Therefore, 80°C was the optimum temperature for the grafting reaction.

Compare with samples 5, 8, and 9, which illustrate the effect of polymerization time on the grafting ratio. Prolongation of the reaction time increased grafting extent from 88 to 120%. Thus, 2 h reaction time resulted in 88% of GR. Evidently, the grafting reaction was rapidly completed under such reaction conditions. Extension of the reaction time to 6 h resulted in a grafting ratio increase of only 8%, a slightly higher GR than that achieved within 4 h.

Samples 10, 11, and 12 show the effect of styrene concentration on the grafting parameters. It is seen that the GR (%) increased significantly by increasing the styrene concentration within the range studied. When using a high concentration of styrene, a high proportion of polystyrene was grafted to the acryloylated starch. However, not all of the styrene was grafted, because non-grafted (homo-polymerized) polystyrene was also isolated from the reaction mixture.

TABLE IV
Effect of Various DS Acryloylated Starch and Styrene on GR (%)

Sample no.	AS (g)	K ₂ S ₂ O ₈ (g)	Styrene (mL)	Temperature (°C)	Time (h)	GR (%)
13	AS0.8	0.2	12	80	4	106
14	AS0.8	0.2	9	80	4	88
15	AS0.8	0.2	6	80	4	81
16	AS0.8	0.2	3	80	4	60
17	AS0.5	0.2	12	80	4	102
18	AS0.5	0.2	9	80	4	78
19	AS0.5	0.2	6	80	4	64
20	AS0.5	0.2	3	80	4	46
21	AS0.2	0.2	12	80	4	80
22	AS0.2	0.2	9	80	4	70
23	AS0.2	0.2	6	80	4	60
24	AS0.2	0.2	3	80	4	48

Reaction conducted at a 1% (w/w) aqueous acryloylated starch solution.

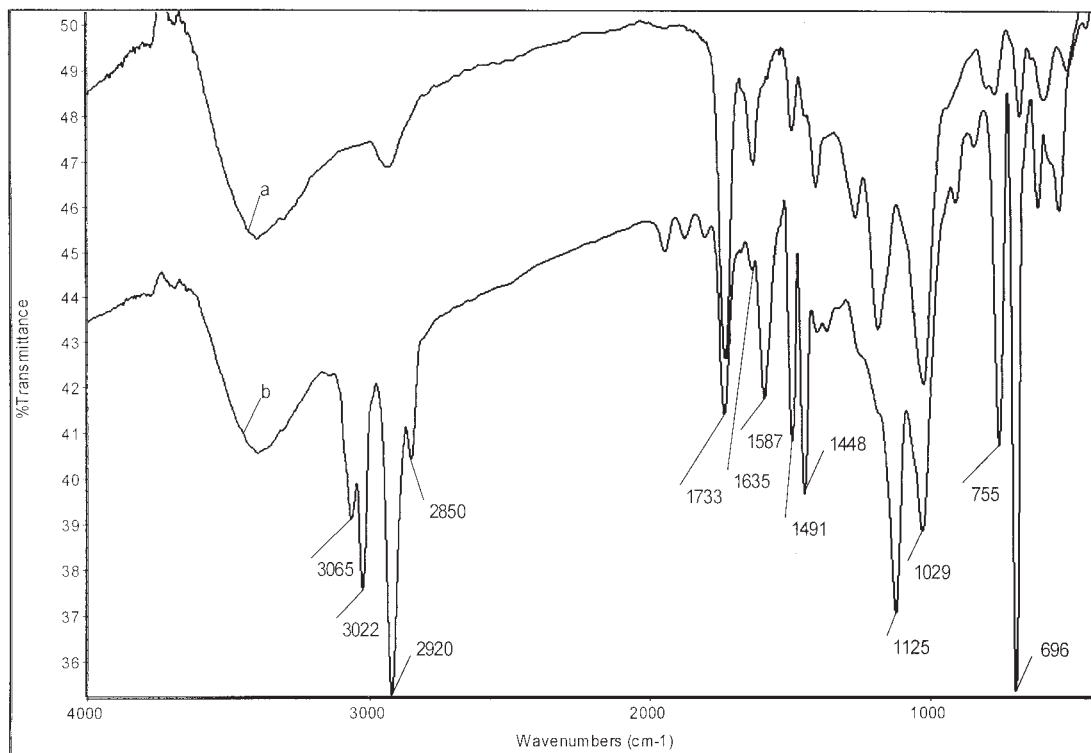


Figure 3 FT-IR spectra of acryloylated starch (a, DS = 2.0) and styrene-acryloylated starch copolymer (b).

