

Effects of molecular structure of acrylates on sizing performance of allyl grafted starch

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In order to improve the performance of allyl starch-*g*-poly(acrylic acid-co-acrylate) sizes, effect of molecular structure of the acrylate monomers grafted onto allyl starch has been studied. A series of acrylates including methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA) have been grafted onto allyl starch with the same degree of substitution through the initiation of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2/\text{H}_2\text{O}_2$ redox system respectively. Meanwhile, acrylic acid (AA) is also graft copolymerized to maintain good water-dispersibility of the grafted starch. Then the properties of the grafted allyl starch, such as the apparent viscosity, viscosity stability, and adhesion to polyester fibres and the mechanical properties of sizing film, have been studied. It is found that by grafting acrylates onto the molecular chains of starch, the sizing performance of the allyl starch is improved markedly. Under the same feed ratio of the acrylic monomers to allyl starch, allyl starch-*g*-poly(AA-co-MA) shows higher paste viscosity, viscosity stability, and film elongation than the other kinds of grafted allyl starch. Allyl starch-*g*-poly(AA-co-EA) also shows higher film strength than the other ones. Both of the allyl starches grafted with MA and EA show higher abrasion resistance of sizing film and better adhesion to polyester fibres.

Keywords: Acrylate monomer, Allyl starch, Graft copolymerization, Mechanical property, Sizing performance, Viscosity

1 Introduction

Warp sizing is a key procedure during the whole weaving process. Sizing agents are basic materials in warp sizing and their consumption in textile industry ranks only second to fibre materials. Starch possesses many advantages, such as abundant source, low cost, and better biodegradability. Therefore, starch and its derivatives always stand in the first place among all kinds of sizing agents and it accounts for approximately 70% of the total sizes consumption^{1,2}. However, natural starch shows poor adhesion to fibres and its film is rigid and brittle. Lots of experiments and industrial trials have demonstrated that chemical modification provides an effective way to extend starch suitability to various fibres as sizing agents³⁻⁵.

Among various chemical modification methods, graft copolymerization is a commonly used one to improve sizing properties of starch⁶⁻⁸. In previous study, allyl etherification of starch was proved to be an effective method to enhance the two essential parameters, i.e. grafting efficiency and grafting ratio, in the graft copolymerization of starch with vinyl monomers^{9,10}. According to our investigation, grafting

efficiency and ratio increased from 53.2% and 5.21% to 73.7% and 7.18% respectively, when acrylic acid (AA) was utilized as grafting monomer⁹. Increasing grafting efficiency and ratio means that the amount of vinyl monomers, converted to grafted branch on the starch, is enhanced. In other words, the probability of occurrence of the side reaction – the homopolymerization of vinyl monomers is decreased substantially. Consequently, the performance of the copolymers is improved and the production cost is reduced. Therefore, more attentions should be paid to the development of allyl starch graft copolymers as a new type of sizing agent.

Up to today, few polymers are appropriate to be used as sizing agents for polyester yarns. Taking the difficult problem into consideration, some investigations on the preparation and property of starch-*g*-polyacrylates have been carried out^{11,12}. The results showed that the grafted starch has good adhesion to polyester fibres, is environment friendly, and possess potential to replace PVA, which is difficult to biodegrade and banned in sizing process by many European countries¹³. In addition, the starch grafted with acrylates has many other satisfactory properties for warp sizing, such as stable apparent viscosity and good film properties. It can be

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speculated that more economic and environmental benefits will be brought if starch-g-polyacrylates, which meets various sizing requirements, is prepared using less amount of acrylate monomers.

In the present study, the native starch is pretreated with allyl chloride and polymerizable double bonds are introduced onto the molecular chains of starch. After the allyl etherification of starch, acrylate monomers with different carbon chain lengths, i.e. methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and 2-ethylhexyl acrylate (EHA), are grafted onto the allyl starch through Fenton's initiator. Effects of the molecular structure on the properties of the grafted starch for warp sizing are revealed. In textile field, sizing operation is based on an aqueous paste. This demands sizing agents to be water-soluble or at least water-dispersible. However, the water-dispersibility of the starch tends to deteriorate upon grafting acrylates. In order to maintain good water-dispersibility of the starch, a certain amount of hydrophilic monomers (AA) is graft copolymerized onto the allyl starch with acrylates in the study. In terms of the main sizing properties, the apparent viscosity, contact angle on polyester fabric, adhesion-to-polyester fibres and film properties of the allyl starch-g-poly(AA-co-acrylate), are evaluated systematically. Finally, the appropriate acrylate type is recommended as the grafting monomer for the preparation of allyl starch-g-poly(AA-co-acrylate) sizes.

