

Microwave Irradiated Synthesis of Grafted Cationic Starch: Synthesis, Characterization, Application, and Biodegradation

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ABSTRACT: A biodegradable copolymer was synthesized by grafting copolymerization of acrylamide, β -hydroxyethyl methacrylate, and *n*-butyl acrylate onto corn cationic starch (CS) by microwave irradiation. The grafted cationic starch (GCS) was characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, and X-ray diffraction. The optimum conditions on graft copolymerization with respect to reaction temperature, exposure time, and initiator concentration were investigated. Physicochemical properties of GCS, such as swelling power, solubility, intrinsic viscosity, and apparent viscosity, were studied, and its application performances as textile sizing agent were tested. Results showed that compared with CS, physicochemical properties of GCS were significantly improved, including decreased crystallinity, weakened granular, increased hydration capacity, and rheological property. Polyester/cotton blended yarns sized with GCS obtained more reinforced mechanical properties than samples sized with CS and exhibited higher tensile strength and abrasion resistance than polyvinyl alcohol (PVA) sized yarns. The mechanisms that the starch physicochemical properties affected on the sizing performances were discussed as well. Biodegradation analysis on these sizing agents showed that BOD_5/COD_{cr} of GCS was 0.263, which outclasses that of PVA ($BOD_5/COD_{cr} = 0.009$). This novel biomaterial could be expected to have promising applications especially in textile industry and be an ideal substitute for PVA. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Polyvinyl alcohol (PVA) has been widely used as textile sizing agent because of its good permeability, viscosity stability, film-forming ability, and high film mechanic strength. But PVA has insufficient adhesion to synthetic fibers and exorbitant cohesion due to the single side group and regular molecular structure. Moreover, PVA has difficulties in desizing, and its non-biodegradability could create serious environmental pollution.^{1,2}

Starch is one of the most abundant natural polymers in the world and as an important ether derivative of raw starch (RS), cationic starch (CS) has many good properties, such as relatively high water dispersion, solubility, paste stability, and low gelatinization temperature. Moreover, owing to positively charged groups, CS has affinity to synthetic fibers which eases to accumulate anion charges during textile processing.³ Studies by Ben and Guo⁴ showed that CS had good viscosity and thermal stability, good adhesive property for cotton/polyester blended yarn, and good miscibility with PVA. The size film of

CS was flexible and intact and had high strength. Study on the compatibility of CS and PVA was carried out by Zhu and Zhou⁵; it was found that the cationization could reduce the extent of phase separation of starch/PVA blends, therefore stabilized the size paste. Hebeish et al.⁶ had investigated the sizing properties of CS derived from pre-oxidized maize starch. Results showed that the oxidized-cationized maize starch enhanced the tensile strength and decreased the elongation at break of light cotton fabric compared with oxidized maize starch. Previous studies indicated that CS had high application potential in textile industry. However, due to the lack of hydrophobic groups, CS still lacks enough adhesion to synthetic fibers.

Graft copolymerization is the most important method to improve the hydrophobicity and overcome the structural shortcoming of RS. In recent years, the research on grafted starch is developing in the direction of multi-constitute graft copolymerization and compound modification. Lv et al.⁷ studied the preparation of corn starch graft copolymers from acrylamide (AM)/dimethyl diallyl ammonium chloride binary monomers

by a simultaneous gamma radiation. Han et al.⁸ (our research group) reported the graft copolymerization of acrylic acid and butyl methacrylate on corn starch by microwave irradiation with rheological phase reaction, in order to meet the sizing requirements of polyester/cotton blended yarn. In the report of Li et al.,⁹ the esterification of hydrolyzed starch with acryloyl chloride was applied before graft copolymerization. Results showed that acryloylation of starch before copolymerization was an effective method for substantially enhancing the grafting efficiency and improving the performances such as adhesion-to-fibers and mechanical properties of grafted starch film. Another report by Zhu et al.¹⁰ indicated that the introduction of allyl groups into starch before the copolymerization could evidently enhance the fiber adhesion and film behaviors of the copolymer. Although there have been many earlier studies on the grafting polymerization of starch and its derivatives aimed at textile sizing,^{11–13} less attention has been paid to the grafting of vinyl monomers onto CS. Moreover, most of the previous studies still remained in the preparation technique and application performance of the product, but deep research on the physicochemical properties of grafted cationic starch (GCS) seemed to be lack. The physicochemical properties, such as crystalline structure, granule configuration, hydration capacity, and rheological property, are considered as the key factors affecting the starch application performance. However, there is some blindness in the aspect of starch grafting modification in present studies.

