마이크로웨이브를 이용한 그래프트된 전분의 합성과 특성분석 및 응용

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Synthesis, Characterization and Application of Grafted Starch Prepared with Microwave-assistance

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Abstract: Butyl acrylate grafted starch (St-*g*-BA) was made by the method of microwave-assisted synthesis, involving the combination of microwave irradiation and a chemical free radical initiator (H_2O_2-Fe^{2+}) to initiate the grafting reaction. The optimal conditions for the graft copolymerization with respect to reaction microwave power, exposure time and type of initiator were investigated. Under the optimal conditions, the percent grafting and grafting efficiency were 26.2% and 85.9%, respectively. The grafted starch was characterized by using Fourier transform infrared spectroscopy and scanning electron microscopy. The St-*g*-BA exhibited good tensile strength, elongation at break and abrasion resistance. Therefore, it is suggested this biomaterial could be used in various industrial applications such as textile sizing and food packaging.

Keywords: microwave irradiation, graft, starch, butyl acrylate, textile sizing.

Introduction

In recent years environmental pollution caused by poly(vinyl alcohol) (PVA), which has been widely used as a textile sizing agent, has become a great concern. In most countries it has been proposed to limit the use of PVA in textile mills. Therefore, the research and development of new textile sizing agents have attracted more and more attention.[1-8]

Having a source-dependent structure, starch is a low-cost biopolymer which is abundantly available. In recent years there has been an increasing interest in the utilization of it as a renewable raw material for industrial applications because it is inexpensive and environmentally-friendly with numerous hydroxyl groups that can be chemically modified, for instance, to design textile sizing agents,[2,5-7] food packaging, and for glass fiber sizing. Some starch is incorporated into plastics to enhance environmental fragmentation and degradation.

Hebeish *et al*. had investigated the sizing properties of starch derived from pre-oxidized corn starch.[9] Results showed that the oxidized corn starch enhanced the tensile strength and decreased the elongation at break of light cotton fabric compared with oxidized corn starch. Study on the adhesion of starch and poly(acrylic acid) was carried out by Li, Zhu, and Pan,[10] it was found that the situation inevitably produces electrostatic repulsion at adhesive layer-fiber interfaces and may damage the adhesion of starch to fibers. However, due to the lack of hydrophobic groups, starch still lacks enough adhesion to synthetic fibers. As an example of its use as a textile sizing agent, starch-*g*-methacrylonitrile was obtained by grafting methacrylonitrile to starch with potassium monopersulfate as initiator and the performance of such grafted starch was greatly enhanced. Fabric samples sized with the polymethacrylic acid pregelled starch graft copolymers acquired higher tensile strength and abrasion resistance than those sized with non-grafted pregelled starch, while the elongation at break was unaltered.[7] Zhang *et al*. prepared a poly(acrylic acid) grafted

starch size with good permeability in fibers. This sizing possessed good breaking strength, elongation, and abrasive resistance,[8] yielding comfortable fuzzy yarns.

Grafting is a method wherein monomers are covalently bonded onto polymer chain backbones. Grafting has been utilized as an important technique for modifying the physical and chemical properties of natural polysaccharides. Various techniques of graft copolymerization, such as irradiation, chemical initiation, etc., have been reported in the literature.[2,7,8,11]

Microwave radiation is an efficient source of thermal energy, providing fast and uniform heating to create free radical sites on polysaccharide backbones where the grafting takes place. Consequently, under microwave dielectric heating, numerous molecules become energized, and this usually results in high reaction rates.[12] Using microwave irradiation, grafting and homopolymerization have been studied without initiators.[13-15] The microwave-assisted technique uses a combination of microwave energy and chemical-free radical initiator to initiate the grafting reaction.[16-19] The details of the microwave-based synthesis of grafted polysaccharide have been well described in the literature.[20]

Many studies have reported the microwave assisted chemical modifications of starch, such as methyl starch,[21] starch acetates,[22,23] etc. However, we know of no reports about the grafting of vinyl monomers onto starch by microwave-assisted modification.

