Grafting Acrylonitrile and Acrylic Acid Monomers on Cellulosic Materials

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Synopsis

Graft copolymers of acrylonitrile and of acrylic acid monomers on cellulosic materials were obtained by use of ceric ion initiator in aqueous medium at a 50% (w/w) cellulose-monomer ratio. The variations of poly(acrylonitrile) grafts and of the efficiency of grafting with ceric ion concentration, and of poly(acrylic acid) grafts with temperature are examined. The dependence of water retention capacity of the grafted fibers with the graft level is reported.

INTRODUCTION

Graft polymerization of acrylonitrile on cellulose followed by alkaline hydrolysis of the graft poly(acrylonitrile) into a copolymer of sodium polyacrylate and polyacrylamide has been shown to result in the formation of modified fibers with outstanding water absorbency.[1] Because of the possible industrial application of these modified fibers, it was thought that a method of preparing analogous copolymers (that is, by grafting acrylic acid monomer on cellulosic materials), would provide further information on the effect of alkaline conversion of the nitrile group on the poly(acrylonitrile) graft to the carboxylate group on the water absorbency of the cellulosic materials. Besides, such a method would provide useful materials for investigating the metal ion binding properties of the grafted polyelectrolyte on a cellulosic substrate.

In this communication, the influence of ceric ion concentration and temperature on graft polymerization and water absorbency are examined for the grafting of acrylonitrile and of acrylic acid, respectively, on holocellulosic materials from a tropical hardwood, *Gossweilerodenron balsmiferum*. An attempt is made to compare the grafting characteristics of the hardwood cellulose with the reported data for cotton linters and softwood graft pulp.[2-8]

EXPERIMENTAL

Materials

Acrylonitrile and acrylic acid monomers were obtained from Hopkin and Williams Limited. The acrylonitrile monomer was extracted with aqueous sodium hydroxide-sodium chloride solution to remove the hydroquinone stabilizer. The hydroquinone-free monomer was dried over calcium chloride and distilled through a Vigreaux column. The fraction boiling at 76–77°C was collected as pure monomer. Acrylic acid monomer was distilled under vacuum. The middle fraction was collected as pure monomer.

Ceric ammonium nitrate from BDH Limited was used without further purification. *Gassweilerodenron balsmiferum* meal was obtained from a commercial sawmill in Benin City. It was air dried and sieved through a 300-μm mesh. The portion retained on the mesh was used in the preparation of the holocellulose.

Preparation of Holocellulose

The chlorite method[9,10] was used for the preparation of holocellulose from the hardwood. A 25-g sample of the air-dried wood meal was extracted with 95% ethanol to remove resinous matter. Preliminary Soxhlet extractions showed that most of the resinous matter (3% w/w) could be removed by a single ethanol extraction.

The air-dried sample (25 g) was suspended in 800 cm^3 of hot water in a 2-L conical flask containing 3 cm^3 of glacial acetic acid, and then 7.5 g sodium chlorite was added. The flask was stoppered with an inverted 50-cm^3 conical flask and heated on a steam bath in a ventilated hood. After 1 h, the heating was interrupted and fresh portions of acetic acid (3 cm^3) and sodium chlorite (7.5 g) were added. The procedure was repeated for a total heating period of 3 h and total amounts of acetic acid and sodium chlorite of 9 cm^3 and 22.5 g, respectively.

The mixture was filtered and the white holocellulose washed thoroughly with cold water and then air dried. The α-cellulose content of the holocellulose (50.3%) was determined according to the method described by Corbett.[11]

Graft Polymerization

The polymerization procedure was based on the method described by Lepoutre et al.[12] Preliminary studies showed that the addition of monomer to a dispersion of the substrate in a solution of a ceric ammonium nitrate initiator produced higher graft levels than adding the initiator to a mixture of the substrate and the monomer in an aqueous medium. Although the latter method of mixing the reagents gave higher values of conversion of monomer to polymer, it was accompanied by low graft levels, indicating an inefficient grafting system.

Graft polymerizations were carried out under the following conditions: (1) for acrylonitrile grafting, both the temperature of grafting (40°C) and the substrate-monomer ratio 0.5 (w/w) were kept constant and the ceric ion concentration was varied; (2) for acrylic acid grafting, the substrate-monomer ratio and the ceric ion concentration (0.018 mmol Ce^{4+}) were kept constant and the temperature of grafting was varied between 35 and 60°C. Polymerization was allowed to proceed for (1) between 0.5 and 3 h and (2) 1 h, respectively.