Microwave irradiation emerges as an efficient source of thermal energy and constitutes a very original procedure of heating materials, different from the classical ones. Microwave assisted free radical polymerization is also emerging as a novel technique in the field of polymer science to get grafted biomaterial. Comparing with traditional methods, “microwave assisted” synthesis of grafted starch is a method of time-saving, high efficiency, low energy consumption, and less pollution.

As above, in order to combine the virtues of both CS and grafted starch, a novel starch-based copolymer, GCS, was synthesized via microwave irradiation in this present work. The optimum reaction conditions for graft copolymerization were discussed. The main aim of this work was to investigate the combined effect of microwave irradiation and grafting modification on the physicochemical properties of GCS and to study the mechanisms that how these properties affected the sizing performances. The application of the product in textile industry and the biodegradability were also studied.

EXPERIMENTAL

Materials

CS [substitution degree (DS) \approx 0.03] was purchased from Jinshan Modified Starch Co., Shandong, China). AM and *n*-butyl acrylate (BA) were supplied by Guangfu Fine Chemical Research Institute, Tianjin, China. Dimethyl sulfoxide (DMSO) was purchased from Kemiou Chemical Reagent Co., Tianjin, China. β -Hydroxyethyl methacrylate (HEMA), ammonium persulfate (APS), sodium bisulfate (SBS), ethanol, and acetone were purchased from Fengchuan Chemical Reagent Science and Technology Co., Tianjin, China. All the chemical reagents were analytically pure.

Microwave-Assisted Grafting Copolymerization of GCS

Of CS, 20 g was dispersed in 160 mL double distilled water and transferred into a two-necked flask, then 40 μ L of DMSO, 3 g AM, 3.4 mL HEMA, and 6 mL BA were successively added. The suspension was mixed by magnetic stirring in a thermostatic water bath at 25°C for 10 min, then 0.92 g APS and 0.28 g SBS were added. After thorough stirring, the flask was placed into the MCR-3 microwave chemical reactor equipped with condenser and magnetic stirring. At the same time, a platinum resistance thermometer probe was projected into the flask to monitor and control the system temperature. The grafting copolymerization was performed at 55°C for 25 min. Once the microwave irradiation for the intended amount of time was complete, the reaction mixture was filtered and washed with ethanol–water solution (50/50, v/v), then with absolute ethanol for several times and dried at 60°C in air oven; thus, the crude product was obtained. Non-grafted homopolymer was removed from the crude product by Soxhlet extraction with water then with acetone as solvent for 10 h, successively. The resulting precipitate was dried, pulverized, and sieved. And after dried in air oven at 60°C to a constant weight, the pure graft copolymer was obtained.

Characterization

Fourier-Transform Infrared Spectroscopy. Fourier-transform infrared (FT-IR) spectra were recorded with Gang Dong FTIR-650.

Fourier-transform spectrometer, at a resolution of 4 cm^{-1} over the wavenumber region 4000–400 cm^{-1} , using KBr pellet.

Scanning Electron Microscopy. The granule configuration of CS and GCS samples were studied using a scanning electron microscope SEM of Hitachi S-4800. The micrographs were taken at magnifications of 2000 and 9000, using 10 kV accelerating voltage.

X-Ray Diffraction. D/MAX-2200 X-ray powder diffractometer was used for the X-ray diffraction (XRD) studies with copper as target material in an X-ray tube under the operational conditions of 40 kV, 150 mA, and wavelength of 1.54 Å. The samples were scanned between 10° and 80°.

Graft Level Determination. The purified sample (2 g) was hydrolyzed in 100 mL of 1N HCl solution under reflux for 4 h at 98°C. The solution was neutralized with 1N NaOH, and the copolymer side chains were obtained by filtration. The side chains were then dried in air oven at 105°C to constant weight. The grafting ratio (GR) and grafting efficiency (GE) were calculated as follows:

$$\text{GR} (\%) = \frac{M1}{M2} \times 100$$

$$\text{GE} (\%) = \frac{M1}{M1+M3} \times 100$$

where *M1* is the weight of grafted chains, *M2* is the weight of grafted starch, and *M3* is the weight of homopolymers.