The main objective of this work was to carry out graft copolymerization of butyl acrylate onto starch using an assisted microwave irradiation technique. We also further explored the application of starch and butyl acrylate grafted starch as textile sizing agents for the textile industry.

Experimental

Materials. Corn starch, iron (II) sulfate (initiator), and hydrogen peroxide were obtained from Aldrich Chemical Co. (U.S.A.). Dimethyl sulfoxide (DMSO), n-butyl acrylate (BA) and sodium bisulfate (SBS) were purchased from Sigma Co. (U.S.A.). Benzoyl peroxide (BPO), ammonium persulfate (APS), ceric ammonium nitrate (CAN) as initiator, ethanol and acetone were purchased from Tokyo Chemical Industry Co. Ltd. (Japan). All the chemicals were used as-received without further purification.

Graft Copolymerization of Starch under Microwave Irradiation. 5.0 g of starch was dissolved in 100 mL distilled water. Desired amounts of BA and 2 mL of DMSO, were dis-

solved in 10 mL water and then added to the starch solution. As an interface agent, DMSO influences the permeation and contact of the reactants with each other. It is better at absorbing microwave. Therefore, DMSO can help the reaction of starch and n-butyl acrylate. They were mixed well and transferred to an open-necked flask (500 mL), H_2O_2-Fe^{2+} was added and the dispersion was stirred at the speed of 40 r/min for good-mixing. The open-necked flask was subsequently placed on the turntable of a microwave oven. Then, microwave irradiation, at 30-150 W of power was applied for 5 min first. The irradiation process lasted for 35 min, with the alternation of 5 min on with 5 min off. Therefore, there was a total of 20 min irradiation.

The primary grafted products were obtained and purified with acetone for 12 h with a Soxhlet extraction device to remove homopolymers. The resulting precipitate was dried, pulverized and sieved, and then dried in air oven to a constant weight to obtain the pure graft copolymer. The percentage and efficiency of grafting were calculated using the following relation.[24]

$$G = \%\ grafting = (W_1 - W_0)/W_1 \times 100\% \tag{1}$$
$$E = \%\ efficiency = (W_1 - W_0)/W_2 \times 100\% \tag{2}$$

where, W_1, W_0, and W_2 denote, respectively, the weight of the grafted starch, the weight of the starch, and the weight of the butyl acrylate used.

FTIR Analysis. The Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra of starch and the St-g-BA were recorded at room temperature with an FTIR spectrometer (FTS 175C, Bio-Rad Laboratories Inc., U.S.A.) in the range of 4000-500 cm^{-1} at the resolution of 2 cm^{-1}.

Scanning Electron Microscopy. Starch and St-g-BA were characterised by using scanning electron microscopy (SEM, JEM-1010, JEOL, Japan). The samples were pressed into thin slices and fractured in liquid nitrogen. The fracture surface was sputtered with gold for 5 min in vacuum before observation.
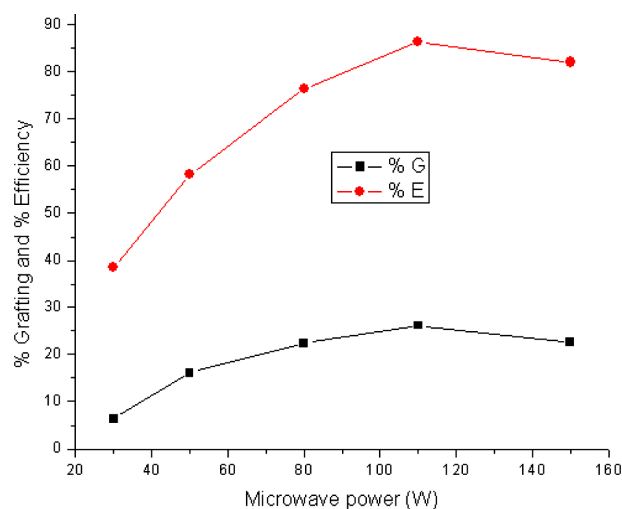
Tensile Testing. The tensile strength and the elongation were measured using a universal testing machine (Instron 4200, Instron, U.S.A.) according to ASTM procedure D-2256. The testing of the abrasion resistance was carried with a Zweigle abrasion tester (Zweigle, Germany). Polyester/cotton blended yarn (T/C 60/40) was sized by dipping in the cooked starch and the modified St-g-BA solution (6% w/v) at 90 °C for 5 min and dried in an oven at 100 °C for 3 min. The sized yarns were finally kept at ambient conditions for at least 48 h

before use. The tensile strength, elongation at break and abrasion resistance were measured five times for each sample and averaged.