Extraction of Homopolymer

The ungrafted poly(acrylonitrile) and poly(acrylic acid) homopolymers were extracted using suitable solvents[2,12]—dimethyl formamide and dioxane, respectively. The grafted cellulosic material was then dried again and

reweighed. The measured weight increase divided by the weight of the substrate, multiplied by 100, was reported as the percentage graft level. The percentage efficiency of grafting was taken as the weight of polymer grafted divided by the weight of the polymer grafted plus the weight of homopolymer, multiplied by 100.

Hydrolysis of Polyacrylonitrile Grafts

Grafted fibers were introduced into 100 cm³ of boiling 3% sodium hydroxide solution stirred with a magnetic stirrer. The slurry was kept boiling for 30 min, and the cellulosic material was filtered while hot on a Buchner funnel and washed with deionized water until pH 9.[2]

Determination of Water Retention Capacity

The water retention capacity of the grafted fibers was measured by a suction technique. An oven-dried (80°C) sample (1 g) was placed in a previously dried and weighed sinta glass funnel (porosity 4), which was then filled with water (60 cm³). Suction was gently applied from a vacuum of water pump (2 drops/min) until the sample was completely drained. The glass funnel was weighed, dried overnight at 80°C, and then reweighed. The amount of water in grams retained per gram of the dry material was expressed as the water retention capacity.

RESULTS AND DISCUSSION

The variations of the graft level and efficiency of grafting with ceric ion concentration and polymerization time for acrylonitrile grafting are shown in Figure 1. It can be seen that, at a constant initiator concentration, both the graft level and efficiency of grafting increase with time, tending to level off at longer durations of polymerization. Although an increase in ceric ion concentration is accompanied by an increase in graft level, the efficiency of grafting decreases with increase in initiator concentration. During polymerization, ceric ions are consumed by the initiation process and by adsorption onto the cellulosic materials in amounts that have been shown to correspond to the total carbonyl content of the cellulosic substrate.[6,8] Any unreacted or unadsorbed ceric ion in the polymerizing system could be initiated homopolymerization by transfer to monomer. Ogiwara and Kubota[6] have estimated the equilibrium amount of ceric ion absorbed per gram of dissolving pulp and commercial bleached semichemical pulp from a 10 mmol/L ceric ion solution. The results indicate that up to 70% of the ceric ion was unadsorbed by the cellulosic substrate. The decrease in efficiency of grafting with increase in the initial ceric ion concentration and the general low efficiency of grafting acrylonitrile on the holocellulosic substrate is an indication that a relatively large proportion of the ceric ions is present in the continuous aqueous medium rather than at the substrate/aqueous medium interface.

The effect of temperature on the grafting of acrylic acid on the holocellulosic substrate is shown in Table I. The results show a decrease in the level of incorporation of poly(acrylic acid) grafts onto the cellulose backbone
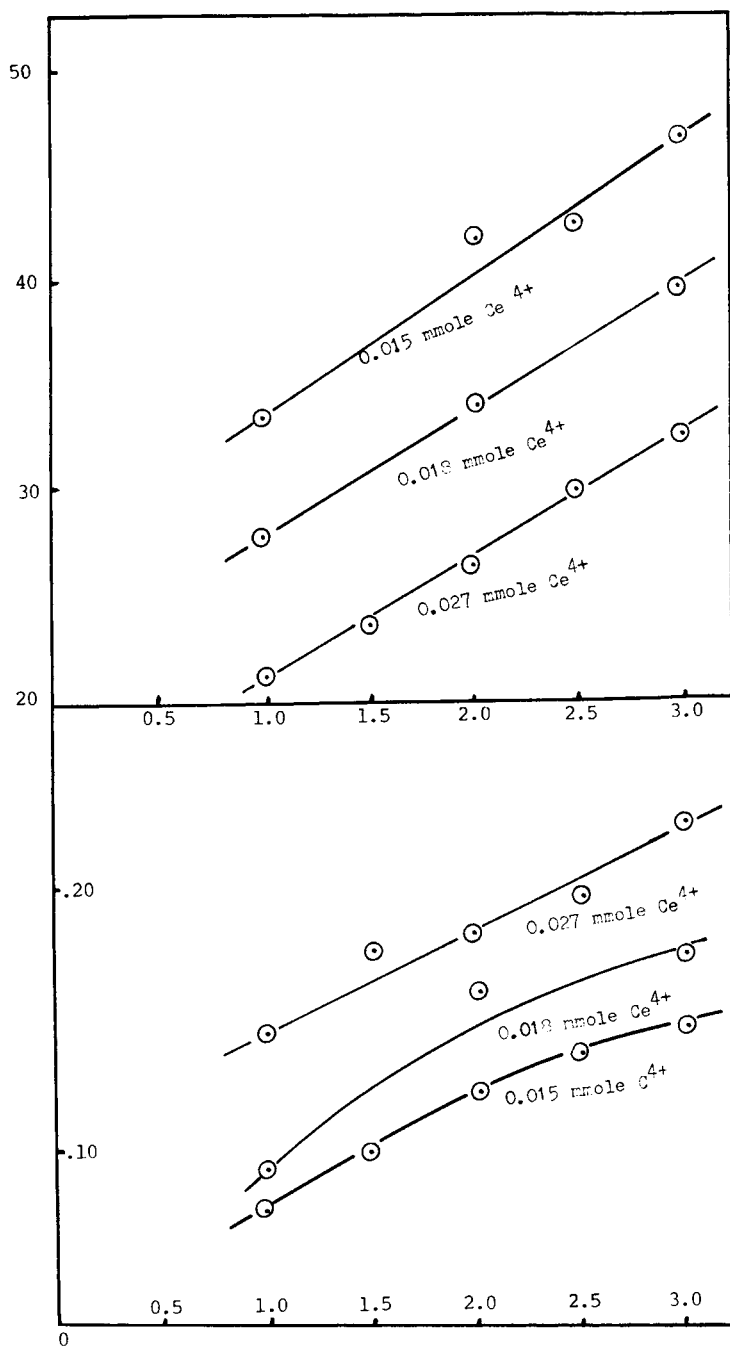
Fig. 1.   Variations of (a) graft level (%) and (b) efficiency of grafting (%) with initiator concentration and polymerization time (h) using a 1:1 substrate-monomer ratio at 40°C.