Swelling Power and Solubility. Starch sample (1 g) was accurately weighed and mixed with 50 mL of distilled water; the

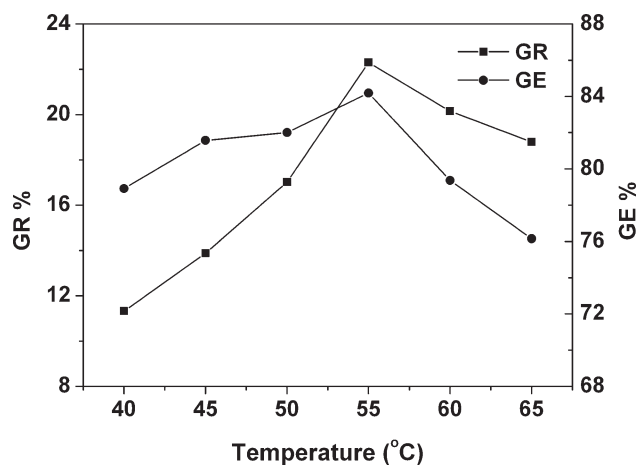


Figure 1. Effect of temperature on graft polymerization.

slurry was stirred and heated in water bath at a temperature of 90°C for 30 min. The mixture was cooled to room temperature and centrifuged at 3000 rpm for 20 min. The supernatant was carefully dumped into an already weighed plate dish, evaporated at 80°C, and then dried to constant weight at 105°C. Solubility and swelling power and were calculated as follows:

$$S\% = \frac{A}{W} \times 100$$

$$SP(\text{g g}^{-1}) = \frac{P}{W(1-S\%)}$$

where A is the weight of residues of supernatant after evaporation, P is the weight of centrifugal precipitate, and W is the weight of starch sample (dry basis).

Rheological Properties. The intrinsic viscosity of sample was determined with an Ubbelohde viscometer at 25°C in DMSO solution; a series of specific viscosity (η_{sp}) were measured with different concentrations, then reduced viscosity (η_{sp}/C) were calculated, and the intrinsic viscosity $[\eta]$ was obtained from extrapolating η_{sp}/C to zero concentration. Apparent viscosity (η_a) of cooked starch paste (6%, w/w) was determined at 95°C using NDJ-79 rotary viscometer.

Application Test in Textile Sizing. Polyester/cotton blended yarn (T/C 65/35, 32 S) was sized with mixed sizing agent (6%, w/w) at 90°C by ASS3000 automatic single-yarn sizing equipment for application test. CS, PVA, and GCS were used as the major components in the mixed size, respectively. Sizing performances including tensile strength, elongation at break, abrasion resistance, and hairiness index were measured with YG061F single-strand strength tester, A-2071.TM cohesion testing machine, and YG172A fluff tester, respectively.

Biodegradability Analysis. The chemical oxygen demand (COD_{cr}) and biochemical oxygen demand (BOD_5) of samples were determined by potassium dichromate method and iodometry, respectively. In this study, 1 g L^{-1} sample solution was diluted with 5 times for COD_{cr} determination and 100 times

for BOD_5 determination. The biodegradability of sample was expressed by a ratio of $\text{BOD}_5/\text{COD}_{cr}$.

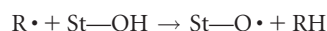
RESULTS AND DISCUSSION

Reaction Mechanism

Under microwave irradiation, when the initiator APS is heated in aqueous medium, it decomposes into SO_4 -free radicals. The oxidation–reduction reaction also happens between the APS and SBS to generate $\text{SO}_4\cdot$ and $\text{HSO}_3\cdot$ free radicals. These all types of radicals abstract hydrogen atom from starch molecules producing the starch macro radicals. The monomer molecules, which are close vicinity of reaction sites, become acceptor of starch macro radicals, resulting in chain initiation and thereby themselves become free radical donor to neighboring molecules leading to the propagation. These grafted chains are terminated by coupling to give graft copolymer on the basis of experimental results as shown by the following scheme:

M: monomers, R: free radicals, St: starch

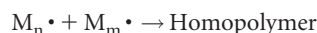
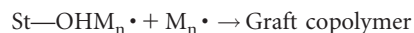
Initiation:



Propagation:



Termination:



Optimal Grafting Conditions under Microwave Irradiation

Effect of Reaction Temperature. Figure 1 shows that the increase in reaction temperature from 40°C to 55°C results in an increase of GR and GE. The reason could be that under relatively high reaction temperature, the swelling extent of starch granules becomes great as well as the motion of monomer molecules accelerates, which enhance the diffusion of monomer and initiator to the starch backbone and then increase the chance of reaction collision. The higher temperature is also benefit to increase the decomposition rate of initiator, resulting into more free radical generated for graft copolymerization. However, beyond 55°C, GR and GE decrease. It is possible that at temperatures higher than 55°C too high a rate of free radical generation is attained, which then increases the rate of chain transfer and chain termination.¹⁴ The rising temperature is also in favor of the homopolymerization occurrence at the expense of the graft copolymerization.

