

Graft Polymerization of Acrylonitrile and Methyl Acrylate onto Hemicellulose

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Synopsis

Graft polymerizations of acrylonitrile onto both a commercial larchwood hemicellulose and a purified (low lignin) wheat straw hemicellulose could be initiated by ceric ammonium nitrate. The resulting hemicellulose-*g*-polyacrylonitrile (PAN) copolymers were fractionated by extraction at room temperature with dimethylformamide and dimethylsulfoxide. Fractions were characterized by determining both the wt % PAN in each polymer fraction and the molecular weight of grafted PAN. Saponification of the PAN component of hemicellulose-*g*-PAN gave a water-dispersible graft copolymer with good thickening properties for water systems. An absorbent polymer, similar to the starch-based absorbents (Super Slurpers), was produced when saponified hemicellulose-*g*-PAN was isolated by methanol precipitation and then dried. Larchwood hemicellulose was also graft-polymerized with methyl acrylate using ceric ammonium nitrate initiation, and the hemicellulose-*g*-poly(methyl acrylate) was extrusion-processed into a tough, leathery plastic. Although ceric ammonium nitrate could be used as an initiator for graft polymerizations onto low-lignin hemicelluloses, it was inert with crude wheat straw hemicellulose containing 11% lignin. The ferrous sulfate-hydrogen peroxide redox system was used to initiate graft polymerizations onto this high-lignin material, and properties of the resulting hemicellulose-*g*-poly(methyl acrylate) and saponified hemicellulose-*g*-PAN graft copolymers were evaluated.

INTRODUCTION

Hemicelluloses¹ are complex mixtures of polysaccharides, the compositions of which will vary with the particular plant species examined. Moreover, most of these polysaccharides are heteroglycans and can contain a number of different sugar units. The polysaccharides are usually branched and are often partially acetylated. Hemicelluloses are commonly removed from plant materials by extraction with dilute alkali and are isolated by neutralization of the alkaline extracts and by alcohol precipitation. Examples of some specific polysaccharides which may be found in hemicellulose are D-xylan (usually bearing side chains of other sugars, such as 4-O-methyl- α -D-glucopyranosyluronic acid or L-arabinose), D-gluco-D-mannan, D-galacto-D-gluco-D-mannan, and L-arabino-D-galactan.

Although graft copolymers of starch² and cellulose³ have been extensively studied, analogous polymerizations with a hemicellulose as the substrate have received comparatively little attention. O'Malley and Marchessault^{4,5} prepared and characterized graft copolymers of aspenwood 4-O-methylglucuronoxylan by allowing the fully methylated polysaccharide to react with either living

* 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.

polystyrene or living poly(2-vinylpyridine). Church⁶ has reported the preparation of aspenwood 4-O-methylglucuronoxylan graft copolymers by the ammonium persulfate-sodium thiosulfate-initiated reaction with sodium acrylate.

Hemicellulose comprises roughly one-fourth to one-third of most plant materials,⁷ and this amount will vary according to the particular plant species. The preparation and properties of new polymers from hemicellulose should thus be an important part of any research program aimed at utilizing annually renewable, agriculturally derived polymers as extenders and replacements for polymers prepared from petrochemicals. Since earlier work at this Center dealt with graft polymerization of a variety of vinyl and acrylic monomers onto starch, we hoped to use this research as a basis for graft polymerizations with hemicellulose. Of particular interest was (1) the preparation of thickeners⁸ and absorbents⁹ by the graft polymerization of acrylonitrile and its subsequent saponification and (2) the preparation of plastics by graft polymerization of methyl acrylate.¹⁰ This report will describe these two processes with larchwood hemicellulose and wheat straw hemicellulose as substrates for graft polymerization.

EXPERIMENTAL

Materials

Acrylonitrile (Eastman) and methyl acrylate (Polysciences) were distilled at atmospheric pressure through a 14-in. Vigreux column, and center cuts were collected. Ceric ammonium nitrate, ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and 30% hydrogen peroxide were Fisher Certified ACS Grade.