Table IV lists three sets of experiments using different DS-value acryloylated starches (DS = 0.8, DS = 0.5, and DS = 0.2) with different quantities of monomer (12, 9, 6, and 3 mL), to prepare copolymers with grafting ratios from 46 to 106%. In general, under the same reaction conditions, highly (DS = 0.8) acryloylated starch yielded a high grafting extent (106%) with styrene, whereas the lower (DS = 0.2) acryloylated starch resulted in 80% grafting. This is evidently due to the presence of more grafting sites in the high DS acryloylated starch. This favors the grafting of larger amounts of monomer onto the acryloylated starch. The experiments also confirmed that GR (%) was related to styrene concentration, with a higher styrene concentration yielding higher GR (106%), and similarly, low styrene concentration giving lower GR (46%). The results corresponded to Table III (samples 8, 10, 11, and 12).

Evidence for grafting

FT-IR analysis

To determine that the grafting reaction had taken place with the acryloylated starch and styrene, the samples were subjected to analysis by FT-IR spectroscopy. FT-IR spectroscopy has been used extensively for the confirmation of graft copolymer formation.² The FT-IR spectra of acryloylated starch (DS = 2.0) is shown in Figure 3(a); the corresponding spectrum,

following styrene grafting, is shown in Figure 3(b). The most important features of the spectra are the carbonyl absorption occurring at 1733 cm^{-1} (which is due to the ester bond between the starch and the acryloyl moiety), and the weak absorption at 1635 cm^{-1} (due to the C=C bond).¹⁰ The presence of strong absorptions at 755 and 696 cm^{-1} is due to the phenyl group of styrene.^{14,15} The significant change in Figure 3(b) is that the C=C peak almost disappears after reaction with styrene. This confirms that the majority of the double bonds in the acryloylated starch are reactive towards free radically initiated graft polymerization under these conditions.

Saponification of grafted and ungrafted samples

This is an indirect method, but it is used to unambiguously prove that styrene was grafted onto acryloylated starch. Styrene-grafted and ungrafted acryloylated starch were treated with sodium hydroxide to hydrolyze the ester linkage between starch and the adduct. FT-IR spectroscopic analysis of the hydrolysis product showed that the saponified acryloylated starch no longer contained absorptions at 1733 cm^{-1} (C=O) nor 1635 cm^{-1} , indicating in Figure 4(a) that the acryloyl group had been removed by this treatment. In the case of the grafted material, the C=O absorption at 1733 cm^{-1} was still present after saponification, showing in Figure 4(b) that the acryloyl