Effect of Exposure Time. From Figure 2, GR and GE are observed to increase with the increase in exposure time and reach a maximum value at 25 min. The reason might be that with increasing exposure time, more microwave energy is

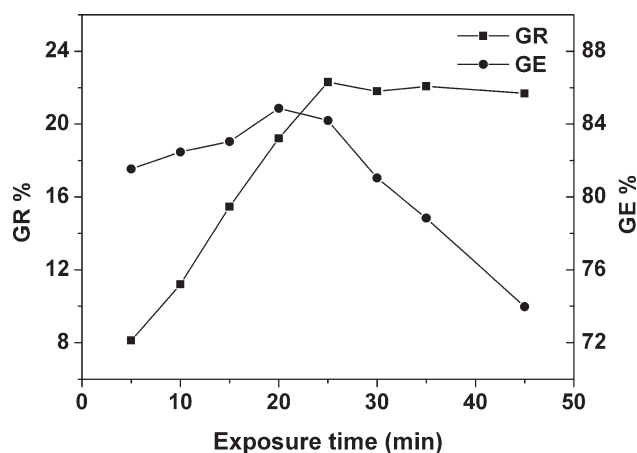


Figure 2. Effect of exposure time on graft polymerization.

absorbed, resulting into more free radical generation, leading to higher grafting and efficiency.¹⁵ After 25 min of exposure GR and GE level off. This might be due to the depletion of monomer and initiator. Another possible reason lies in that along with the formation of homopolymer, the viscosity of reaction system increases, which would make it difficult for monomer molecules to reach reaction sites.¹⁶

Effect of Initiator Concentration. Figure 3 shows that GR and GE increase with increasing the concentration of initiator, reach an optimum value, and then decrease. Free radicals are generated as a result of decomposition of initiator in the polymerization media to initiate, propagate, and terminate the growing polymer chains. An increase in concentration of initiator increases the chance of hydrogen abstraction from the starch backbone; thus, the number of free radicals on the starch backbone increases and more radical sites are produced, leading to the formation of graft copolymer. This accounts for the substantial increment in GR and GE up to a certain initiator concentration. However, the excessive increase in initiator concentration produces extra free radical species from the decomposition of APS and SBS to give the termination reaction with starch macroradicals or the growing polymer chain or a

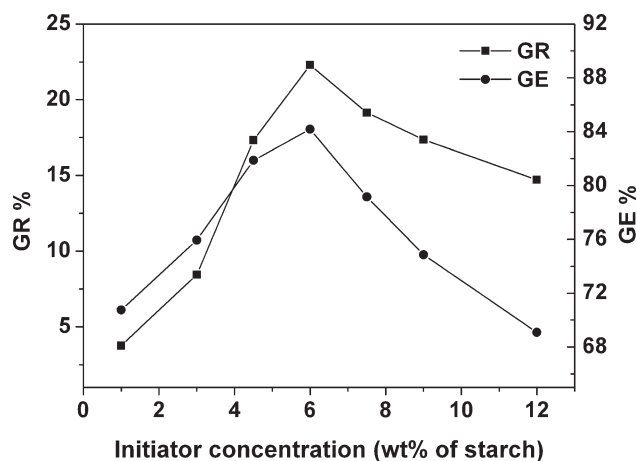


Figure 3. Effect of initiator concentration on graft polymerization.

combination reaction between them.¹⁷ Consequently, GR and GE decrease.

Structural Characterization and Physicochemical Properties

FT-IR Study. The FT-IR spectra of CS and GCS are shown in Figure 4. CS shows broad peak at 3385 cm^{-1} due to stretching vibration of O–H, a smaller peak at 2927 cm^{-1} is attributed to the C–H stretching vibration, and the bands peak at $1155\text{--}1017\text{ cm}^{-1}$ are assigned for C–O–C stretching vibration and 1417 cm^{-1} for C–N stretching vibration of cationic group.¹⁸ In case of GCS, N–H stretching band of $-\text{CONH}_2$ presents in AM, and O–H stretching band of hydroxyl group of starch overlaps with each other and leads to a peak at 3424 cm^{-1} . The absorption peaks at 1652 cm^{-1} , 1637 cm^{-1} , and 1455 cm^{-1} are attributed to C=O stretching vibration (amide-I), N–H bending vibration (amide-II), and C–N stretching vibration of the amide group.¹⁹ Furthermore, the carbonyl stretching located at 1735 cm^{-1} has clearly appeared, which is attributed to the ester group of HEMA and BA.²⁰ These results have confirmed the grafting process.