Larchwood hemicellulose was purchased from Vega Biochemicals under the name Xylan and was used as received. The moisture content was 9.4%; and the lignin content, as determined by the method of Bagby et al.¹¹ was 1.3%. When a 1.2% dispersion of hemicellulose in water was stirred overnight at room temperature, 40% of the polysaccharide remained insoluble after centrifugation at $1500 \times g$. The remaining 60% of the polysaccharide was dispersed in the cloudy supernatant. Dispersibility in water increased to 64% and 67% when the hemicellulose-water slurry was heated for 30 min at 85°C and 100°C, respectively.

Wheat straw hemicellulose was isolated without prior removal of lignin by the method of Whistler and Feather.¹² Before extraction with 10% sodium hydroxide, the straw was dried for about 2 h at 90°C and then Wiley-milled through a 1-mm² screen. The hemicellulose A fraction was precipitated by neutralization of the alkaline extract with acetic acid. The precipitate was washed twice with 50% ethanol-water, dialyzed against distilled water, and freeze-dried. Lignin content was 11%.

Purified wheat straw hemicellulose (lignin content = 3%) was isolated from milled straw, which was first extracted with 2:1 (vol) benzene-ethanol and then delignified by treatment with acetic acid-sodium chlorite.¹³

Hemicelluloses were analyzed for neutral sugars after hydrolyzing 10-mg samples for 24 h at 100°C in 1.5 mL of 1.0*N* trifluoroacetic acid (sealed vials). Samples were evaporated to dryness and were then converted to the peracetylated aldonitrile derivatives by the method of Seymour et al.,¹⁴ with minor

modifications (ethyl acetate substituted for chloroform, and ethyl acetate solutions extracted with aqueous sulfuric acid to remove pyridine). Dry ethyl acetate solutions were analyzed by gas chromatography (3% neopentyl glycol succinate on Supelcoport, $\frac{1}{8}$ in. \times 7 ft. stainless-steel column, 170–220°C at 20°C/min, holding at the limit), and area percentages were calculated.

Graft Polymerizations

Acrylonitrile, Ceric Ammonium Nitrate (CAN) Initiation. A stirred slurry of 10.0 g (dry basis) of hemicellulose (from either larchwood or purified wheat straw) in 167 mL of water was sparged with a slow stream of nitrogen for 1 h at either room temperature or 85°C. Under the latter conditions, the dispersion was cooled back to room temperature. Acrylonitrile (10.0 g) was added, followed after 5 min by a solution of 0.338 g of CAN in 3 mL of 1*N* nitric acid. The temperature was controlled with an ice bath, and the mixture was allowed to stir for 2 h at 25–30°C. The polymer was isolated by centrifugation, washed with water and with ethanol, and vacuum-dried at 60°C. Water washings were dialyzed against distilled water and freeze-dried. Polymers were subjected to repeated extractions, first with dimethylformamide (DMF) and then with dimethylsulfoxide (DMSO), and solids were separated by centrifugation (20 min at 1500 \times *g*). Extracted solids and concentrated supernatants were blended with water, and polymers were isolated by filtration, washed with water and with ethanol, and dried.

Methyl Acrylate, CAN Initiation. A stirred slurry of 75.0 g of larchwood hemicellulose in 3 L of water was sparged with a slow stream of nitrogen for 1 h at room temperature, methyl acrylate (93.8 g) was added, and the mixture was stirred for 5 min. A solution of 5.1 g of CAN in 45 mL of 1*N* nitric acid was then added in four equal portions, allowing 15 min between each addition. The mixture was stirred for 2 h while the temperature was maintained at 25–30°C, and the polymer was isolated by filtration. The polymer was resuspended in water, the pH was adjusted to 7 with sodium hydroxide solution, and the polymer was again isolated by filtration. Repeated extraction of the wet filter cake with acetone at room temperature removed 19.3 g of ungrafted poly(methyl acrylate) (PMA). Air-drying the extracted solid yielded 130.7 g of hemicellulose-*g*-PMA with a moisture content of 5.2%.