2 Materials and Methods

2.1 Materials

Commercial corn starch provided by Yixing Starch Factory (Jiangsu Province, China), having a moisture content of 12.8% and an apparent viscosity of 58 mPa·s. (6%, 95°C) was used. The apparent viscosity of starch paste was measured by NDJ-79 rotary viscometer at a shear rate of 2028 s⁻¹. The starch was refined to remove protein¹⁴, hydrolyzed to reduce excessive viscosity with diluted HCl to 15 mPa·s for increasing the fluidity of starch paste¹⁵, and dried at 80°C in a vacuum oven¹⁶. All the reagents were chemically pure and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Polyester roving (400 tex, twist factor: 49.8) was offered by Yizheng Co. Ltd. of Chemical Fibre (Jiangsu province, China). The length and fineness of the polyester fibres were 38 mm and 1.73 dtex (~14 micron diameter) respectively.

2.2 Allyl Etherification of Starch

Two hundred and thirty-five grams (dry weight) of hydrolyzed cornstarch were mixed with distilled water-isopropyl alcohol (20/80, w/w) mix to form a 30 % (w/w) suspension. After 59 mL of 4% (w/w) sodium hydroxide solution was added, the suspension was heated to 30°C in a water bath and stirred with a mechanical stirrer. After 30 min, 3g of allyl chloride dissolved in a certain amount of isopropanol was added into the flask and the reaction lasted at 30°C for 24 h. The allyl etherification is shown in Scheme 1. The starch was filtered, re-dispersed in distilled water-alcohol solution (18:82, v/v), and neutralized with diluted HCl to pH 6-7. Finally, the product was filtered, washed thoroughly with distilled water, dried at 50°C, pulverized, and sieved for passing through a 100-mesh sieve.

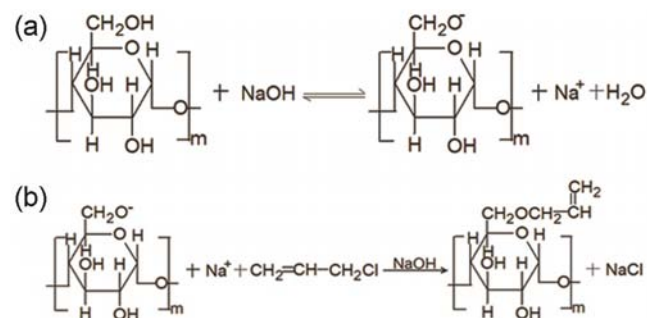
2.3 Characterization of Allyl Starch

The amount of allyl groups introduced onto the starch was measured by titrimetric analysis. The double bonds of allyl groups reacted with bromine and the residual bromine was then reacted with iodine. The excessive iodine was titrated with sodium hyposulfite¹⁷. The degree of substitution (DS) was calculated using the following equations:

$$DS = \frac{162x}{79.904 \times (2 - 0.5006x)} \quad \dots(1)$$

$$x = \frac{(V_1 - V_2) \times C \times 0.0799}{W} \times 100 \quad \dots(2)$$

where $x(\%)$ is the bromine value; V_1 (mL) and V_2 (mL), the volumes of the standard sodium hyposulfite solution consumed in blank and sample titrations respectively; C (mol·L⁻¹), the concentration of the sodium hyposulfite solution; and W (g), the dry weight of allyl starch sample.



Scheme 1—(a) Alkalinization of starch and (b) allyl etherification of starch

In order to obtain high grafting parameters and satisfactory sizing performance from the allyl grafted starch, DS value of allyl starch prepared for further grafting must be in an appropriate range. According to our previous experimental results⁹, DS value of allyl starch should be in a range of 0.011-0.025. In this study, DS value of the allyl starch is taken as 0.023.

