Synthesis and Properties of Graft Oxidation Starch Sizing Agent

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Received 5 December 2001; revised 23 May 2002; accepted 23 May 2002

ABSTRACT: In this article, a graft, oxidation starch sizing agent was synthesized and its structure and surface morphology were analyzed by infrared (IR) spectroscopy and scanning electron microscopy (SEM). The results show that the synthesized graft oxidation starch has good gelatinizing ability, good film properties, good desizing ability, and lower hygroscopic properties. The sized yarns (T/C65/35, 13.5tex), sized with graft oxidation starch and emulsive copolymer size EM, exhibit good tensile strength and elongation at break, good abrasion resistance, and lower counts of fluff when poly (vinyl alcohol) (PVA) is substituted by $\leq$ 80% with graft oxidation starch. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1563–1566, 2003

Key Words: graft copolymers; tension; strength; resists

INTRODUCTION

Poly (vinyl alcohol) (PVA) has been widely used as a sizing agent for polyester/cotton yarns because of its superior adhesion to synthetic fibers. Because of environmental protection concerns, PVA now has been banned for use in the sizing process in Europe because of its pollution problem. There is also a propose to limit the use of PVA in textile mills in China. Research on and development of new textile sizing agents have been carried out.[1–8] Graft oxidation starch copolymer, which exhibits excellent behaviors of a starch sizing agent as well as good synthetic polymer size, is potentially the ideal replacement for PVA. Other graft oxidation starches have been reported, but they didn't meet the need for a PVA replacement because of drawbacks, such as high cost, incomplete gelatinization, poor film ability, deposition during weaving, etc. In this paper, we report the synthesis of a green sizing agent, graft oxidation starch, which has properties of excellent performance as well as low cost. This agent could substitute for 80% of the PVA used for sizing of fine terylene/cotton yarns.

EXPERIMENTAL

Preparation of grafting oxidation starch

Materials

Commercial cornstarch, sodium hypochlorite, acrylic acid (AA), methyl acrylate (MA), vinyl acetate (VA), sodium hydroxide, and hydrochloric acid were all chemical pure agents. The redox initiator was confected by our laboratory.

Preparation of oxidation starch

Starch (30 g, which was dryed before weight) water (100 mL), and catalyst (0.1 g) were mixed by stirring in a three-necked flask for 10 min. Next, a certain volume of sodium hypochlorite solution (content of effective chlorine is 0.8%), adjust to and kept at pH 8–9, was added to this mixture at 30°C and allowed to react for 1h. Then, the pH was adjusted to 6, and a small quantity of a sodium sulfite solution was added to remove the unreacted sodium hypochlorite. After filtration, washing, and drying, 39 g of oxidation starch, with a viscosity value of 8 mPa.s (95°C$^-$, 6% solution) was obtained.

Preparation of grafting oxidation starch

Thirty grams of the oxidation starch (obtained as just described) and 100 mL of water were combined in a three-necked flask and stirred for 15 min. Next, of 10 g monomer mixture (which is composed of 7.5 g of methyl acrylate, 0.5 g of acrylic acid, and 2 g of vinyl acetate) was added and the mixture was stirred for 10 min. The grafting copolymerization reaction was initiated with a solution of 20 mL of redox initiator and proceeded at 30–50°C for 2 h. Then the solution was heated to 50°C to saponify at pH 10 for 1–1.5 h. The reaction solution was cooled to room temperature, after neutralization, filtration, washing, and drying. A yield of 33.2 g of grafting oxidation starch was ob-

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TABLE I
Characterization of the Sizing Agent

Parameter items	Characteristic
Appearance	White powder
Viscosity (mPa · s)	34.4 (95°C, 6%)
pH value (6% solution)	4–5
Percentage of graft (%)	11.62
Molecular weight of the side chain	2.0983×10^5

tained. The graft percentage of the product is shown in Table I.

Analysis of the structure and surface morphology of the product

The prepared product is a mixture of graft oxidation starch copolymer and copolymer that doesn't. Participate in the grafting reaction. The pure grafting starch copolymer was obtained by removing the latter copolymer with acetone in a Soxhlet apparatus. The side-chain copolymer grafted onto starch was obtained after complete degradation of starch backbone by acid hydrolysis.

