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Grafting Acrylic Acid Monomer on Cellulosic Materials

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ABSTRACT

Graft copolymers of acrylic acid on cellulosic materials were obtained by use of ceric ion in aqueous medium at different temperatures. The variation in the level of incorporation of poly(acrylic acid) grafts on the cellulosic substrate and the dependence of the water and saline retentions of the graft copolymers on the graft level are examined.

INTRODUCTION

Graft polymerization of acrylonitrile on cellulose followed by alkaline hydrolysis of the poly(acrylonitrile) graft 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 graft co-

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polymers (by grafting acrylic acid on cellulosic materials) would provide further information on the effect on the water absorbency of alkaline conversion of the nitrile group on the poly(acrylonitrile) graft to carboxylate. Besides, this would provide useful materials for investigating the metal ion binding properties of polyelectrolyte grafted on cellulosic substrate.

This communication examines the influence of temperature on the grafting characteristics of acrylic acid on holocellulosic materials from Gasweilerodenron balsamiferum, a tropical hardwood, and the effect of poly(acrylic acid) grafts on the water and saline retention capacities of the cellulosic material.

EXPERIMENTAL

Materials

Acrylic acid monomer from Hopkin and Williams Ltd. was distilled under vacuum. After distillation, the monomer was stored at 7°C until required. Ceric ammonium nitrate from BDH Ltd. was used without further purification. Gosweilerodenron balsamiferum meal was obtained from a commercial saw mill in Benin City. It was air-dried and sieved through a 300-μm mesh screen. The portion retained on the screen was used in the preparation of holocellulose.

Preparation of Holocellulose

The chlorite method [2, 3] was used to prepare the holocellulose from the hardwood. A 25-g sample of the air-dried wood meal was extracted with 95% ethanol to remove resinous material. Preliminary Soxhlet extractions showed that most of the resinous matter (3 wt%) could be removed by a single ethanol extraction. The resin-free wood meal was then air dried.

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 of 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 9 h and total amounts of acetic acid and sodium chlorite were 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 cellulose content of the holocellulose (50.3%) was determined according to the method described by Corbett [4].

Graft Polymerization

The polymerization procedure was based on the method described by Lepoutre and Hui [1]. Graft polymerization was carried out using a constant cellulose substrate/monomer ratio (0.5 w/w) and a ceric ion concentration (0.018 mmol, equiv) over a temperature range from 35 to 60°C. Polymerization was allowed to proceed for 1 h, and then the grafted cellulosic material was filtered, washed, and air dried.

The grafted cellulosic material was Soxhlet extracted with dioxane to remove the ungrafted poly(acrylic acid) homopolymer. The sample was then dried and weighed. The percentage weight increase (in terms of the weight of the cellulosic substrate) was reported as the graft level. The percent efficiency of grafting was taken as the weight of the polymer grafted divided by the weight of the polymer grafted plus weight of homopolymer multiplied by 100.

Determination of Water Retention Capacity

The water retention capacity (WRC) 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 sintered glass funnel (porosity 4) which was then filled with water 60 cm^3). Suction was applied from a vacuum of a water pump and controlled by a valve between the pressure source and the filter flask to allow the sample to drain at 2 cm^3/min. The glass funnel was then weighed, dried overnight at 80°C, and then reweighed. The amount of water retained per gram of the dry material was taken to be the water retention capacity.

The saline retention capacity (SRC) was determined in a similar manner using 1 wt% aqueous sodium chloride solution.

RESULTS AND DISCUSSION

The effect of temperature on the grafting of acrylic acid on the holocellulosic materials is shown in Table 1, which shows a decrease in the graft level 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 by about 30% as the temperature increases from 35 to 60°C.

During polymerization, the initiating ceric ions are either consumed in creating active centers on the cellulosic substrate, adsorbed on the cellulosic substrate (in amounts that have been shown to correspond to the carbonyl content of the cellulosic material [5, 6]), or retained in the aqueous medium where they can initiate homopolymerization by transfer to monomer. The graft level and the efficiency of grafting both depend on the relative amounts of ceric ions initiating polymer formation on the cellulosic substrate and in the aqueous phase.

TABLE 1. Effect of Temperature on the Grafting of Acrylic Acid Monomer on Cellulosic Materials

Polymerization temperature, °C	Graft level, %	WRC, g/g	SRC,[a] g/g
Control	0	1.34	
35	23.8	8.76	6.98
40	19.7	6.83	5.31
45	19.1	6.44	5.02
50	18.5	5.81	4.62
60	18.5	5.78	4.53

[a] Uncorrected for the amount of sodium contained in the retained quantity of the solution.

The results from this study indicate that a relatively high proportion of the initiating ceric ions are in the aqueous medium [5] and that an increase in temperature tends to reduce the amount of ceric ions available to initiate grafting.

The effect of acrylic acid grafting on the water retention capacity (WRC) of the cellulosic material is also shown in Table 1. The water retention properties of cellulosic materials are thought to result from interaction through hydrogen bonding of the hydroxyl groups on the cellulose with water molecules. The effect on water retention by grafting vinyl monomers on cellulose backbone would therefore depend on the frequency of interposition of the grafted polymer chains on the cellulosic backbone, the nature of the grafted polymer, and the fiber-fiber cohesion on the cellulosic substrate. The results (Table 1) show that grafting acrylic acid monomer on the cellulosic substrate increases the water retention capacity of the cellulosic substrate and that the increase is dependent on the increase in graft level. Enhanced water compatibility of the grafted fibers resulting from the presence of hydrophylic poly(acrylic acid) grafts on the cellulosic chain would explain the observed variation of water retention capacity with graft level.

The saline retentions grafted fibers (Table 1) are about 20% lower than the corresponding WRC values. It has been suggested that the presence of sodium chloride causes the grafted polyion chain to undergo configurational changes, resulting in the reduction of the swelling forces [7].

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