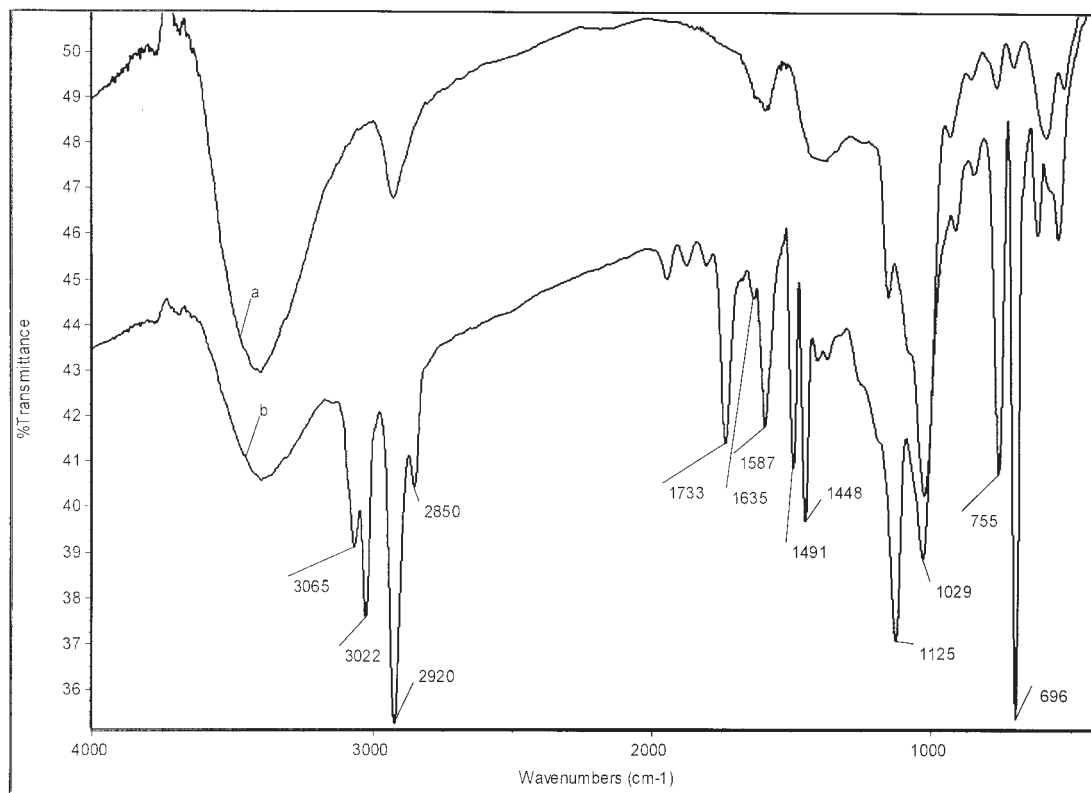


Figure 4 FT-IR spectra of ungrafted (a) and grafted (b) acryloylated starch after hot aqueous NaOH treatment.

group was not removed by such treatment. Furthermore, the absorptions due to styrene at 1587, 755, and 696 cm^{-1} remained. This suggests that grafting of the acryloyl group had occurred, and that as a result the attached styryl chain afforded protection to the attached ester. In other words, as styrene was grafted onto acryloylated starch, the ester bond resisted the alkaline hydrolysis. The ungrafted acryloyl group was, however, easily hydrolyzed. This result corresponded to that reported by Hill and Cetin¹⁵ for the hydrolysis of methacrylic anhydride reacted and styrene grafted wood flour.

Solubility

The starch graft copolymers were synthesized in two steps. Each reaction resulted in the modified starches having significantly different solubilities compared to the native starch. Interestingly, DMSO was a good solvent for potato starch. But the styrene-grafted acryloylated starch did not dissolve in either DMSO, tetrahydrofuran, pyridine, toluene, or chloroform. It partially dissolved in DMF, but that depended on the GR (%). Thus, the sample with high GR (%) was difficult to dissolve in DMF. Even on heating, it merely swelled, indicating the grafting nature of the modified starch. The poor solubility was probably due to chain combination of the growing graft molecules.

Another investigation showed that potato starch gelatinized in water at around 70°C , while the acryloylated starch was easily dissolved in water at room temperature. However, the graft copolymers did not gelatinize even after heating at 100°C , which further confirmed the grafting reaction had occurred with acryloylated starch and styrene.

CONCLUSIONS

Reaction of potato starch in controlled reactions of acryloyl chloride afforded acryloylated starches of defined DS-values. Introduction of the acryloyl group was confirmed with FT-IR and NMR spectroscopies. The spectra indicate the presence of the double bond and its availability for further reaction. Successful grafting with styrene, via free radical polymerization in an aqueous solution using potassium persulfate as an initiator, afforded good yields of styrene starch copolymer. Grafting ratio was determined and related to the conditions of synthesis. The amount of grafted polystyrene with respect to starch varied between 8 and 120% (w/w) by suitable control of the reaction parameters (reactant ratio, reaction time, and temperature). The DS-value of acryloylated starch, the amount of initiator added, and the monomer concentration also affected the graft ratio. On the basis of the above studies, it was found that a maximum GR (%)

was 120 (Table III), when using high DS (2.0) acryloylated starch, styrene (12 mL), 80°C, 6 h. Using a lower temperature (60°C) and a short reaction time (2 h) led to the lowest GR (8%). The starch graft copolymers showed poor solubilities in organic solvents, which hampered further analysis. The structures of graft starch copolymers, however, were confirmed by FT-IR analysis and further confirmation by saponification of the grafted and ungrafted materials. These experiments showed the ease of acryloyl group hydrolysis in the ungrafted starch. Conversely, hydrolysis of the acryloyl group in the grafted material was not facile, indicating that the styrene copolymer afforded a degree of steric protection to the labile ester group.

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