The molecular weight of the side chain was determined from viscosity measurements. Infrared (R) spectra of starch, pure graft oxidation starch copolymer, and the side chain copolymer were recorded with a Nicolet 550-II IR spectrophotometer. The surface morphology of corn starch and pure grafting starch copolymer were investigated with a JSM-848 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The characteristics of the graft oxidation starch sizing agent are shown in Table I. The IR spectra of the starch pure graft oxidation starch copolymer, and the side-chain copolymer are shown in Figures 1–3, respectively. The surface morphology of corn starch and pure grafting starch copolymer are shown in Figures 4 and 5, respectively.

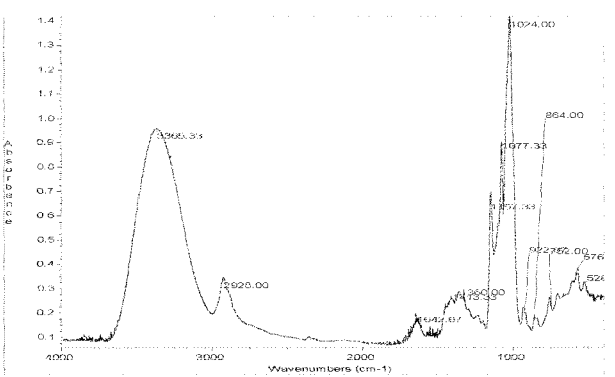

Figure 1 Infrared spectrum of starch.

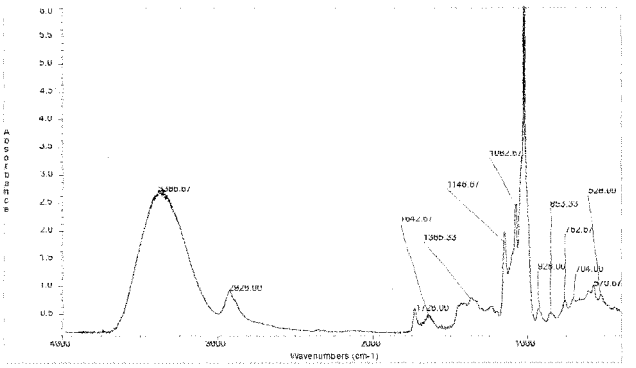

Figure 2 Infrared spectrum of graft oxidation starch polymer.

A comparison of Figures 1 and 2 indicates that the graft oxidation starch has a new characteristic absorption peak of carbonyl group at 1728.00 cm^{-1}, in addition to the absorption peaks of corn starch at 3386.67, 2928.00, 1413.00, 1024.67, 853.33, 762.67, and 570.00 cm^{-1}. According to Figure 3, the side-chain copolymer also exhibits the characteristic absorption peak of a carbonyl group at 1728.00 cm^{-1}, but does not have the characteristic absorption peaks of corn starch. These results confirm that a graft oxidation starch copolymer was obtained.

The SEM results in Figure 4 show that the granules of corn starch are of different sizes and that the surface of the starch granule is very smooth, like a variety of pebbles. As seen in Figure 5, the graft oxidation starch copolymer maintains the granular shape, but the surface of graft oxidation starch granules is very rough and covered with a layer of polymer. This result indicates that the graft reaction takes place mainly on the surface of starch granules.

Application properties of the product

Viscosity property

A suspension of 6% product was heated to 95°C for 3 h, with stirring, and observed to determine whether

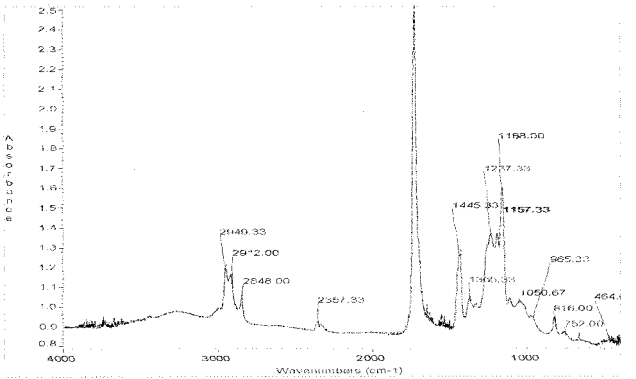

Figure 3 Infrared spectrum of the side-chain copolymer.

