

Carbamoyl Ethylation of Starch for Enhancing the Adhesion Capacity to Fibers

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ABSTRACT: The influence of starch carbamoylethylation upon the adhesion capability of starch to pure cotton, all polyester, and polyester/cotton blend fiber substrates were investigated. The carbamoylethyl starch was prepared by the reaction of starch with acrylamide in an aqueous dispersion. The capability was evaluated in terms of the maximum strength and work-to-break of a roving impregnated with the starch pastes. The mechanical behaviors of the adhesive layers were estimated through a method by casting starch films and then by measuring their behaviors under controlled condition. It was found that the carbamoylethylation is an effective means for enhancing the adhesion of starch to

fibers. No matter what type of the fibers is used, the adhesion capability obviously enhances compared with those of unmodified starch, even if the degree of substitution is at a very low level. The capacity increases steadily as the modification extent increases. Moreover, the experimental results are also discussed and analyzed especially through the failure type, internal stress, stress concentration, and mechanical behaviors of the adhesive layers among fibers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2763–2768, 2007

Key words: carbamoylethylation; starch; adhesion; fiber; film

INTRODUCTION

Starch possesses valuable behaviors such as biodegradable character, abundant sources, less pollution to environment, low price, a certain extent of characteristics like adhesion capacity and film-forming ability, etc. A large amount of starch is used as a sizing agent for warp sizing and paper making every year. However, starch is a polysaccharide consisting of anhydroglucose units that contain three hydroxyls and are linked together through α -D-glucosidic bonds.¹ The cyclic structure and numerous hydroxyls make starch material show brittleness and rigidity. For this reason, starch film cast is inflexible and the adhesion to fibers is never to be good enough.

Whether in textile industry as warp sizing agents or in paper making area as wet-end additives, surface sizing agents, and coating binders, sufficient adhesion to fibers is perceived to be a valuable behavior and essential feature for every kind of sizing agents.^{2,3} The adhesion is capable of enhancing the strength of sized yarns and papers. Such enhancements can be achieved by gluing

fibers together through the adhesion of sizing agents to fibers.^{2,4} In warp sizing operation in textile industry, the adhesion diminishes yarn hairiness by gluing the hairiness back onto the body of the yarns.² Consequently, the adhesion capacity influences the physical and mechanical properties of sized goods and determines how heavily a warp yarn⁴ or paper must be sized. For this reason, the behavior has already received increasing attention recently. A great deal of research work has been done.^{4–6}

Chemical modification provides new opportunity to improve intrinsic defects of native starch. Currently, the research on improving the adhesion of starch to fibers is focused on chemical modification. Several techniques have been adopted to introduce chemical groups or to make some changes to starch molecules to enhance the adhesion.^{2,6} It is as well to emphasize that carbamoylethyl modification also constitutes a powerful means for the variation of intrinsic behaviors for natural polymers. Sharma, Gupta, and their coworkers studied the carbamoylethylation of some gums such as cassia tora gum, cassia occidentalis seed gum, and guar gum, and confirmed that the carbamoylethylated gums show non-Newtonian pseudoplastic behavior.^{7–9}

Carbamoylethyl modification of starch can be achieved by the reaction of starch with acrylamide in a base-catalyzed, Michael-type addition to etherify with amide ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CONH}_2$) substituents.¹ Rupinski and Brzozowski explored the effects

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of temperature, reaction time, and acrylamide concentration on the degree of substitution (DS) of starch.¹⁰ The modified starch shows positive effect in raising the mechanical behaviors of sized cotton yarns when applied to sizing trials.¹¹ Carbamoylethyl group is a polar one and is capable of absorbing water. The steric hindrance effect of the groups and the water absorbed enhance the flexibility of the adhesive layers among fibers. On the other hand, carbamoylethyl group is hydrophilic and is able to increase the dispersibility of starch in aqueous paste. Furthermore, the groups might not only increase the van der Waals force between carbamoylethyl starch and polyester fiber, but also form hydrogen bonding with cellulose fibers. Based on above analysis, both adhesive and cohesive failure would occur only under higher applied forces, and the adhesion of starch to fibers could expect to be improved by the modification. Is the carbamoylethylation really able to enhance the adhesion capacity? How does the adhesion change as the modification extent increase? Unfortunately, little was known about these questions and no research took these problems into serious consideration. For this reason, we made an effort toward clarifying the effect of the carbamoylethylation on the adhesion to fibers. It is necessary and interesting to discuss and analyze the influences of the modification upon the adhesion from the viewpoint of the adhesive and cohesive failures.