Acrylonitrile, Fe⁺²/H₂O₂ Initiation. A stirred slurry of 10.0 g (dry basis) of crude wheat straw hemicellulose was sparged with a slow stream of nitrogen for 1 h at room temperature. Acrylonitrile (either 10.0 g or 20.0 g) was added followed by 0.16 g of FeSO₄·7H₂O. After the resulting mixture had stirred for 5 min, 0.50 g of 30% hydrogen peroxide was added, and the mixture was stirred for 2 h at 25–30°C, while controlling the temperature with an ice bath. The reaction mass was poured into ethanol, and the polymer was isolated by filtration, washed with ethanol, and vacuum dried at 60°C. Polymers were extracted with DMF, as described for CAN-initiated reactions.

Methyl Acrylate, Fe⁺²/H₂O₂ Initiation. A stirred slurry of 75.0 g of crude wheat straw hemicellulose in 3 L of water was sparged with a slow stream of nitrogen for 1 h at room temperature. Methyl acrylate (93.8 g) was added, followed by 1.20 g of FeSO₄·7H₂O. After the resulting mixture had stirred for 5 min, 3.75 g of 30% hydrogen peroxide was added, and the mixture was stirred for 2 h at

25–30°C, while controlling the temperature with an ice bath. The polymer was separated by filtration, washed with water, and neutralized to pH 7. The polymer was allowed to air-dry to yield 141.0 g of polymer with a moisture content of 6.8% and a PMA content (grafted and ungrafted) of 43%, as calculated from the gain in weight of hemicellulose. The turbid water washings contained 32 g of polymer, the infrared spectrum of which showed PMA with little or no carbohydrate. Extraction of a 10-g portion of graft copolymer with acetone removed 10% (by weight) of the polymer as ungrafted PMA.

Characterization of Hemicellulose-*g*-Polyacrylonitrile (PAN) Copolymers

A dispersion of 2.00 g of hemicellulose-*g*-PAN in 150 mL of 2*N* hydrochloric acid was heated under reflux for 1.5 h. The insoluble polymer was separated by filtration, washed with water, and dried under vacuum at 60°C. The infrared spectrum showed PAN with less than 5% carbohydrate. Percent PAN in the original copolymer was calculated from weight loss on acid hydrolysis.

The molecular weight of PAN (\bar{M}_v) was determined from its intrinsic viscosity in DMF.¹⁵

Characterization of Hemicellulose-*g*-PMA

Carbohydrate was removed from larchwood hemicellulose-*g*-PMA by first oxidizing the carbohydrate component with sodium periodate and then degrading the oxidized carbohydrate with sodium methoxide in methanol. 2 g of hemicellulose-*g*-PMA were added to a solution of 4.278 g of NaIO₄ in 200 mL of water, and the mixture was allowed to stand in the dark with occasional stirring for 1 week. The oxidized polymer was removed by filtration, washed with water and with methanol, and then suspended in 20 mL of methanol. After this suspension had been cooled to about 0°C, 2 mL of 1*N* sodium methoxide in methanol was added, and the mixture was allowed to stand overnight at 0°C with occasional stirring. The supernatant liquid was decanted, and the polymer was washed several times with cold methanol and allowed to air-dry. To remove final traces of methanol, the polymer was taken up in benzene and freeze-dried. The yield was 1.108 g, which corresponds to 55% PMA in the original polymer, as calculated from loss in weight. The infrared spectrum showed less than the detectable limit of 5% carbohydrate, and the polymer was 93% soluble in acetone.

Analysis of the acetone-soluble PMA by gel permeation chromatography (GPC) showed $\bar{M}_w = 546,000$ and $\bar{M}_n = 387,000$. GPC was carried out at ambient temperature on a Waters Model ALC/GPC 244 Liquid Chromatograph. Four Waters μ -Styragel columns were used (10⁵, 10⁴, 10³, and 500 Å) with an injection volume of 200 μ L and a flow rate of 1 mL/min. Polymer concentration was 0.08% in tetrahydrofuran. Polystyrene standards were used, and the *Q* factor (46.7) was verified with a PMA secondary standard obtained from Scientific Polymer Products, Inc.

The sodium periodate–sodium methoxide degradation procedure did not significantly alter \bar{M}_w and \bar{M}_n of a PMA homopolymer. The PMA was first deposited on cellulose fibers and then isolated after degrading the polysaccharide component of the synthetic mixture. \bar{M}_w and \bar{M}_n of PMA before treatment: 498,000 and 432,000; after treatment: 509,000 and 438,000.