2.4 Graft Copolymerization

Before grafting, 130g of allyl starch was dispersed in 390 mL of distilled water. Then the dispersion was adjusted to pH 3-4 with diluted H₂SO₄ and transferred into a 1000 mL four-neck flask. The flask was maintained at 30°C in a water bath. After the reaction system was deoxygenated by passing nitrogen gas for approximately 30 min, the Fenton's initiator including H₂O₂ and FeSO₄·(NH₄)₂SO₄ was prepared. The molar ratio [H₂O₂/FeSO₄·(NH₄)₂SO₄/anhydroglucose unit of starch] was kept at 20/1/1000. Then 13g of monomers (10 wt%, to allyl starch; constant molar ratio 3/7, AA/acrylate) and Fenton's initiator solutions were added continuously through dropping funnels and the addition was completed uniformly in 20-30 min respectively. The graft polymerization was carried out under vigorous stirring using a laboratory mixer under nitrogen atmosphere for 3h. The graft copolymerization of the starch with acrylates and AA is shown in Scheme 2. After adding 3.5 mL of 2% paradioxybenzene solution to terminate the copolymerization, the product was neutralized to pH 6-7, filtered, washed thoroughly with distilled water, dried at 50°C, pulverized, and sieved using a 100-meshed sieve.

2.5 Characterization of Grafted Starch

The amount of residual monomer (AA and acrylates) after grafting was determined by titrating

the double bonds of the monomer in the filtrate after the graft polymerization. The amount of residual monomer in filtrate can be titrated through a bromination method. The principle of this method is that double bonds of the acrylate monomers react with bromine, which is derived from the oxidation of HBr with KBrO₃. Then the residual bromine reacts with iodine and the excessive iodine is titrated with sodium thiosulfate finally¹⁷. The weight of residual monomer was calculated using the following equation:

$$W = \frac{(V_0 - V_1) \times C}{V} \times \frac{V_f}{1000} \times \frac{M_a}{2} \quad \dots (3)$$

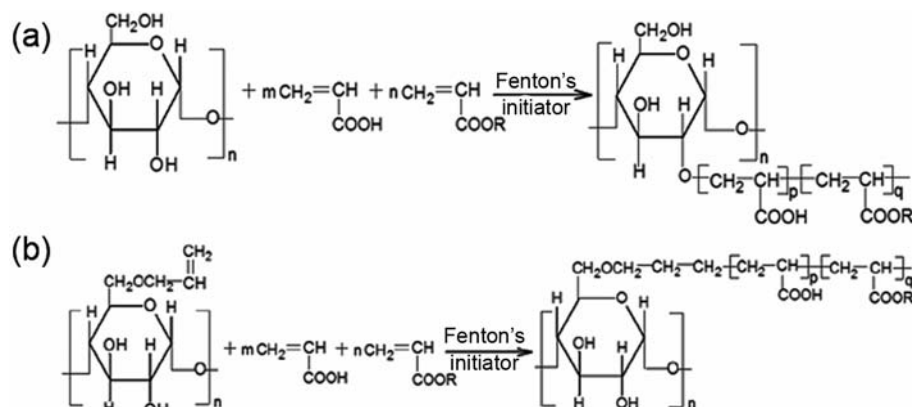
where W (g) is the weight of the residual monomer; V_0 (mL) and V_1 (mL), the volumes of the standard sodium thiosulfate consumed in blank and filtrate titration respectively; V (mL), the volume of the filtrate taken for titration; C (mol/L), the concentration of the standard sodium thiosulfate; V_f (mL), the total volume of the filtrate; and M_a , the molecular weight of the monomer which was equal to the molar weight mean of AA and acrylates.

After obtaining the weight of the residual monomer, % Monomer conversion was calculated using the following equation:

$$\% \text{ Monomer conversion} = \frac{W_1 - W_2}{W_1} \times 100 \quad \dots (4)$$

where W_1 and W_2 are the weights of the total and the residual monomer respectively.