Results and Discussion

Mechanism of Grafting. The mechanism of microwave-assisted grafting is depicted in Scheme 1. Grafting was carried out in aqueous medium, with the water absorbing the microwave energy. This results in dielectric heating of the reaction medium. Microwaves have also been reported to have the special effect of lowering the Gibbs energy of activation of the reactions.[25] The free radical sites thus created on the starch backbone (by H_2O_2-Fe^{2+}) and on the BA (by microwave irradiation) interact through usual free radical reaction mechanisms, to yield the graft copolymer.

Effect of Microwave Power. The reaction was carried out using 30 to 150 W to optimize the microwave power (Figure 1). The G and E increased up to 110 W microwave power at the fixed monomer concentration (35%) and for the fixed exposure time of 20 min. The increase in %G and %E with the increase of microwave power to 110 W may be due to the for-

Initiation

$$H_2O_2 + Fe^{2+} \rightarrow HO\cdot + HO^- + Fe^{3+}$$

$$HO\cdot + M \rightarrow M\cdot$$

$$HO\cdot + St\text{–}OH \rightarrow H_2O + St\text{–}O\cdot$$

$$M + St\text{–}O\cdot \rightarrow St\text{–}OM\cdot$$

Propagation

$$St\text{–}O\cdot + M \rightarrow St\text{–}OM\cdot$$

$$St\text{–}OM\cdot + M \rightarrow St\text{–}OMM\cdot$$

$$St\text{–}OMM_{n-1} + M \rightarrow St\text{–}OM_n\cdot$$

Termination

$$St\text{–}OM_n\cdot + St\text{–}OM_n\cdot \rightarrow St\text{–}OM_n\,M_nO\text{-}St \text{ (Grafted copolymer)}$$

where St-OH is the starch, St-O· is starch with a free radical site, and M is the monomer.

Scheme 1. Schematic representation of the microwave assisted synthesis of St-*g*-BA.

Figure 1. Effect of microwave power on % grafting (%G) and % efficiency (%E) at 35 min, H_2O_2-Fe^{2+} (4.0×10^{-3} M).

mation of more $M_n\cdot$ and St-O· radicals, resulting in the availability of more grafting sites and thus higher grafting. The decrease in the grafting when the microwave power was increased beyond 110 W may be due to the microwave energy is transformed into heat. Initiator decomposed rapidly at a higher temperature. The reactions between monomers and primary radicals could result in PBA homopolymers and thus leaded to low graft ratio and graft efficiency.

Effect of Exposure Time. It is obvious from Figure 2 that with the increase in polymerization time at 110 W, the percentage grafting increased and reached a maximum value at 35 min at the fixed monomer concentration, after which it decreased. As above, this may be due to the fact that beyond the exposure time of 35 min, 5 min on, 5 min off.

This might be due to the microwave energy is transformed into heat. When the temperature was increased, the graft ratio and graft efficiency of the reaction showed a little decline. This was due to that initiator decomposed rapidly at a high temperature and more collisions occurred between primary radicals and BA or between two radicals. These collisions brought about PBA homopolymers or radicals termination. Both cases could result in the decrease of graft ratio. Figure 2(b) showed the GPC analyses to monitor the changes of the molecular weight the distribution during the microwave irradiation.