Alkaline Saponifications

A suspension of 1.0 g of hemicellulose-*g*-PAN in 9 mL of 0.7*N* sodium hydroxide (in a 25-mL Erlenmeyer flask) was heated on a steam bath for 5–10 min until the mixture thickened sufficiently to preclude settling. The flask was loosely stoppered (to permit escape of ammonia) and heated for 3 h in a 95–100°C oven. The reaction mass was then diluted with 150 mL of water and dialyzed against distilled water. A known weight of the dialyzed dispersion (pH about 7) was freeze-dried to determine % solids. The dispersion was then diluted with water to 0.25% solids, and the viscosity was obtained with a Brookfield viscometer at 30 rpm. To reduce viscosity and polymer swelling, the dispersion was acidified with hydrochloric acid to pH 4, and a portion of this dispersion was centrifuged at 1500 × *g*. The supernatant was then allowed to filter by gravity through fluted Whatman 54 paper. The % soluble polymer was calculated from the % solids in both the filtrate and the unfiltered dispersion, as determined by freeze-drying.

Reactions in which saponified polymers were isolated by methanol precipitation were carried out in the same way, except that reaction mixtures after saponification were blended at high speed with 350 mL of methanol. The polymer was separated by filtration, washed with methanol, and dried overnight under vacuum at 60°C. To determine water absorbency, an accurately weighed 5–10-mg sample of saponified polymer was allowed to soak for 30 min in 50 mL of deionized water. The swollen polymer was then separated from unabsorbed water by screening through a tared 280-mesh sieve. The polymer on the sieve was allowed to drain for about 20 min, and the sieve was then weighed to determine the weight of water-swollen gel. Absorbency was calculated as g water/g polymer and was not corrected for percent solubles. Absorbencies were run in duplicate, and averages were recorded to two significant figures. Duplicate determinations agreed to within 10%.

Extrusion of Hemicellulose-*g*-PMA and Testing of Plastics

Hemicellulose-*g*-PMA polymers were extruded through a 3/4-in. C. W. Brabender extruder with *L/D* ratio of 20:1. The screw had a 3:1 compression ratio and was driven by a variable speed Brabender Plasti-Corder. Temperature of the slit die (1 × 0.020 in.) and the end of the barrel was 140°C, while the inlet zone was 90–115°C. Plastic specimens used for testing were given three passes through the extruder. Dumbbell-shaped tensile specimens were tempered 4 days at 22.2°C and 50% relative humidity before testing on an Instron testing machine at either 5 or 50 cm/min crosshead speed.

RESULTS AND DISCUSSION

Larchwood Hemicellulose

Polymerizations were carried out with a commercial sample of larchwood hemicellulose. The complexity of this polysaccharide was shown by an analytical method for neutral sugars, in which the hemicellulose was hydrolyzed with aqueous trifluoroacetic acid, and the resulting sugars were then converted to the peracetylated aldonitrile derivatives. Analysis was then carried out by gas

chromatography. Xylose made up about 30% of the mixture; the remaining sugars consisted of mannose and glucose in a ratio of about 4.5:1. A trace of arabinose was also present. The portion of this hemicellulose that was water-insoluble contained a higher percentage of xylose, whereas the soluble fraction contained more glucose and mannose. This suggests that, in addition to xylan, one component of our larchwood hemicellulose is a water-soluble glucomannan.

Graft polymerizations of acrylonitrile onto larchwood hemicellulose were carried out in water with ceric ammonium nitrate as the initiator (Table I). Two different pretreatment conditions were used for the polysaccharide. Under the first set of conditions, hemicellulose was merely slurried in water at room temperature prior to graft polymerization, whereas in the second polymerization, the hemicellulose-water slurry was heated for 1 h at 85°C before room temperature reaction with monomer and initiator.

Polymerizations occurred readily and yielded insoluble polymers, which were isolated by centrifugation and washed with water. About 14–15% of the original hemicellulose could be recovered from the aqueous supernatants; this polysaccharide fraction was apparently ungrafted, since infrared spectra showed no nitrile absorption. The water-insoluble hemicellulose-*g*-PAN reaction products were fractionated by extraction at room temperature with DMF, and the DMF-insoluble polymers were finally subjected to a further extraction with DMSO.