In the experiment, the grafted starch with homopolymers, i.e. PAA and polyacrylates (PMA, PEA, PBA and PEHA) was initially washed with distilled water thoroughly till no PAA exists in the filtrate. The method used to test the presence of the homopolymers PAA in the filtrate was according



Scheme 2—(a) Principle of forming grafted branches connected with oxygen in hydroxyls by Fenton's initiator and (b) principle of forming grafted branches through the double bonds

to the one reported by Bayazeed *et al.*¹⁸. After the removal of PAA, the remaining homopolymers - polyacrylates were removed completely by repeated refluxing in Soxhlet with acetone for 24 h, which is a good solvent for polyacrylates¹⁹. The grafted starch product obtained was later dried at 80°C for 4 h in a vacuum oven in order to remove acetone.

In this study, grafting ratio (GR) describes the weight percentage of PAA and polyacrylate branches grafted onto the allyl starch to the allyl starch, and grafting efficiency (GE) describes the weight percentage of PAA and polyacrylate branches grafted onto the allyl starch to the sum of PAA and polyacrylate, including grafted branches and un-grafted homopolymers. Both GR and GE were determined using the following equations:

$$W_3 = W_b - W_a \quad \dots (5)$$

$$\text{GR}(\%) = \frac{W_1 - W_2 - W_3}{W_0} \times 100 \quad \dots (6)$$

$$\text{GE}(\%) = \frac{W_1 - W_2 - W_3}{W_1 - W_2} \times 100 = \frac{\text{GR}}{\text{MC}} \times \frac{W_0}{W_1} \times 100 \quad \dots (7)$$

where W_b and W_a are the weight of the products before and after the washing by distilled water and the extraction by acetone respectively; W_3 and W_0 , the weights of the homopolymers and allyl starch respectively; and MC, % the monomer conversion.

2.6 FTIR Study

Fourier transform infrared spectrometer (FTIR) was used to verify the grafting of AA and MA onto the allyl starch. The allyl starch-g-poly(AA-co-MA) was initially washed with distilled water thoroughly and extracted by acetone for 24 h in order to remove the homopolymers (PAA & PMA), adhered to the grafted starch completely. Then I₂-KI ethanol-water solutions were dripped into the water and acetone to identify the color change. The results showed that the water and acetone did not turn blue or violet and still kept colorless. This validated that starch were not lost during the extraction. Measurements were done on Thermo Nicolet (Avatar 380) spectrophotometer through the diffuse reflectance technique with a spectral resolution of 2 cm⁻¹ for 64 scans.

2.7 Measurement of Apparent Viscosity

The apparent viscosity and viscosity stability of the grafted allyl starch were measured using an NDJ-79

viscometer purchased from electrical machinery plant of Tongji University (Shanghai China). The starch sample was suspended into distilled water to form 6% (w/w) dispersion. The dispersion was heated to 95°C and maintained at this temperature for 1 h under mechanical stirring. Then the apparent viscosity of gelatinized starch paste was measured at 95°C with a shear rate of 2028 s⁻¹. Viscosity stability of the paste denoted the percentage of the viscosity invariability over a period of 2.5h at 95°C¹⁴. The stability was measured over the period of 1-3.5 h after starch gelatinization. The viscosity of the starch paste was measured after every 30 min and the stability was calculated from the following equation²⁰:

$$\text{Viscosity stability of starch paste}(\%) = \left(1 - \frac{V_{max} - V_{min}}{V} \right) \times 100 \quad \dots (8)$$

where V is the apparent viscosity of the paste; while V_{max} and V_{min} , the maximum and minimum of the viscosity over the period respectively.

2.8 Measurement of Contact Angle

One per cent (w/w) of starch-distilled water dispersion was cooked in a flask at 95°C with mechanical stirring for 1 h. Then 0.1 mL of the starch paste was extracted from the flask using a syringe and dripped onto the surface of a tensioned polyester woven fabric (10 tex × 10 tex; 370/10 cm × 390/10 cm). Contact angle of the starch paste on the polyester fabric was measured using a JC2000D2 contact angle meter purchased from Zhongchen Digital Technology Co. Ltd. (Shanghai China). Five samples were measured to obtain the mean value.