SEM Analysis. Figure 5 shows the SEM micrographs of CS and GCS. CS granules mostly exhibit integrated structure and smooth surface which are similar to raw corn starch. Slight rough and small holes observed on the surface of some CS granules are probably caused by the corrosion of alkaline reagent during the process of cationization. By contrast, granule configuration of GCS has been significantly changed. A polymeric layer has been observed coating on the granules, thus causing a wrinkle-like surface. The size of GCS granules increases, and some of the granules have cracked. By magnifying the image of cracked granules, the grafted polymers can be observed not only coating on the granule surface but also existing inside the granules. The reason could be that with microwave-heating effect, the starch granules swell and their structures become loose, thus enhancing the permeability for monomer molecules. As a result, the grafting copolymerization occurs not only on the surface of the granules, but also within the amorphous regions, even inside the crystalline regions. This phenomenon indicates that a combination of microwave irradiation and grafting copolymerization has altered and weakened the granular structure of starch.²¹

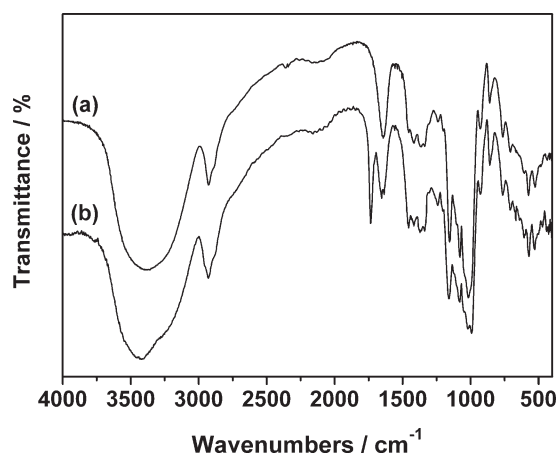


Figure 4. FT-IR spectra of (a) CS and (b) GCS.