Polymer fractions were characterized by first removing the carbohydrate component by acid hydrolysis and then calculating the wt % PAN in the original polymer (% add-on) from the loss in weight. The molecular weight of the remaining PAN was then determined from its intrinsic viscosity in DMF.

Table I shows that the amount of polymer extractable with DMF and DMSO was not greatly different for the larchwood hemicellulose products prepared at the two pretreatment temperatures. Also, under both reaction conditions, a DMF-extractable fraction was obtained that contained 72–74% PAN, indicating that some hemicellulose-*g*-PAN had been extracted along with any PAN homopolymer formed in the reaction. PAN molecular weights showed little variation with the particular fraction examined and did not depend significantly on pretreatment temperature. The independence of graft molecular weight on carbohydrate pretreatment is in marked contrast to starch-*g*-PAN polymers, which show large increases in PAN molecular weight when the starch granules are heated in water at 85°C.¹⁶

Since the PAN component of starch-*g*-PAN may be saponified with sodium or potassium hydroxide to yield hydrophilic polymers that are useful as thickeners⁸ and as water absorbents,⁹ the saponification of larchwood hemicellulose-*g*-PAN and the physical properties of the resulting saponified polymer were likewise investigated. The polymer used for saponification was the DMF-insoluble fraction isolated from the 25°C-pretreated product.

After purification by dialysis, a 0.25% water dispersion of saponified hemicellulose-*g*-PAN had a Brookfield viscosity (30 rpm) of 800 cp. The graft copolymer was 54% water soluble, and the remainder was in the form of a highly swollen but insoluble gel, similar to that typically encountered with saponified starch-*g*-PAN. In comparison, a saponified starch-*g*-PAN prepared from granular starch had a viscosity of 260 cp at 0.25% solids and was 26% soluble in water.

TABLE I
Graft Polymerization of Acrylonitrile onto Hemicellulose. Fractionation of Graft Copolymers^a

| Hemicellulose (pretreatment) | Product wt (g) | Extraction with dimethylformamide (DMF) | | Extraction of DMF-insoluble fraction with dimethylsulfoxide | |
|---------------------------------|----------------|--|---------------|--|-----------------------------|
| | | Extractable (%) | Insoluble (%) | Extractable (%) | Insoluble (%) |
| Larchwood 25°C | 17.1 | 34 | 66 | 45 | 55 |
| | | 72% PAN; \bar{M}_v 95,000 | | 49% PAN; \bar{M}_v 91,000 | 39% PAN; \bar{M}_v 85,000 |
| Larchwood 85°C | 17.6 | 29 | 71 | 37 | 63 |
| | | 74% PAN; \bar{M}_v 113,000 | | 49% PAN; \bar{M}_v 103,000 | 40% PAN; \bar{M}_v 95,000 |
| Purified wheat straw 25°C | 15.6 | 59 | 41 | 99+ | <1 |
| | | 43% PAN; \bar{M}_v 260,000 | | 30% PAN; \bar{M}_v 280,000 | |

^a Amounts used: 10.0 g hemicellulose, 10.0 g acrylonitrile, 167 mL water, 0.338 g ceric ammonium nitrate dissolved in 3 mL of 1N nitric acid. Values for percent polyacrylonitrile (PAN) in the individual fractions refer to weight % PAN present in these fractions and not to homopolymer content. PAN homopolymer will be present in the DMF-extractables but not in the DMSO-extractable fraction.