2.9 Measurement of Adhesion

A sized roving method was initially utilized by Faasen & Van Harten to evaluate the adhesion of sizing agents on cotton fibres²¹. About 30 years later, Behera and Pakhira²² reported that the adhesion between size materials and polyester fibres could be determined by measuring the tensile strength of sized polyester-fibre roving. If spun yarn is used as sizing object for adhesion evaluation, its high twist and tensile strength have marked influences on tensile properties of sized yarns. Thus, it is very inaccurate to take tensile strength of the sized spun yarns as adhesive strength of a sizing agent on fibres due to the inherently high tensile strength of unsized spun yarns. Even if the same sizing agent and fibre are used for adhesion evaluation, different results will be produced

in case of using spun yarns with various twists or tensile strengths. As a result, roving is more appropriate to be used as sizing object for adhesion evaluation because twist and strength of unsized roving are so low that their influences on tensile strength of the sized roving can be neglected. Therefore, slight sizing of rovings has become a relatively accurate and simple method for evaluating the adhesion of a sizing agent on fibres. Nowadays, this method has become a standard to estimate the adhesion of a sizing agent to fibres in China (FZ/T 15001-2008, a criterion regulated by Textile Association of China). In the measurement, a slightly sized roving is drawn to tensile failure. Tensile strength of the sized roving is considered as adhesive strength of a sizing agent on fibres. The detailed steps of roving method to evaluate the adhesion are given below.

One per cent (w/w) of starch-distilled water dispersion was cooked in a flask at 95°C with mechanical stirring for 1 h. Then the roving wound onto a stainless steel frame was impregnated with the paste for 5min at 95°C. The samples were taken out, dried in air and conditioned at 65% relative humidity and 20°C temperature for 24 h before tensile test. Tensile strength and elongation of the roving samples were measured on a BZ2.5/TNIS Zwick material tester with 100mm initial chuck distance and 50mm/min drawing speed under the same humidity and temperature. Twenty samples were measured for obtaining the mean value of the data required.

2.10 Size Film and its Mechanical Properties

Starch films were cast with 400g of starch paste (6%, w/w). The preparation of starch paste was the same as in the experiment for viscosity measurement. The paste prepared was poured onto a 650mm × 400mm polyester film spread on a same size glass plate and dried at 65% relative humidity and 20°C temperature. Finally, the starch film was peeled carefully from the polyester film.

Tensile strength and tensile elongation of the starch films were measured on a BZ2.5/TNIS Zwick material tester. Twenty samples were measured to obtain the mean value. Abrasion resistance of sizing film is closely related to wear resistance of sized yarns. In actual weaving production, sizing film formed on the surface of warp yarns plays a major role in the resistance to abrasion. Thus, abrasion resistance of starch film was also evaluated in terms of wear loss of the film weight using a G552 Zweigle

abrader. Ten samples were abraded reciprocally for 1000 times to obtain the mean value. The abrasion material was KP915C abrasion paper produced by ITAS Co. Ltd. The wear loss was obtained from the following equation:

$$\text{Wear loss (mg/cm}^2\text{)} = \frac{W_1 - W_2}{S} \quad \dots(9)$$

where W_1 and W_2 are the weights of the films measured before and after the abrasion respectively; S , the area of the films for abrasion.

2.11 Statistical Analysis

The data were analyzed using SAS software (SAS Institute, Inc., Cary, NC). Comparison of multiple means is often done using Tukey's HSD test, which is a specialized single-step multiple comparison procedure and statistical test. Therefore, Tukey's HSD test was utilized to compare the multiple means in this paper. The confidence interval was set at 95% and a 'p' value smaller than 0.05 was considered to be a statistically significant difference by Tukey's HSD test. According to the operation results of the analysis, small letters, such as a, b, c, were inserted above or below the data points in all the figures except Fig. 1. The data points with the same small letter were not statistically significantly different from each other.