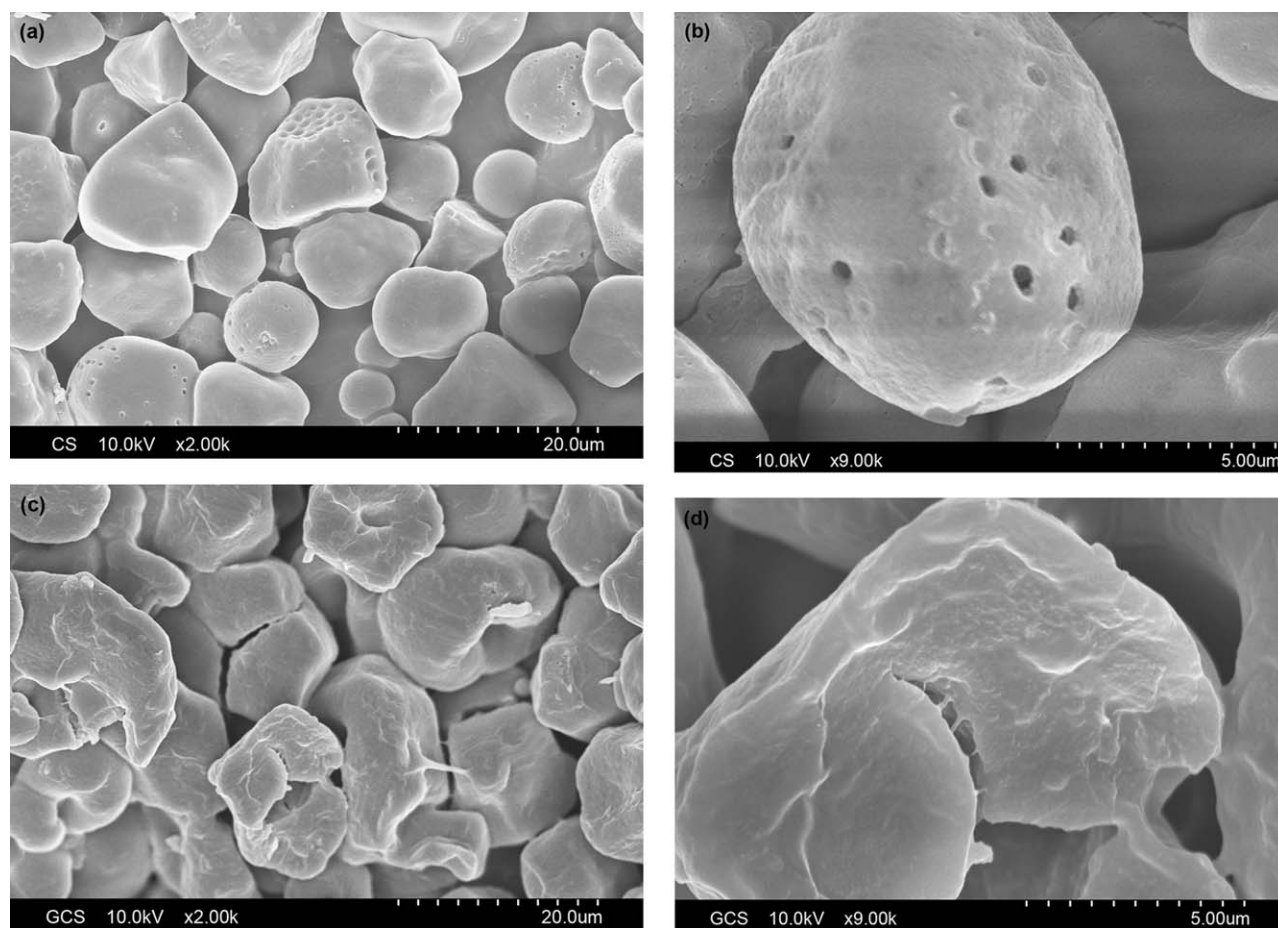


Figure 5. SEM micrographs of (a) CS 2000 \times , (b) CS 9000 \times , (c) GCS 2000 \times , (d) GCS 9000 \times .

X-Ray Diffraction. Starch is known to be semi-crystalline in nature due to the amylopectin fraction that exists in it. As seen in Figure 6, CS has diffraction peaks at 2θ 15.1 $^\circ$, 17.2 $^\circ$, 18.0 $^\circ$, and 23.0 $^\circ$, showing that CS maintains the diffraction patterns of cereal starch (A type structure). By contrast, the XRD pattern of GCS obviously changes, the diffraction intensity has reduced, and the peak shape has switched from spike to diffuse peaks, which indicates the decreased crystallinity. These phenomena are also attributed to the combination of microwave irradiation and grafting copolymerization. Firstly, in microwave field, the starch is heated and swells; the water molecules permeate into the granules, accelerated by microwave energy, and keep colliding with starch molecular chains not only in amorphous region but also on the surface of crystalline region. Some of the water molecules with higher motion velocity could enter the crystalline region and form hydrogen bonds with starch molecules, leading to the unwinding of starch double-helix structure and the destruction of crystalline structure. On the other hand, the grafted side chains introduced onto the starch backbone bring about a steric effect which reduces the formation of intermolecular hydrogen bonds and prevents the starch molecules from arranging orderly and forming crystalline structure. Following the reduction of crystal structure, some of the monomer molecules could permeate into the crystalline region and react with

starch molecules therein, thus further promoting the amorphization of starch.²² Under the interactions of both two factors, crystallinity of GCS significantly decreases. The results also evidence that the grafting copolymerization takes place both on the granular surface and inside the granular. Along with amorphous region, the crystalline region of starch is also involved in grafting; this is consistent with the results observed by SEM.

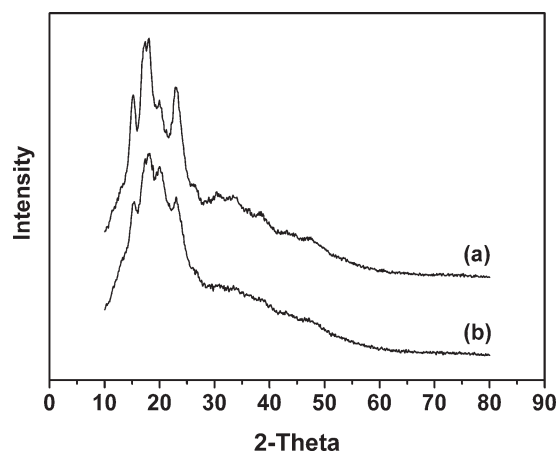


Figure 6. XRD pattern of (a) CS and (b) GCS.