When saponified hemicellulose-*g*-PAN was isolated by methanol precipitation and dried, its absorbency was 430 g distilled water/g polymer, and it was 57% soluble in water. Saponified starch-*g*-PAN prepared from granular starch typically has an absorbency of 150–200 g/g and is about 20% water soluble.¹⁷

We next synthesized a PMA graft copolymer from larchwood hemicellulose to see if an extruded plastic prepared from such a polymer would have properties similar to comparable graft copolymers synthesized from starch. Polymerization was readily initiated with ceric ammonium nitrate to yield a graft copolymer containing 55% PMA after extraction of homopolymer with acetone. Grafted PMA, remaining after degradation and removal of the polysaccharide component, was 93% soluble in acetone; \bar{M}_w and \bar{M}_n of this soluble PMA were 546,000 and 387,000, respectively. Both the % add-on and the solubility of grafted PMA are similar to results encountered with starch as the substrate for graft polymerization.¹⁸

As observed with starch-*g*-PMA, extrusion of hemicellulose-*g*-PMA through a slit die at 140°C produced a smooth, well-formed plastic ribbon that was tough and leathery and that exhibited little or no die swell. The absence of die swell in these carbohydrate-thermoplastic graft copolymers is ascribed¹⁰ to the fact that polymers do not melt under the conditions of extrusion because of the rigid, high-melting nature of the carbohydrate component. A continuous plastic is instead formed by the sintering of heat-softened particles under the high pressure encountered in the extruder die. The ultimate tensile strength (UTS) of extruded hemicellulose-*g*-PMA was 2.25 kg/mm² at a crosshead speed of 50 cm/min, and test specimens showed 150% elongation before break. These figures may be compared with a UTS of about 2.7 kg/mm² and 80% elongation before break for a typical starch-*g*-PMA plastic having about the same carbohydrate:thermoplastic ratio.¹⁸

Wheat Straw Hemicellulose

The hemicellulose A fraction was isolated from milled wheat straw by extraction with dilute sodium hydroxide followed by precipitation of the hemicellulose by acidification of the alkaline solution with acetic acid.¹² Since any practical process for the utilization of hemicellulose would use crude rather than purified polysaccharide, the hemicellulose A used in most experiments was isolated from wheat straw without prior removal of organic solubles or lignin. This hemicellulose was a tan-colored solid that contained about 11% lignin. Gas chromatographic analysis for neutral sugars, using the method employed for larchwood hemicellulose, showed about 10% arabinose, 88% xylose, and 2% glucose. A purified hemicellulose A was also prepared from a sample of wheat straw which was first Soxhlet-extracted with 2:1 (vol) benzene-ethanol and then delignified with acetic acid-sodium chlorite.¹³ This polysaccharide was a white solid that contained only about 3% lignin.

Ceric-initiated graft polymerization of acrylonitrile onto purified wheat straw hemicellulose was carried out under the same conditions used for larchwood hemicellulose (room temperature pretreatment), and the resulting polymer was similarly fractionated by extraction with DMF and DMSO (Table I). It is apparent that wheat straw hemicellulose-*g*-PAN has a higher solubility in DMF and DMSO than its larchwood counterpart. Extraction with DMF removed 59%

of the polymer, and this extractable fraction contained 43% PAN, as opposed to 72% PAN for the larchwood polymer. The higher solubility of wheat straw hemicellulose could be due either to a lower molecular weight or to its different chemical composition. In addition to solubility differences between the polymers depicted in Table I, higher PAN molecular weights were obtained in polymerizations with wheat straw hemicellulose.

Unlike purified hemicellulose, crude wheat straw hemicellulose was unreactive toward acrylonitrile when attempts were made to initiate polymerizations with ceric ammonium nitrate, probably because of the higher (11%) lignin content of this polysaccharide. Reactivity was not improved by extracting the crude hemicellulose with 2:1 (vol) benzene-ethanol. In contrast to ceric ion, the ferrous sulfate-hydrogen peroxide redox system was an effective initiator for graft polymerization. Apparently, the chain transfer reaction of hydroxyl radicals with hemicellulose is not as easily inhibited by lignin as the complexation and reaction of ceric ions with the polysaccharide.

Graft polymerizations of acrylonitrile onto 10 g of crude wheat straw hemicellulose (room temperature pretreatment) were carried out with $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ initiation using either 10 g or 20 g of acrylonitrile in the polymerization recipe (Table II). As observed with ceric initiation onto purified wheat straw hemicellulose (Table I), over half of the polymer was extractable with DMF at room temperature.