3 Results and Discussion

3.1 Evidence of Grafting

FTIR spectra of purified natural starch, allyl starch, purified allyl starch-g-poly(AA-co-MA) and allyl

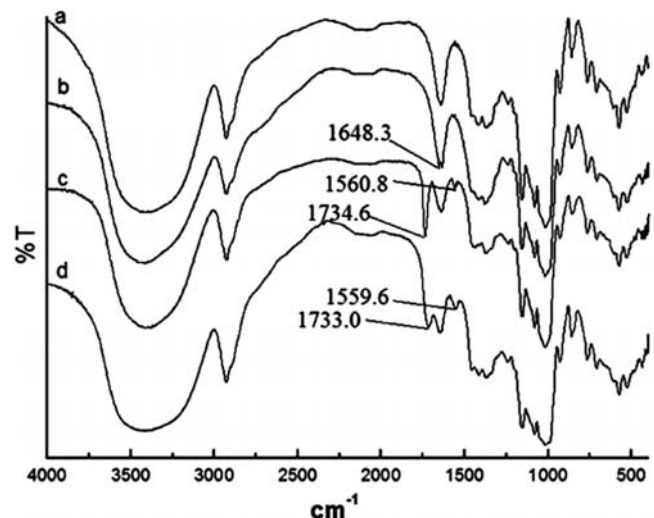


Fig. 1 — FTIR spectra of purified natural starch (a), allyl starch (b), purified allyl starch-g-poly(AA-co-MA) (c), and allyl starch-g-poly(AA-co-MA) with homopolymers (d)

starch-*g*-poly(AA-co-MA) with homopolymers are showed in Fig. 1. It could be observed that an absorption peak appeared at 1648 cm^{-1} in the infrared spectrum of allyl starch due to the stretching vibration of double bonds of allyl groups⁹. For the spectrum of purified allyl starch-*g*-poly(AA-co-MA), the peak at 1735 cm^{-1} corresponds to the stretching vibration of carbonyl group of methyl ester, which proves the existence of grafted branches²³. In addition, the new peak appearing near 1561 cm^{-1} corresponds to reverse stretching vibration of the carbonyl²⁴. The new peak proves the existence of grafted branches (PAA). The peaks at 1733 cm^{-1} and 1560 cm^{-1} also appear in the spectrum of the allyl starch-*g*-poly(AA-co-MA) with homopolymers (i.e. PAA & PMA).

3.2 Influences of Monomer Structure

3.2.1 Effect on Grafting Parameters

The monomer conversion, grafting efficiency and ratio of the prepared allyl starch-*g*-poly(AA-co-acrylate) are shown in Fig. 2. With the increase in carbon chain length of acrylate monomers, the grafting efficiency and ratio decrease, while all the monomer conversions are higher than 95% and show no significant change.

As for the monomer conversion, the conversion of each type of monomer exceeds 95%. The high monomer conversion indicates that nearly all the monomers are converted to polymers under the polymerization conditions. With the increase in the carbon chain length of the acrylates, the grafting ratio gradually decreases. In the graft copolymerization, grafted branches are formed through the bonding of starch radical with monomers. The longer the carbon chain of the monomer, the larger the space monomer occupies. As a result, when the acrylate monomers are

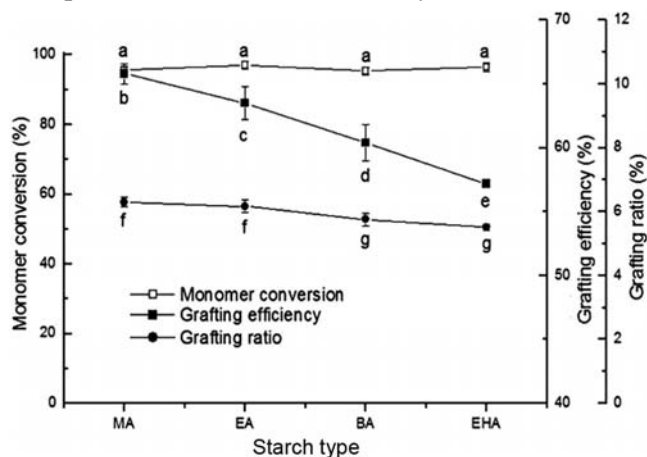


Fig. 2—Influence of monomer structure on grafting parameters

in the vicinity of allyl starch radicals, the acrylates with longer carbon chain are more difficult to be grafted onto the allyl starch than the ones with shorter carbon chain. It is great steric hindrance that inhibits the grafting of the acrylates with longer carbon chain. Therefore, the greater the steric hindrance, the lower is the grafting ratio. According to Eq. (7), the grafting efficiency also decreases with the increase in carbon chain length of the monomers due to the similar monomer conversions of the acrylates.