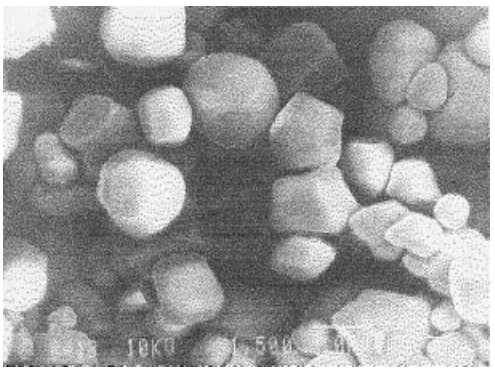

Figure 4 SEM picture of corn starch.

it completely gelatinized. In addition, the variation of viscosity of the solution was determine every 30 min with a NDJ-79 viscometer. The results, shown in Table II, indicate that the graft oxidation starch sizing agent gelatinizes completely, which ensures good film ability. The 6% solution also exhibited low and stable viscosity, which enhances the ability of the agent to penetrate into yarns.

Hygroscopic and water-soluble properties of the sizing film

To determine the hygroscopic properties of the sizing agent, a 0.1-mm thick film was mode with a 3% solution of the product. This film was dried to a constant weight, and 1 g of film was placed in a container at 75% R. H. for 10 days. The change in weight of the film was used to calculate the hygroscopy of 9.5%. To determine solubility, 1 g of film was placed in water at 80°C, and the time until the film was completely dissolved was determined. This film dissolved in < 0.5 min. The very low hygroscopy (9.5%) indicates there would be little readhesion between sized yarns. Also, the film could be dissolved completely in 80°C water within 30 s, so sized yarn would be easy to desize in hot water.

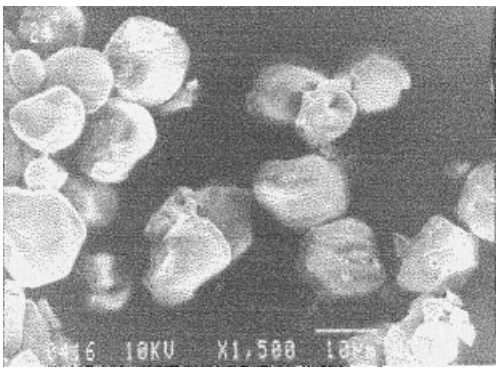

Figure 5 SEM picture of graft oxidation starch.

TABLE II
Viscosity of 6% Solution of the Sizing Agent

Time (min)	Viscosity (mPa · s)[a]
0	38.5
30	35.0
60	34.4
90	34.0
120	35.5
150	35.8
180	34.0

[a] Percent variation = 8.89%.

Sizing properties of the product

Tensile strength and extension, abrasion resistance, and counts of fluff of the sized yarns are critically important for weavability in fabric manufacturing. The components different sizing agents are shown in Table III. In Table III, A is a sizing agent that is widely used in textile mill. Six percent solutions of each of the sizing agents described in Table III were headed to 95°C and kept at this temperature for 1 h with stirring. Then, yarns (T/C65/35,13.5tex) were immersed in the sizing solutions for 15 min at 95°C. The sized yarns were patted dry under the same conditions and then conditioned at R.H., 65% for at least 24 h before testing. The tensile strength and elongation at break, abrasion resistance, and counts of fluff of the sized yarns were measured with a YGO21 A single-strand strength tester, LFY-20 yarn abrasion tester, and YG171 fluff tester, respectively. The results are presented in Table IV. The cost of each agent, calculated according to the marketing price of every components of each recipe, is also shown in Table IV.