Calculation of % PAN in the fractions of Table II by weight loss on acid hydrolysis and determination of molecular weights of the resulting PAN components were not possible because of the presence of significant amounts of lignin in the samples. Since lignin is at most only partially solubilized by dilute refluxing mineral acid, it remains as an impurity in the insoluble PAN remaining after acid hydrolysis of the hemicellulose component. The compositions of the various polymer fractions in Table II are thus expressed not in terms of % PAN but in terms of percent hemicellulose. Subtraction of % hemicellulose values from 100% gives the values for % PAN plus % lignin.

The water-insoluble PAN + lignin remaining after acid hydrolysis of the two DMF-extractable fractions contained largely PAN, as judged from infrared spectra. In contrast, acid hydrolysis of the DMF-insoluble fractions produced PAN + lignin that was only partially soluble in DMF, and infrared spectra clearly showed the lignin component. Since extraction of PAN + lignin hydrolysis products with DMF did not cleanly remove PAN from lignin, it is a reasonable assumption that graft polymerization of acrylonitrile has taken place not only on the carbohydrate but on the lignin component as well.

Saponification reactions were carried out with the two polymers of Table II under the same conditions used for larchwood hemicellulose-*g*-PAN. Graft copolymers used for saponification were not extracted with DMF. Although large differences in water absorbencies and water solubilities were not observed for the two methanol-precipitated saponified polymers, the Brookfield viscosity of a 0.25% water dispersion of saponified polymer was higher when less acrylonitrile was used in the graft polymerization reaction.

Methyl acrylate graft polymerized readily onto crude wheat straw hemicellulose in the presence of ferrous sulfate-hydrogen peroxide initiator to yield a polymer containing 43%, by weight, of PMA. This polymer was then extruded, without prior removal of ungrafted PMA, under the same conditions used for

TABLE II
Graft Polymerization of Acrylonitrile onto Crude Wheat Straw Hemicellulose^a

| Acrylonitrile (g) | Product, wt (g) | Extraction with dimethylformamide | | Saponified, not dried | | Saponified, ppt. with methanol, dried | |
|----------------------|--------------------|--------------------------------------|----------------------|---|-------------------|--|-------------------|
| | | Extractable (%) | Insoluble (%) | Viscosity at 0.25% (cp) ^b | Solubility (%) | Absorbency (g/g) | Solubility (%) |
| 10 | 17.4 | 52 (36% hemicel.) | 48 (73% hemicel.) | 1,050 | 40 | 430 | 40 |
| 20 | 26.3 | 61 (25% hemicel.) | 39 (57% hemicel.) | 150 | 30 | 500 | 38 |

^a Amounts used: 10.0 g hemicellulose, 167 mL water, 0.50 g 30% H₂O₂, 0.16 g FeSO₄·7H₂O.

^b Brookfield viscosity at 30 rpm.

larchwood hemicellulose-*g*-PMA. Although 10% (by weight) of this polymer consisted of acetone-extractable PMA homopolymer, the extruded plastic ribbon showed little or no die swell and exhibited a UTS of 2.6 kg/mm² (crosshead speed: 5 cm/min). The plastic was more brittle than the corresponding larchwood hemicellulose product and showed only about 10% elongation before break. Use of the lower testing speed was necessary to get reproducible results. The observed brittleness of this polymer, as compared to the larchwood hemicellulose product, could be caused by the difference in chemical composition between hemicelluloses isolated from larchwood and wheat straw, or it could simply be due to its lower PMA content.

CONCLUSIONS

Experiments with larchwood and wheat straw hemicelluloses show that useful graft copolymers can be prepared from the hemicellulose component of plant materials. Saponification of hemicellulose-*g*-PAN affords a product that functions as both a thickening agent for water systems and as a water absorbent. Moreover, extrusion processing of hemicellulose-*g*-PMA yields a well-formed plastic that exhibits little or no die swell.

Although graft polymerizations onto low lignin hemicelluloses can be readily initiated with ceric ammonium nitrate, this initiator does not function when lignin contents are high (11%). The ferrous sulfate-hydrogen peroxide redox system may be used to initiate graft polymerizations onto high-lignin hemicelluloses. There is evidence that graft polymerization takes place onto the lignin component as well as onto the polysaccharide.

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