Effect of Different Initiator Systems. In order to investigate the property of the initiator on graft copolymer, we selected three types of initiators: oil-soluble initiators, water-soluble initiators, and complex initiators. The effect of initiators on grafting was studied with an initiator concentration
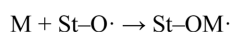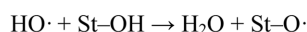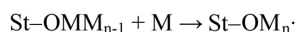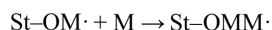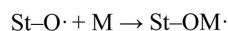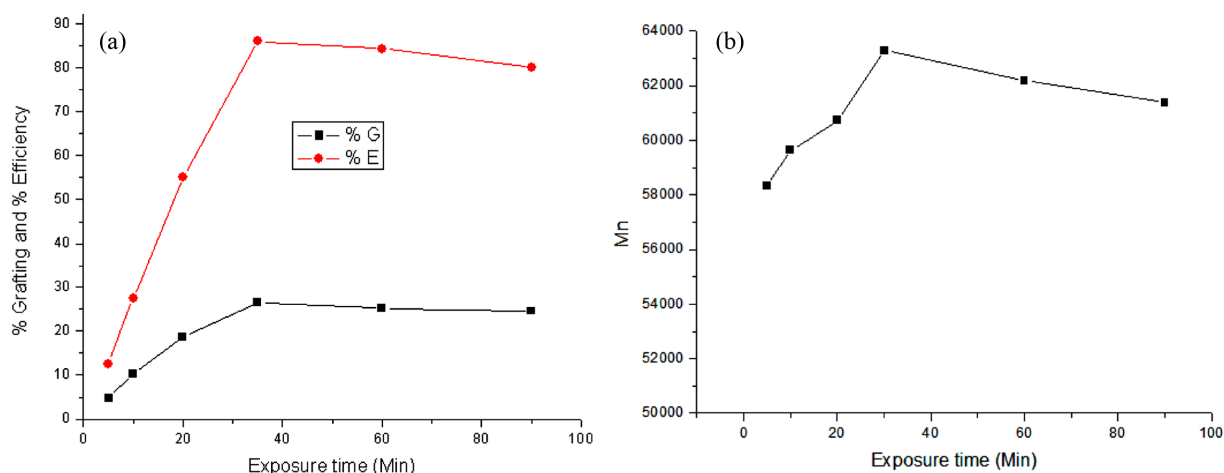
Figure 2. Effect of exposure time on (a) % grafting and % efficiency; (b) Molecular weight of St-*g*-BA at 110 W microwave power, H_2O_2-Fe^{2+} (4.0×10^{-3} M).

**Table 1. Effect of Initiators for Graft Copolymer Systems at 110 W Microwave Power, 35 min**

Initiator	BPO	APS	CAN	H_2O_2-Fe^{2+}	APS-BPO	Ce^{4+}-BPO	Ce^{4+}-APS
Grafting (%)	3.02	7.43	7.92	9.72	6.31	6.56	8.06
Efficiency (%)	34.28	66.11	67.35	72.21	57.65	61.33	70.47

*Water soluble: APS, CAN, H_2O_2-Fe^{2+}, **Oil soluble: BPO, ***Complex initiators: Ce^{4+}-APS, Ce^{4+}-BPO, APS-BPO.

of 4.0×10^{-3} M and fixed concentrations of BA (1.0 g), and starch (5.0 g) in 100 mL of water at 110 W microwave power for 35 min (intermittent irradiation, 5 min on, 5 min off) exposure. The effect of the type of initiators on the % G and % E is shown in Table 1. It is shown that the water-soluble initiators were better than oil soluble initiators. The degree of grafting and the efficiency of H_2O_2-Fe^{2+} were the best of the water-soluble initiator systems. On the one hand, starch is water-soluble, so the compatibility was good with the water-soluble initiator systems and the effect of grafting was better. On the other hand, the Fe^{2+} of H_2O_2-Fe^{2+} system was recycled, and the inhibition of Fe^{2+} to free radicals led to the highest graft ratio for this system. Finally, the primary radicals generated from H_2O_2-Fe^{2+} are OH· owing to stronger electronegativity shown by OH·. Thus OH· can abstract hydrogen atoms more easily and more starch macroradicals were formed, then those macroradicals polymerized with butyl acrylate.[26] As a result, the grafting efficiency and ratio of the graft copolymers using H_2O_2-Fe^{2+} as initiator were higher than that of the other initiators. Therefore, H_2O_2-Fe^{2+} was chosen as the initiator for further studies of the graft copolymerization of starch with BA so as to increase the efficiency and the ratio.