EXPERIMENTAL

Materials and reagents

Commercial cornstarch with a viscosity of 41 mPa s was supplied by The Yixing Starch Factory (Jiangsu Province, China). Before use, the starch was purified by the method described in our former publication.¹² Acrylamide was of a chemically pure grade and was obtained from The National Chemical Reagents. Sodium hydroxide and anhydrous sodium sulfate were all chemically pure grades and used as received.

Pure cotton roving (456 tex, twist factor: 128) was obtained from Qingfeng Textile Co. Ltd (Jiangsu province, China). All polyester roving (361 tex, twist factor: 49.8) and polyester/cotton blend roving (352 tex, twist factor: 56.8) were supplied by Yizheng Co. Ltd of Chemical Fiber (Jiangsu province, China). The parameters of polyester and cotton fibers in all-polyester and pure cotton rovings were 38 mm × 1.73 dtex and 27.44 mm × 1.91 dtex, respectively. And in polyester/cotton roving, the parameters were 38 mm × 1.73 dtex for polyester fibers and 29.0 mm × 1.67 dtex for cotton ones.

Synthesis of carbamoylethyl starch

The refined cornstarch was hydrolyzed to reduce the viscosity before use. The acidification was carried out by dispersing 900 g (dry weight) starch in 1350 mL distilled water. After having heated the mixture to 50°C, 80 mL of 2M HCl was added and the dispersion was stirred at 50°C for 1.5 h. The product was neutralized with 0.8% NaOH solution (w/w) to pH 6–7, filtered, washed thoroughly with distilled water, dried at 60°C, ground, and sieved for passing a 100-meshed sieve. Apparent viscosity and viscosity stability of the acidified starch were 18 mPa s and 91.7%, respectively.

One hundred thirty grams (dry weight) of the acidified cornstarch was dispersed in 264 mL of distilled water containing 1.3 g sodium hydroxide and 6.5 g anhydrous sodium sulfate. The pH value of the dispersion obtained was 9 and the dispersion was transferred into a 500-mL three-necked flask that was immersed in a thermostatic water bath. A certain amount of acrylamide was dissolved in 20 mL distilled water and the solution was added into the flask. The reaction was carried out under continuous stirring at 45°C for 24 h. Then, the products were neutralized with 0.5M HCl, filtered, washed with ethanol/water mixture (volume ratio 70 : 30) three times, and then with pure ethanol one time. Finally, the modified starch was dried at 60°C. A series of carbamoylethyl starch with different DS were prepared by changing the amount of acrylamide used.

Characterization of carbamoylethyl starch

The DS of carbamoylethyl starch was determined by measuring the nitrogen content of the starch with Kjeldahl method.¹³ The DS was calculated as follows:

$$DS = \frac{162(N - N_0)}{1400 - 71(N - N_0)} \quad (1)$$

where $N_0(\%)$ and $N(\%)$ were the nitrogen contents of purified and carbamoylethyl starch, respectively.

Apparent viscosity of the starch samples were measured as follow: the starch was dispersed with distilled water to form 6% dispersion. The dispersion was heated to 95°C and maintained at the temperature for 1 h under stirring. Then, apparent viscosity of starch paste was measured by a NDJ-79 rotary viscometer at a shear rate of 2028 s⁻¹.

The viscosity stability indicates the stability in value of apparent viscosity of starch paste over a period of up to 2 h at 95°C under mechanical stirring. The determination was carried out over a period from 1–3 h after starch gelatinization. Meanwhile,

the viscosity readings were taken every 30 min. The stability was calculated from the eq. (2):

$$\text{Viscosity stability of starch paste (\%)} \\ = \left(1 - \frac{v_{\max} - v_{\min}}{v}\right) \times 100\% \quad (2)$$

where v_{\max} and v_{\min} were the maximum and minimum of the viscosity measured over the period, respectively. v was the apparent viscosity of starch.