between 35 and 40°C. The graft level remaining virtually constant between 40 and 60°C. The effect of temperature on the efficiency of grafting is more significant, decreasing from 54% at 35°C to 24% at 60°C.

TABLE I
Influence of Temperature of Polymerization on the Graft Level and Water Retention
Capacity (WRC) of Acrylic Acid-Cellulose Graft Copolymers

Polymerization temperature (°C)	Graft level (%)	WRC (g/g)
35	23.81	8.76
40	19.71	6.83
45	19.10	6.44
50	18.53	5.81
60	18.45	5.78

Water Retention Capacity

The water retention capacity of the ungrafted holocellulose, acrylonitrile-grafted fibers, and hydrolyzed poly(acrylonitrile) grafted fibers are shown in Table II.

The water retention capacity of cellulosic materials is generally thought to result from the interaction through hydrogen bonding of the hydroxyl groups on cellulose with water molecules. The effect on water retention by the introduction of vinyl grafts on the cellulose backbone would depend on the frequency of interposition of the grafted polymer, the nature of the grafted polymer, and the fiber-fiber cohesion of the substrate. The results (Table II) show that grafting of acrylonitrile onto cellulose reduces the water retention capacity; the retention capacity decreasing with increase in graft level. This leads to the suggestion that the relatively hydrophobic nature of the poly(acrylonitrile) grafts has completely compensated for the effect of reduced interfiber cohesion due to grafting on the swelling properties of the cellulosic materials.

The water retention capacity of the hydrolyzed poly(acrylonitrile) grafts is higher than the capacities of both the ungrafted substrate and the un-hydrolyzed grafts. Alkaline conversion of the nitrile group on poly(acrylonitrile) graft to carboxylate group, leading to enhanced water compatibility,[2] would explain the higher levels of water retention by the hydrolyzed grafted fibers.

TABLE II
Water Retention Capacity of Acrylonitrile-Cellulose Copolymer

Poly(acrylonitrile) graft level before hydrolysis	Water retention capacity (g/g)	
	Unhydrolyzed grafts	Hydrolyzed grafts
0.00	1.34	—
7.73	1.27	3.47
11.00	1.21	4.22
14.50	1.20	4.46
17.59	0.99	5.50
20.59	0.95	6.57

The effect of acrylic acid grafting on the water retention capacity of the cellulosic materials is shown in Table I. For the same order of magnitude of graft level, the acrylic acid-grafted fibers show higher levels (by about 5%) of water retention than hydrolyzed poly(acrylonitrile) grafts. Alkaline hydrolysis of poly(acrylonitrile)-grafted fibers has been shown to be accompanied by scission of some of the grafted polymer chains from the cellulosic backbone,[2] thereby resulting in hydrolyzed poly(acrylate) grafts with lower graft levels than in the unhydrolyzed grafts. Besides, alkaline conversion of the nitrile group on poly(acrylonitrile) grafts to carbonylate group passes through an amide intermediate. The loss of grafted polymer chains during hydrolysis, the deficit in the carboxylate group due to intermediate amide formation, and that the amide group could be less compatible with water than the carboxylate group would explain the higher levels of water retention by the acrylic acid-grafted fibers.

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