The tensile strengths of yarns sized with mixtures A*, B*, C*, D*, and E* are obviously superior to those sized with the mixtures A, B, C, D, and E. This difference may be due to the low viscosity and high ester group content of EM, properties that make penetration into yarns easy and that improve adhesion to synthetic fibers. The tensile strength, abrasion resistance, and the counts of fluff of yarns sized with C*, D*, and E*, in which graft oxidation starch was used to replace 50, 60, and 80% PVA, respectively, are similar to those parameters of yarn sized with A. However, the elongation at break of yarns sized with C*, D*, and E* are superior to that of yarn sized with A. These results demonstrate that the graft oxidation starch, which can substitute up to 80% of the PVA when it is used with emulsive copolymer sizing agent EM, can effectively size yarns (T/C65/35 13.5tex) and that the cost can be decreased 150 yuan per kettle (see Table IV).

CONCLUSION

A graft starch sizing agent was synthesized, and its structure and surface morphology were analyzed by

TABLE III
Composition of Sizing Agents[a]

Agent	Viscosity (95°C, mPa · s)	PVA (g)	CS (g)	GS (g)	AA (g)	EM (g)	NaOH (g)	2-Naphnol (g)	Emulsive Oil (g)	Substitution of PVA (%)
A	26.0	37.50	45.00	0.00	20.00	0.00	0.3	0.08	0.15	—
B	35.5	0.00	50.00	32.50	20.00	0.00	0.3	0.08	0.15	100
C	34.0	7.50	45.00	30.00	20.00	0.00	0.3	0.08	0.15	80
D	33.2	15.00	45.00	22.50	20.00	0.00	0.3	0.08	0.15	60
E	32.0	18.75	45.00	18.75	20.00	0.00	0.3	0.08	0.15	50
A*	23.6	37.50	45.00	0.00	0.00	20.00	0.3	0.08	0.15	—
B*	33.0	0.00	50.00	32.50	0.00	20.00	0.3	0.08	0.15	100
C*	29.2	7.50	45.00	30.00	0.00	20.00	0.3	0.08	0.15	80
D*	27.2	15.00	45.00	22.50	0.00	20.00	0.3	0.08	0.15	60
E*	27.0	18.75	45.00	18.75	0.00	20.00	0.3	0.08	0.15	50

[a] CS, corn starch; GS, graft oxidation starch; AA, liquid commercial sizing agent that was synthesized mainly with acrylic acid, acrylonitrile, and acrylamide; EM, emulsive copolymer sizing agent made in our research group (solid content is the same as that for sizing agent AA), which was synthesized mainly with vinyl acetate, acrylamide, and acrylic acid.

TABLE IV
Properties of Sized Yarns

Yarn	Tensile Strength (cN)	Break Elongation (mm)	Abrasion Resistance (times)	Fluff Counts Longer than 2 mm	Cost per Kettle (yuan)
Unsized	265.10	12.70	16.4	63.7	—
A	328.98	10.65	69.7	22.3	675.00
A*	345.26	10.61	74.6	16.75	675.00
B	318.90	10.56	48.9	26.45	455.00
C	315.35	10.60	54.2	25.36	525.00
D	315.35	10.04	56.4	24.50	562.50
E	320.14	10.73	60.5	24.22	581.25
B*	309.82	10.59	52.8	25.64	455.00
C*	326.64	11.77	65.6	21.12	525.00
D*	326.59	11.26	69.5	18.50	562.50
E*	333.28	11.50	70.1	17.49	581.25

IR spectroscopy and SEM. The IR spectra show that the graft reaction between starch in a particulars state and the monomer mixture (which is made up of MA, AA, and VA in a suitable proportion) really takes place. Furthermore, the SEM results show that the graft reaction takes place mainly on the surface of the starch granules.

The synthesized graft oxidation starch can be gelatinized completely in hot water. It has good film properties, good desizing ability, and low hygroscopic properties. In solution (6% solid content, the sizing agent exhibits low and stable viscosity.

The yarns (T/C65/35, 13.5tex) sized with the graft oxidation starch and emulsive copolymer (EM) sizing agents exhibit good tensile strength and elongation at break, good abrasion resistance, and lower counts of fluff when PVA is substituted by 80% with graft oxidation starch sizing agent. Finally, the graft oxidation starch is environmentally friendly and could significantly reduce the cost of sizing yarns.

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