Measurement of the adhesion

The adhesion of starch to fibers was measured by impregnating roving with a 1% starch paste (w/w) and handing the sized roving to drawing test to failure. It was the failure loads or mechanical behaviors that were adopted to exhibit the adhesion capacity of starch to fibers. Generally, the behaviors adopted include the maximum strength (S_m), breaking extension (E_b), and work-to-break (W_b). S_m denotes the bonding strength of sizing agents to fibers, and W_b indicates an ability of the roving to resist drawing break by bonding.^{2,3,5} Therefore, the adhesion capacity can be easily measured and evaluated by the indexes. The bigger the value, the better is the adhesion.

The impregnation of roving with starch paste was carried out as follows: 22.0 g (dry weight) of starch was dispersed into 2178 mL of distilled water. The dispersion was heated to 95°C and maintained at the temperature under mechanical stirring for 60 min. Then the roving that had been carefully wound onto a special frame² was impregnated with the paste for 5 min at 95°C. Finally, the impregnated roving samples were hung, dried in air, and collected for the following drawing test.

After the samples had been kept in an constant temperature and humidity room for at least 24 h under 65% relative humidity and 20°C, the maximum strength, breaking extension, and work-to-break of the roving samples were measured on a BZ2.5/TNIS Zwick Material Tester with an initial chuck-distance of 100 mm and a drawing speed of 50 mm/min under the same humidity and temperature. For each case, the strength, extension, and work reported were the average of 20 successful tests with which the abnormal values had been rejected by statistical analysis.

Mechanical behaviors of film

Starch films were cast with 400 g of starch paste (6%, w/w). The paste was prepared as same as the measurement of starch viscosity. After the starch had been gelatinized for 1 h, the paste was com-

pletely poured onto a 650 mm × 400 mm polyester film spread on a same size glass plate and dried at 65% relative humidity and 20°C. Then, the films were collected and tailored into 200 mm × 10 mm strips.

After the stripped films had been kept under the above condition for 24 h, the breaking strength and elongation of the stripped films were measured by the same tester and under the same condition as the measurement of the roving samples. Twenty samples were measured for each case and the readings given were the average of the test results with which the abnormal values had been rejected by statistical analysis. The breaking strength of the films was calculated as follows:

$$\text{Breaking strength (N/mm}^2\text{)} = \frac{N}{d \times w} \quad (3)$$

where N , d , and w were the breaking force, thickness, and width of starch film, respectively.

Abrasive resistance of the strip samples was evaluated in value of wear loss of the film weight and was measured on a G552 Zweigle abrader. The values reported were mean value of ten tests for each case. The abrasive material used was KP915C abrasive paper manufactured by ITAS Company. The wear loss was obtained from eq. (4)

$$\text{Wear loss (mg/cm}^2\text{)} = \frac{w_1 - w_2}{s} \quad (4)$$

where w_1 and w_2 were the weight of the stripped film measured before and after the abrasion, and s was the area of the strip films for the measurement.

Flexibility of the stripped film was presented in value of the times bent to break and was measured on a Y731 machine. Ten samples were tested for each case.

RESULTS AND DISCUSSION

The samples of carbamoylethyl starch prepared are characterized in the Table I. With a rise in the DS, the apparent viscosity increases and the viscosity stability decreases. The carbamoylethylation introduces carbamoylethyl groups ($\text{NH}_2\text{COCH}_2\text{CH}_2-$) onto starch molecules. The groups are polar and hydrophilic. It has been elucidated that pure starch pastes can be described as a suspension of swollen particles dispersed in a continuous phase.^{14,15} The swollen particles are the broken fragments derived from starch granules that swell and break in starch cooking and are mainly composed of entangled amylopectin. The presence of the polar groups causes the swollen particles to further swell and results in greater expansion of the coiled starch macromole-

TABLE I
Characterization of Carbamoyethylated Starch Prepared

Nitrogen content (%)	Degree of substitution	Reaction efficiency (%)	Apparent viscosity (mPa s)	Paste stability (%)
0	0	—	18	91.7
0.189	0.022	36.9	18	88.6
0.367	0.043	36.6	19	86.5
0.626	0.075	36.5	26	80.8
0.844	0.102	34.6	27	77.8

cules in the continuous phase. Therefore, the apparent viscosity of carbamoyethyl starch is perceived to enhance. The more the polar groups, the greater is the expansion and the swellability. Therefore, the viscosity shows an ascending tendency with the increase of modification extent.