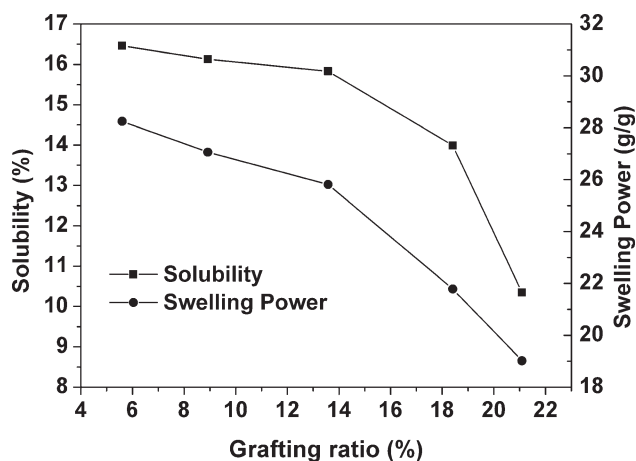


Figure 7. Swelling power and solubility of GCS.

Swelling Power and Solubility. Hydration capacity is the most critical physicochemical property of modified starch used as a sizing agent. Good solubility provides good permeability, wettability, as well as good fluidity for size. While higher swelling power is benefit of increasing the gelatinization properties, resisting retrogradation, stabilizing the paste, and improving the viscosity properties and adhesiveness, the solubility and swelling of starch is influenced by its granular structure, crystallization degree, and functional groups. As seen in Figure 7, the swelling power and solubility of GCS both increase by contrast with untreated CS ($S\%$ and SP of CS is, respectively, 15.22% and 21.08 g g^{-1}) but decrease gradually with the raise of GR. This is because the hydration capacity of GCS is influenced by both positive and negative sides. On one hand, some of the starch macromolecules degrade into soluble smaller molecules due to microwave irradiation, and in addition, the steric hindrance of introduced grafting side chains disrupts the hydrogen-bonding association and reduces the intermolecular force of starch molecules, resulting in the destruction of crystalline structure and the disorganization of granules, which facilitates the percolation of water within the granules and the forming of hydrogen bonds between starch hydroxyl groups and water molecules; thus, the solubility and swelling power of GCS increase.²³ On

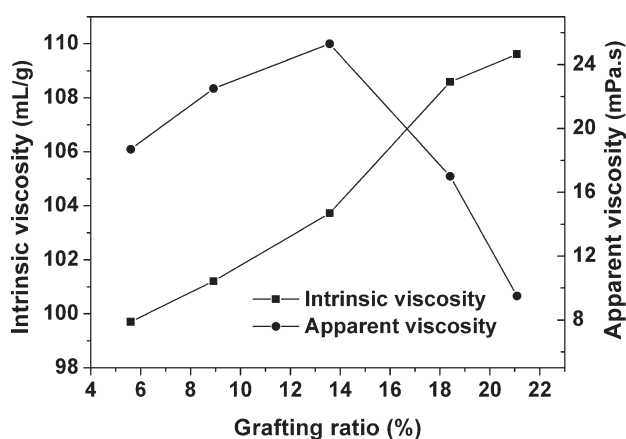


Figure 8. Intrinsic viscosity and apparent viscosity of GCS.

the other hand, however, the introduced grafting side chains on starch also bring about hydrophobicity, and with the raise of GR, the hydrophobicity of GCS becomes more and more obvious; therefore, the swelling and solubility gradually decrease. Since the purpose of the study is to increase the lipophilicity of GCS while also ensure its water-solubility, the effect of the GR on the solubility and swelling must be investigated. According to the experimental results, it can thus be concluded that within a certain range of GR (<15%), the structural disintegration effects of grafting copolymerization on the granules can overcome the negative impacts on starch hydration capacity which was caused by the introduced hydrophobic grafting side chains.

Rheological Properties. The rheological behavior is another important property for starch derivatives used in textile sizing. Good rheological property provides higher fluidity for starch size, thus benefiting for its wetting and spreading on the fiber surface, but excessively low viscosity can cause the decrease of cohesion of sizing film. The intrinsic viscosity $[\eta]$ of starch depends mainly on its relative molecular weight, molecular dimension, and molecular geometries. As shown in Figure 8, after microwave irradiation, the $[\eta]$ and η_a of GCS reduce (intrinsic viscosity and apparent viscosity of CS is, respectively, 157.13 mL g^{-1} and 585 mPa s). This is for that in microwave field, high-frequency vibration of starch macromolecules occurs, leading to the breakage of glycosidic bonds and the decrease of polymerization degree. Meanwhile, branching degree of starch macromolecules also decreases with some of the amylopectin degrade and turn into amylose.²⁴ As a result, the $[\eta]$ and η_a reduce. Further, the $[\eta]$ increases with the raise of GR, since higher GR translates to higher molecular weight, and the introduced graft side chains bring more branch points onto the starch chain backbone, which causes the starch molecular geometries tending to be complicated and results in the $[\eta]$ increasing. Moreover, it is interesting to notice that the η_a increases firstly and then decreases with the raise of GR. The reason would be for that in addition to molecular weight and molecular dimension, the η_a of starch also depends on its swelling power. As GR further rises, the hydrophobicity of starch increases, causing a reduced swelling ability and difficulty in gelatinization; consequently, the η_a of starch decreases.