3.2.2 Effect on Paste Viscosity

Effect of the monomer structure of the acrylates on the viscosity and its stability of allyl starch-*g*-poly(AA-co-acrylate) are described in Table 1. All the allyl starch-*g*-poly(AA-co-acrylate) pastes possess higher apparent viscosity and viscosity stability than non-grafted allyl starch paste. In addition, the viscosity and its stability of the grafted starch paste decrease with increasing carbon chain length.

Two major factors help the grafted allyl starch paste to possess higher apparent viscosity than the non-grafted one. Initially, there are many carboxyl groups on the grafted branches of allyl starch-*g*-poly(AA-co-acrylate). The carboxyl groups are hydrophilic and negatively charged. The hydrophilicity increases the intermolecular forces between the grafted starch and the water. In addition, crosslinking occurs in polymerization when the degree of functionality of a reactant is more than 2. In the graft copolymerization of starch with vinyl monomers, a grafted branch can be achieved in the position of oxygen through the abstraction of hydrogen from hydroxyls and thus primary active radicals can be formed. As for the allyl-etherified starch, the allyl groups containing double bonds on the starch backbones result in the formation of a grafted branch bonded with the groups. These two branches can be grafted onto the same starch molecule. In this case, starch can be regarded as a bifunctional reactant and mild crosslinking can occur

Table 1—Influence of monomer structure on paste viscosity

Starch type	Apparent viscosity, mPa·s	Viscosity stability, %
Hydrolyzed starch	15	86.7
Allyl starch	4	75.0
Allyl starch- <i>g</i> -P(AA-MA)	30	94.0
Allyl starch- <i>g</i> -P(AA-EA)	29	93.1
Allyl starch- <i>g</i> -P(AA-BA)	20	93.0
Allyl starch- <i>g</i> -P(AA-EHA)	12	83.3

between the starch molecules. The mild crosslinking can increase not only the apparent viscosity, but also the viscosity stability. The stability is very important for sizing agents because high stability is the base of a stable size add-on²⁵.

The results show that increasing the carbon chain of the acrylates decreases the apparent viscosity and the viscosity stability of the allyl starch-*g*-poly(AA-co-acrylate) paste. There are two main reasons for the decrease. At first, with the increase in carbon chain length of the acrylates, side chains of the graft copolymers extend and their hydrophobicity increases. Longer hydrophobic side chains tend to collapse / aggregate in water. The hydrophobicity decreases the intermolecular forces between the grafted starch and water. Consequently, the apparent viscosity of the grafted starch paste decreases therewith. In addition, when the graft copolymerization is carried out, both the weight ratio of vinyl monomers to allyl starch and the molar ratio of AA to acrylate are constant. The longer the carbon chain of the acrylates, the higher is their molecular weight. The total weight of vinyl monomers is constant and thus the molar number of the acrylate with longer carbon chain is smaller. As a result, the molar number of AA decreases with the increase in the carbon chain length of the acrylate. It is the grafted branch (PAA) that endows the grafted starch with good hydrophilicity. Decreasing the molar number of AA leads to deterioration in hydrophilicity of the allyl starch-*g*-poly(AA-co-acrylate). Therefore, the apparent viscosity decreases with the increase in the carbon chain length of the acrylate.

It is found that starch-*g*-poly(AA-co-EHA) is the most difficult to dissolve in water among all the grafted starch samples in the study. This means that the other grafted samples, such as starch-*g*-poly(AA-co-MA) and starch-*g*-poly(AA-co-EA), could dissolve in water nearly completely under high temperature (95°C) and mechanical stirring in 1h. However, only part of the starch-*g*-poly(AA-co-EHA) dissolved in water under the same condition in 1h. In order to measure the viscosity stability, it requires more than 2.5 h to obtain viscosity values at different time points. As the testing time passed, the remaining part of the starch-*g*-poly(AA-co-EHA) continues to dissolve in water. The substantial increase in the dissolvability of starch-*g*-poly(AA-co-EHA) would necessarily cause the variation in viscosity. In contrast, after the heating time is over, the increase in the dissolvability of the other grafted samples is

unconspicuous. Therefore, viscosity vibration of the starch-*g*-poly(AA-co-EHA) paste, which was caused by larger increase of the dissolvability, turns higher than that of the other grafted starch.