The effects of the carbamoyethylation on the adhesion to pure cotton, all-polyester, and polyester/cotton blend fiber substrates are presented in Figures 1–3. It is clearly seen that the maximum strength and work-to-break of the three kinds of roving samples impregnated with the carbamoyethyl starch paste increase compared with those with the native one. The strength and work enhance as the DS increases. This implies that the bonding strength or adhesion capability can be enhanced by the carbamoyethylation and the adhesion increases with the increase of the modification extent, no matter what type of these fibers was used as substrates. The results demonstrate that the carbamoyethylation is an effective means to enhance the adhesion of starch to fibers.

It has been broadly accepted that the failure of an adhesive joint can be divided into cohesive failure and interfacial failure (adhesive failure)¹⁶ according to failure position. The former means a failure occurs wholly within a bulk phase of an adhesive layer formed by adhesives. The latter indicates that a failure occurs exactly at the interface between the ad-

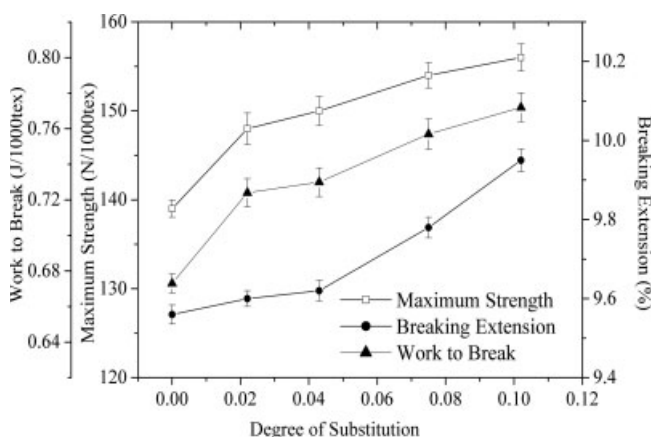


Figure 1 Effect of the carbamoyethyl modification on the adhesion to pure cotton fibers.

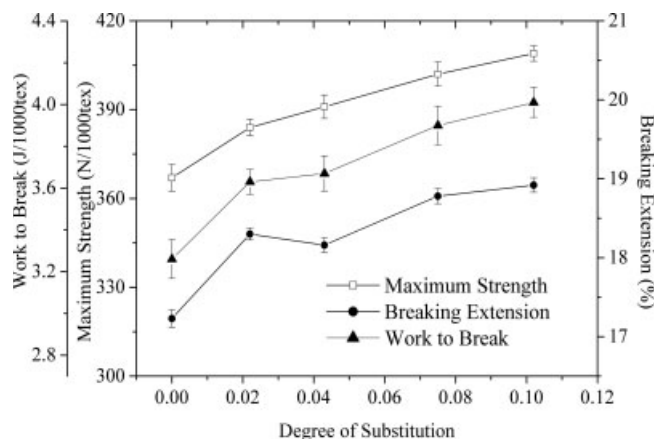


Figure 2 Effect of the carbamoyethyl modification on the adhesion to all-polyester fiber.

herent and the adhesive layer. As an adhesive joint will fracture at its weakest position, the bonding strength of an adhesive joint is determined not only by interfacial attraction, but also by the mechanical properties of the adhesive layer. Generally, a strong bonding can be obtained only when neither cohesive failure nor interfacial failure occurs at low applied loads. To examine the influences of the modification upon the adhesion, we first consider the interactions on the interfaces between adhesive layer and fiber and then the mechanical behaviors of the adhesive layer formed by starch paste by means of evaluating the interfacial and cohesive failure, respectively.

