Grafting Acrylic Acid onto Starch and Poly(vinyl Alcohol) by Photolysis

Acrylic acid graft polymerizes onto starch with low add-on in chemically initiated free radical systems such as ceric ion or ferrous iron-hydrogen peroxide.[1] Higher add-on is obtained using γ radiation or electron beam preirradiation.[2] Irradiation of an aqueous monomer solution in a thin layer has been shown to be effective in maximizing conversion of monomer to polymer.[3] We find that we can graft acrylic acid onto granular starches and poly(vinyl alcohol) by photolysis in a novel cyclic process whereby a slurry of the material in water is pumped continuously past a quartz cell and irradiated while adding acrylic acid. The cell is wrapped with a polyethylene sheet transmitting light at wavelengths longer than 250 nm. This sheet prevents homopolymer from sticking to the quartz element and facilitates good recovery of product. Acrylic acid is added dropwise to minimize homopolymer formation by providing a maximum initial starch:monomer ratio. The method is applicable to ordinary, high-amylose, thin-boiling, oxidized, acid-modified, and hydroxyethylated starches as well as granular poly(vinyl alcohol). Graft copolymers with up to 20% add-on of poly(acrylic acid) are obtainable. Monomer goes 40–66% to graft copolymer and 19–36% to homopolymer. The graft copolymers give clear, thick pastes when heated in aqueous alkali.

EXPERIMENTAL

A 10–20% suspension of granular starch or poly(vinyl alcohol) in 400 ml water was deoxygenated with nitrogen 15 min and pumped continuously from a reservoir through a vessel (210 ml) containing a 450-W mercury vapor lamp (Hanovia 679A) in a water-cooled quartz immersion well that was wrapped in polyethylene (Fig. 1). The slurry was preirradiated 5 min and then acrylic acid was added to the reservoir dropwise over 30 min. Irradiation was subsequently continued 60 min. The reaction mixture was filtered, and the insoluble material was washed with water and alcohol and then air dried to obtain the graft copoylmer. The filtrate was evaporated to obtain homopolymer.

The amounts of grafted poly(acrylic acid) in the graft copolymers were determined by carboxyl content, either indirectly by treatment with excess base followed by back titration with hydrochloric acid[4] or directly by titration to pH 8.5 (ref. 5) to the phenolphthalein endpoint.

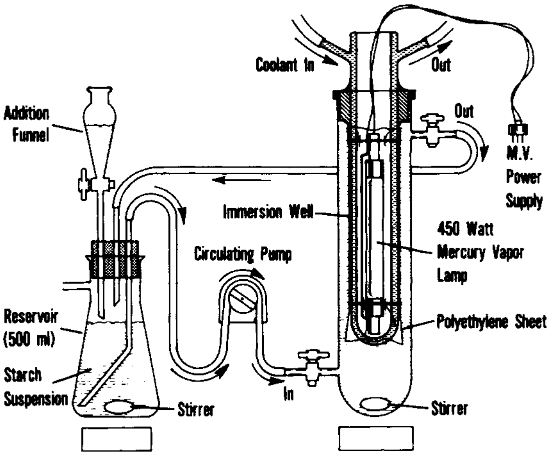

Fig. 1. Method for grafting acrylic acid onto slurried starch or poly(vinyl alcohol) by photolysis.

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TABLE I

Graft Copolymers of Acrylic Acid with Starches and Poly(vinyl Alcohol) Prepared by Photolysis

Starting material	% in water slurry	Monomer: polyol	% Add-on	Conversion of monomer %		Pastes at 90°		
				to grafted copolymer	to homopolymer	% Concentration	pH	Viscosity, (cp)
Pearl corn starch	10	1:5	11.2	65.6	24.6	2.5	8.8	5620
Acid modified starch	10	1:5	8.3	49.6	25.8	1.0	8.0	525
High amylose starch	10	1:5	11.2	61.3	18.8	4.0	8.1	10,000
Hydroxyethylated modified starch	10	1:5	9.3	47.5	27.9	10.0	8.7	226
Poly(vinyl alcohol)	10	1:5	8.4	45.4	36.3	5.0	8.0	124
Oxidized starch	10	1:5	9.4	46.3	35.1	10.0	9.0	260
	10	1:10	4.7	46.2	32.0	10.0	8.6	22
	20	1:10	6.0	58.6	21.9	10.0	8.6	109

TABLE II
Influence of Acrylic Acid Concentration upon Grafting Acrylic Acid onto Oxidized Starch

Monomer: oxidized starch[a]	% Add-on	Conversion of monomer to grafted polymer (%)	7% Pastes at 90° Fully titrated pH	Fully titrated Viscosity cp	Half titrated pH	Half titrated Viscosity cp
1:10	6.0	58.6	7.9	14	6.1	29
1:5	11.3	59.4	8.1	46	5.7	90
3:10	15.3	56.3	8.3	115	6.0	215
2:5	18.9	52.6	8.1	274	6.1	410
1:2	19.7	42.2	8.4	550	6.1	401

[a] Control oxidized starch showed a hot paste viscosity of 4 cp at these pH's and temperatures.

The graft copolymer prepared by photolysis of 1:2 acrylic acid:oxidized starch was refluxed with 0.5N HCl for 2 hr, and the solution was dialyzed to remove the hydrolyzed starch. Freeze drying allowed recovery of the poly(acrylic acid) portion. The number-average molecular weight was obtained by osmometry and grafting frequency from $\overline{M}_n$ and yield of poly(acrylic acid).

Hot paste viscosities of graft copolymer dispersions were determined at 90°C with a Brookfield viscometer at a spindle speed of 30 rpm.

RESULTS AND DISCUSSION

The products obtained in grafting acrylic acid onto various starches and poly(vinyl alcohol) are described in Table I. The native starches such as pearl corn and high amylose showed greater add-on and higher paste viscosities than the modified starches. Since the modified starches were of lower molecular weight and more soluble than the native starches, some soluble grafted polymer may have appeared in the homopolymer fraction at the expense of the insoluble fraction. Conversion of monomer to graft copolymer increased as the concentration of starch in the slurry increased; with oxidized starch, monomer conversion to graft copolymer increased from 46.2 to 58.6% as slurry concentration increased from 10 to 20%.

Increasing amounts of acrylic acid were added to a 20% slurry of oxidized starch in water, and the results are shown in Table II. Hot paste viscosities of the resulting graft copolymers increased as the percent add-on increased. Add-on reached a maximum of about 20% poly(acrylic acid) and may have been limited by a tendency for homopolymer to form on the polyethylene sheet and limit the amount of light reaching the slurry. Higher paste viscosities were usually obtained when only half the carboxyl groups were neutralized. The large viscosity increases encountered upon grafting acrylic acid onto starches may be related to the unusual associative properties of acrylic acid with water.[6] Polymerization would lead to stereoregular molecular aggregates, which would show higher viscosities than similar polymerization carried out in nonpolar solvents.

The graft copolymer of highest add-on in Table II had $\overline{M}_n$ 250,000 and an average of 6100 AGU/grafted chain. Add-on from weight of recovered poly(acrylic acid) was 20.1% and in close agreement with titration values.

Interestingly, a graft copolymer of starch and poly(acrylic acid) prepared by electron preirradiation[7] and containing 18.2% poly(acrylic acid) had $\overline{M}_n$ 220,000 and 6100 AGU/grafted chain.

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

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