**Effect of Monomer Concentration.** Variations in both the
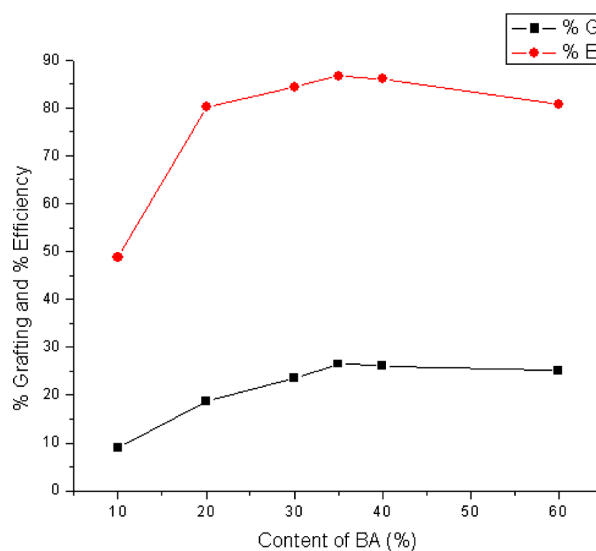
Figure 3. Effect of monomer concentration on % grafting and % efficiency at 110 W microwave power, H_2O_2-Fe^{2+} (4.0×10^{-3} M), 35 min polymerization time.

grafting and efficiency with variations in BA/starch ratio are shown in Figure 3. The efficiency increased slightly by incorporating BA up to 35%. However, further increase in the BA content resulted in a deterioration of efficiency and grafting.

The grafting also increased steadily as BA content increased up to 35% and then decreased slightly. We suggest this is because once the graft copolymer radical has formed, the excess monomer will shield the graft copolymer, which may decrease the rate of graft copolymerization. In addition to this, with excess monomer concentration, the competing homopolymer formation reaction becomes significant, leading to depletion of the monomer and reduction in the percentage of efficiency and grafting.

FTIR Analysis. The IR spectra of pure starch and St-*g*-BA are shown in Figure 4. In the starch spectrum, a broad, strong absorption band at 3384 cm^{-1}, due to the stretching vibrations of O-H, and a peak at 2923 cm^{-1} (C-H stretching) were present. Peaks at 1650 cm^{-1} are assigned to C=O and at 1023 cm^{-1} to C-O-C stretching vibrations. A comparison of curves a and b in
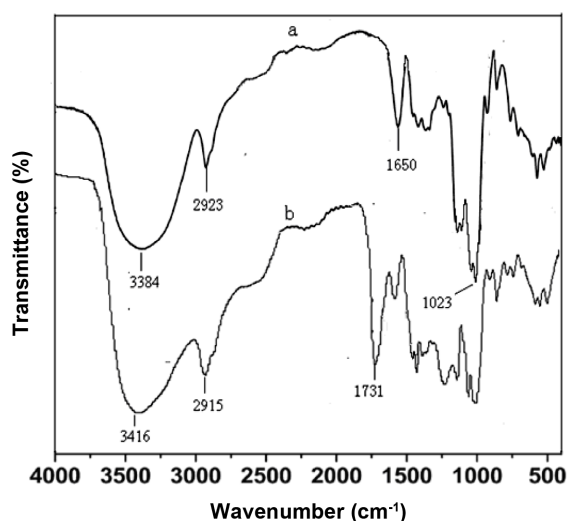
Figure 4 indicated that the grafted starch had a new, characteristic absorption peak of carbonyl groups at 1731 cm^{-1}, but the new peak was not found on the starch spectrum. These results confirmed that a grafted starch copolymer was obtained.

SEM Observations. SEM micrographs of non-grafted starch and grafted starch are shown in Figures 5(a) and 5(b), respectively. The pure starch granules were of different sizes with oval particle shape, and the surfaces were very smooth, as shown in Figure 5(a).