The paste must be to wet and spread evenly on the surface of fibers to be glued. Apparently, the carbamoyethylation of starch introduces hydrophilic groups onto both amylose and amylopectin, which increases the dispersibility of starch in aqueous pastes. This can be interpreted as an increased fraction in the continuous phase and a decreased amount and a greater expansion of the swollen granules

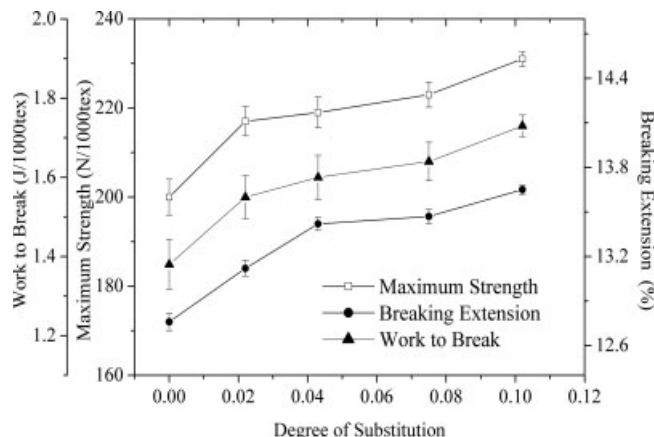


Figure 3 Effect of the carbamoyethyl modification on the adhesion to polyester-cotton blend fibers.

dispersed in the modified starch paste compared with unmodified starch paste. It should be noted that the starch in swollen granular form plays much less role in adhesion than those in the continuous phase, because the swollen particles cannot uniformly spread onto the surfaces of fibers, especially for the particles with low expansion. The particles in starch paste evidently induce incomplete wetting and spreading onto the fibers to be glued. Obviously, the situation results in interfacial defects and causes stress concentration around unwetted or outspreaded interfacial defects as an adhesive joint is subjected to forces. When the local stress exceeds the local strength, local interfacial failure occurs. Therefore, incomplete wetting and spreading makes the interfacial failure occur at low applied loads and is deleterious to adhesion. Secondly, polarized carbamoylethyl groups introduced onto starch can form hydrogen bonds with the hydroxyls of cotton molecule and enhance intermolecular forces on the interface between the starch layer and cotton fiber. This situation is favorable to the enhancement of the adhesion to cotton fibers. On the other hand, carbamoylethyl groups possess the same group (carbonyl) as polyester. This indicates an increase in van der Waals force on the interfaces between carbamoylethyl starch and polyester fiber.¹⁷ As a result, the interfacial actions were reinforced. Accordingly, the probability of the interfacial failure would expect to decrease, and the adhesion of the modified starch to fibers increases if the cohesive force of the adhesive layer is strong enough and the interfacial failure is mainly responsible for the failure of adhesive joint.

It is commonly accepted that the cohesive failure of an adhesive joint also depends on the mechanical behaviors of adhesive layers among fibers. Therefore, the behaviors should be determined for the evaluation of the cohesive failure. It should be noted, however, that it is almost impossible to strip the adhesive layers among fibers for determining their real mechanical behaviors. Accordingly, an attempt had been made by casting films with carbamoylethyl starch, and it is the cast films that are adopted to estimate the mechanical behaviors. The mechanical behaviors such as breaking strength, breaking elongation, flexibility, and wear loss of the film are shown in Table II. The strength, elongation, and flexibility of carbamoylethyl starch films increase compared with unmodified starch. And with a rise in value of DS, the elongation and flexibility enhance whereas the breaking strength reduces. This suggests that the flexibility of the films or adhesive layers could be improved by carbamoylethylation. And the improvements can be enhanced with the increase of the modification extent. Carbamoylethyl groups introduced disturb the association of starch hydroxyls and interfere with the regular arrangement of the

TABLE II
Influence of the Carbamoylethyl Modification on the Behaviors of Starch Films

Degree of substitution	Breaking strength (N/mm ²)	Breaking elongation (%)	Flex resistance (times)	Wear loss (mg/cm ²)
0	29.59	1.93	899	0.57
0.022	34.97	2.47	2267	0.47
0.043	32.25	2.76	2485	0.45
0.075	31.14	3.04	2678	0.44
0.102	30.33	3.61	2287	0.42

amylose due to steric hindrance effect. In addition, the carbamoylethyl groups are hydrophilic and are capable of absorbing water into the films. The groups on starch molecules and the water absorbed play a plasticization role to starch films and enhance their elasticity. Therefore, the groups enhance the elongation and flexibility of starch films and introduce toughness to the film. Furthermore, the steric hindrance of the groups increases the distance of starch molecules and reduces cohesive force of starch. Accordingly, the strength of starch films shows a descending trend as the modification extent of starch increases.