Application Studies of Textile Warp Sizing

As shown in Table I, mechanical properties of yarns sized with GCS are obviously enhanced compared with yarns sized with CS; the tensile strength and abrasion resistance indexes of GCS sized yarn even exceed those sized with PVA. Since GCS has

Table I. Sizing Performances of CS, PVA, and GCS

	Tensile strength enhancement (%)	Elongation reduction (%)	Abrasion resistance enhancement (%)	Hairiness reduction (%)
CS	16.08	19.17	155.82	90.73
PVA	22.5	14.89	216.59	96.24
GCS	23.81	15.62	248.17	95.58

Table II. Biodegradability indexes of RS, CS, PVA, and GCS

	COD _{cr} (mg L ⁻¹)	BOD ₅ (mg L ⁻¹)	BOD ₅ /COD _{cr}
RS	823	270	0.328
CS	837	267	0.319
PVA	1480	13	0.009
GCS	926	244	0.263

relatively high swelling ability, high adhesion to polyester/cotton blended yarn, and moderate viscosity, it has better film-forming ability, sizing film integrity, and covering capability to yarn, which is benefit of reducing yarn hairiness. Meanwhile, the introduction of grafted side chains restrains the intermolecular hydrogen bonding of starch, which plays a role in plasticization of size adhesive layer.^{25,26} Hence, the tenacity of adhesive layer and the elongation at break of yarn are increased. Furthermore, higher solubility and better rheological property of GCS give it better permeability and wettability, which favor the penetration of sizing agent into yarns, hence increasing the adhesion and cohesion between fibers. Therefore, the GCS sized yarns could bear more external mechanical forces after the surface film is destroyed, as a result the yarn tensile strength and abrasion resistance are significantly improved.

Biodegradation Analysis

PVA has been widely considered “impurity” size for the desizing waste water of which is non-biodegradable and could cause serious environmental problem. For this reason, as a potential substitute for PVA, the biodegradability of GCS has become an important indicator. Starch biodegradability could be measured by BOD₅/COD_{cr} ratio, where higher BOD₅/COD_{cr} value means better biodegradation. Table II shows that biodegradation of CS is fairly near that of RS, while BOD₅/COD_{cr} of PVA is only 0.009, which means it is almost impossible to be biodegraded in a short time. Compared with CS, the biodegradability of GCS slightly drops, because the grafted polymer side chains are presumed to make up the hardly biodegraded part of GCS. But the BOD₅/COD_{cr} value of GCS is above 0.25, so it could still classified as a biodegradable sizing agent,²⁷ which means it has an incomparable advantage in environmental protection over PVA.

CONCLUSION

A novel biopolymer-based sizing agent GCS was synthesized through grafting polymerization of AM, HEMA, and BA onto CS. Microwave irradiation had significantly accelerated the reactions. The optimum conditions worked out on the basis of present work was exposure time of 25 min, polymerization temperature at 55°C, and an initiator concentration of 6 wt % of starch. Products of different grafting ratios could be obtained by adjusting the monomer additions. The continuous microwave output mode is adopted in the study instead of pulse microwave so as to avoid the fluctuations of system temperature and protect the organic molecule structure. Hence, the homogeneity and reproducibility of the grafting modification could be ensured.

Physicochemical properties of GCS were improved significantly, and mechanisms that these properties affect the sizing performances of GCS were studied. The enhanced rheological property provided higher fluidity and permeability for GCS size. The disintegration of crystalline region and the weakening of starch granule resulted in the raise of swelling capacity, which increased the film-forming ability and coverage performance of size. Meanwhile, the introduced grafted side chain reduced the intermolecular forces of starch, enhanced the macromolecules flexibility, and thus increased wettability and spreadability of size on fiber surface. It could be concluded that the modified physicochemical properties of GCS played a critical role in its sizing performance improvement.

In the application as a sizing agent in textile, yarns sized with GCS obtained more reinforced mechanical properties than those sized with CS, and some of the indicators such as tensile strength and abrasion resistance even surpassed over those of PVA. Since these two indicators were considered the most important sizing properties which directly determine the weavability of yarns, GCS could become an ideal substitute of PVA in fabric/yarn sizing. Together with the good biodegradation, GCS could be expected to have a promising application in textile industry.

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