After the BA was partly grafted onto the starch, however, there were changes in the morphological structure of the grafted starch. As shown in Figure 5(b), the surface of the particles of the grafted starch was rough and some holes were distributed on the surface as well. This result indicated that the grafting reaction occurred not only on the surface of the starch particle, but also on the molecular chains in the initiator of the corn starch.

Application Studies as a Textile Warp Sizing. Tensile strength, extension and abrasion resistance of the sized yarns are critically important for weavability in fabric manufacturing. The work presented in this section was aimed at applying the newly tailored polymeric grafted starch products as the sizing of textiles and testing their suitability as sizing agents of yarns. Table 2 shows the important mechanical properties, that is, tensile strength, elongation at break and abrasion resistance of yarns sized with starch, and St-*g*-BA. Mechanical properties of the yarns sized with St-*g*-BA were obviously enhanced compared with the yarns sized with a modified starch. The graft polymerization of BA to the chemically modify starch greatly improved the sizability irrespective of the backbone of the starch as evidenced by the data.

Figure 4. FTIR spectra of (a) starch; (b) St-*g*-BA.
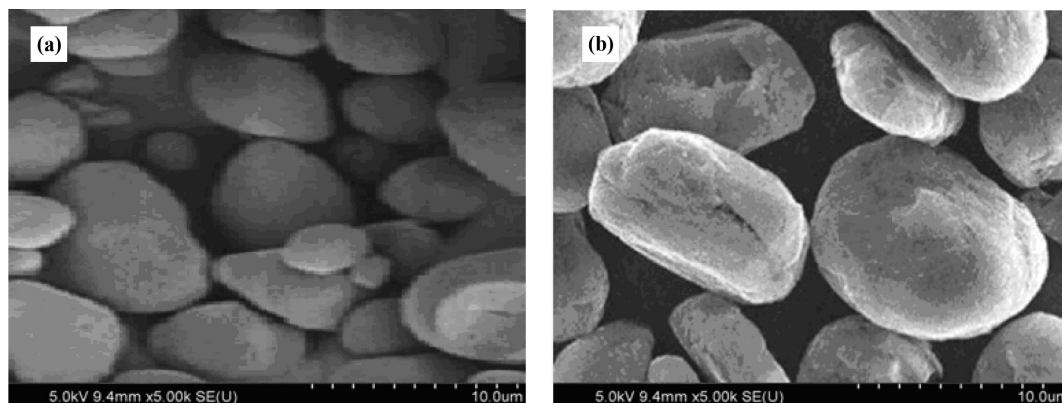
Figure 5. SEM micrographs of (a) starch; (b) St-*g*-BA.

Table 2. Mechanical Properties and Abrasion Resistance of Sizing Performances of Starch and St-*g*-BA

	Tensile strength enhancement (%)	Elongation reduction (%)	Abrasion resistance enhancement (%)
Starch	16.22±0.32	18.96±0.18	157.76±1.15
St-*g*-BA	24.43±0.41	15.17±0.09	254.38±2.43

Table 2 reveals that the yarns sized with the modified starch under investigation exhibited relatively higher elongation at break than the yarns sized with the pure starches. The introduction of the grafted side chains restrained the intermolecular hydrogen bonding of starch, which plays a role in increasing the plasticization of their sizing adhesive layer, increasing its tenacity.[27] As a result, the elongation at break of the yarn increased. Starch and St-*g*-BA are permanent sizing through washing. Further, the abrasion resistance enhancement of St-*g*-BA sized yarns was also higher than that of the starch sized yarns, being 254.38% against 157.76% for starch sized yarns.

Conclusions

St-*g*-BA was synthesized using a microwave assisted reaction, and small concentration of initiator (H_2O_2-Fe^{2+}). The % grafting and % efficiency were found to be highest with in exposure time of 35 min and with 110 W microwave power. The percentage grafting and the percentage efficiency for the BA/starch ratio of 35/65 were found to be higher as compared to other ratios. The yarn samples sized with the BA grafted starch exhibited good tensile strength, elongation at break, and good abrasion resistance. St-*g*-BA could be expected to have application in the textile industry.

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