In dry process, starch paste among fibers shrinks and forms an adhesive layer. As the adhesive layer-fiber contact area is constrained by adhesion, the shrinkage induces the internal stresses both on the interfaces and within the bulk phase of adhesive layers. The stresses developed might result in such a failure that the stress loaded does not exceed the layer strength. Consequently, internal stresses often increase the possibility of cohesive and interfacial failures and are deleterious to an adhesion, especially when the adhesive layers consist of brittle materials like starch. However, the internal stresses will relax as long as the adhesive layer shows sufficient flexibility. The magnitude of internal stresses developed depends on the flexibility of adhesive layer, and the stress relaxation as a function of time is also dependent on the flexibility. As elucidated previously, the flexibility of adhesives is important for reducing the stress concentration¹⁸ and the increment in the flexibility favors to decrease the internal stresses. For this reason, the modification of starch increases the adhesion capacity to fibers.

With an increased level of the modification, the dispersibility of starch increases, and the amount of the swollen granules dispersed in starch paste decreases and the granules further expand. Moreover, the interactions on the interfaces produced by the van der Waals force or hydrogen bonds increase. Consequently, the occurrence of the interfacial failure would be expected to decrease. On the other hand, with a rise in the modification extent, the flexi-

bility and deformability of the layers increase and the internal stresses reduce. Therefore, the cohesive failure of the adhesive joints is expected to happen only at higher loads. For this reason, increasing the modification extent enhances the adhesion capability to the fibers.

It is well known that polyester and cotton fibers are quite different in nature. To achieve strong adhesion, the polarities of the adhesive and the adherent should be equal.¹⁹ This means that a strong bonding may be obtained when adhesive and adherent are either polar or nonpolar, and a polar/nonpolar pairs never form strong adhesion. Starch and cotton are all polar polymers whereas polyester is nonpolar. Undoubtedly, only according to adhesion based on polarity, a strong adhesion would be achieved between cotton fibers and starch. And for polyester/starch, weak adhesion should be logical. However, the experimental results are quite different. This is mainly due to the length of fibers used as substrates. The length of polyester fibers is much longer than that of cotton ones. The loads transferred through the boundary between fiber and adhesive layer enhances as the fiber length increase.²⁰ For this reason, the bonding strength of starch to polyester fibers is greater than those to cotton ones.

CONCLUSIONS

Based on the experimental results and discussions presented above, the following conclusion can be obtained.

1. The investigation demonstrates that the carbamoylethylation of starch is an effective manner for enhancing the adhesion of starch to pure cotton, all polyester, and polyester/cotton blend fibers. The bonding strength or adhesion capability of carbamoylethyl starch to the three kinds of fibers evidently enhances compared with those of unmodified starch, even if the DS is at very low level. The adhesion capacity enhances obviously as the modification extent increases.
2. The mechanical behaviors of starch film can be varied by the carbamoyl ethylation of starch. The breaking strength, breaking elongation, and flexibility of the modified starch film increase compared with those of unmodified starch one. With a rise in value of the DS, the elongation and flexibility of carbamoylethyl starch film increases whereas the breaking strength reduces. This suggests that an improvement in flexibility of starch films can be achieved

through the carbamoyl ethylation. And the improvement enhances as the modification extent increases.

3. Due to the hydrophilicity, chemical structure and steric hindrance effect of carbamoylethyl groups introduced, the modification induces increased dispersibility of starch, which results in a reduced amount of swollen granules and further expansionary particles dispersed in starch paste. The modification might reduce incomplete wetting and stress concentration on the interfaces. Secondly, the interfacial forces between starch layers and fibers can be increased, by means of the modification, through van der Waals force or hydrogen bonds. Thirdly, the flexibility and deformability of adhesive layers increase and the internal stresses both on the interfaces and in the bulk phase of the layers reduce. Therefore, both the interfacial and cohesive failure is expected to happen at higher loads. For this reason, the modification enhances the adhesion of starch to fibers.

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