3.2.3 Effect on Film Properties

Sizing operation requires starch film to possess good mechanical properties, such as appropriate tensile strength, great tensile extension and high abrasion resistance. Therefore, we also investigated the effects of monomer structure on the mechanical properties of starch film. Figure 3 shows that the film properties of the allyl starch-*g*-poly(AA-co-acrylate) are better than those of the non-grafted starch. In addition, with the increase in carbon chain length of the acrylate, the tensile strength of the film initially increases, reaches the maximum when EA is chosen as the grafting monomer, and then decreases. As for the tensile elongation and abrasion resistance, it gradually decreases with increasing the carbon chain length of the acrylate.

Due to the steric effect of grafted branches introduced onto the molecular chains of starch, the association of starch hydroxyls gets disturbed and the regular arrangement of starch molecules is restrained. Besides, the grafted branches are found flexible as compared to starch backbone and thus the branches introduced improve the film toughness. Therefore, the grafted allyl starch has higher tensile elongation than the non-grafted starch. As mentioned above, mild crosslinking could occur between the starch molecules in the graft copolymerization and the crosslinking could increase the molecular weight of the grafted starch. As a result, cohesive strength of the allyl starch-*g*-poly(AA-co-acrylate) is

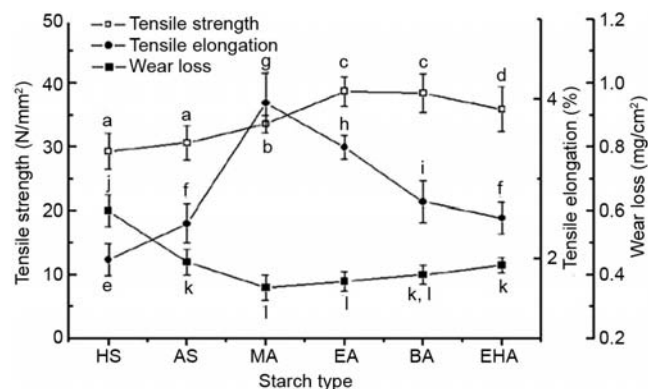


Fig. 3—Effects of monomer structure on mechanical properties of sizing film [HS - hydrolyzed starch; AS - allyl starch; MA, EA, BA, and EHA - the allyl starch grafted with MA, EA, BA, and EHA as acrylate monomers respectively]

increased and tensile strength of the starch film becomes higher.

As described in preceding part of the paper, the molar number of AA decreases with the increase in carbon chain length of the acrylate. The decrease causes the allyl starch-*g*-poly(AA-co-acrylate) to have fewer carboxylic groups which are hydrophilic and hence more water is adsorbed by starch. It should be noted that the water absorbed by the PAA branches plays a role in plasticizing the film. The plasticization can increase the tensile elongation of the film but decrease the tensile strength. Therefore, allyl starch-*g*-poly(AA-co-MA) film has higher tensile elongation but lower tensile strength than allyl starch-*g*-poly(AA-co-EA) film. As mentioned above, the longer the carbon chain of the acrylate, the less water-dispersible is the corresponding allyl starch-*g*-poly(AA-co-acrylate). The lower water-dispersibility of starch is harmful for the thermal motion of macromolecular chains and for the diffusion among particles during film formation. As a result, the brittleness of the starch film increases. Therefore, the tensile elongation of the allyl starch-*g*-poly(AA-co-acrylate) film decreases with increasing the carbon chain length of the acrylate. With the continuous increase in the carbon chain length, the water absorbed by the PAA branches of the grafted starch turns less and the plasticization effect due to water gets weakened. The weakened plasticization contributed to the increase in tensile strength of the film. However, the longer the carbon chain of acrylate, the less rigid is the molecular chain of the corresponding polyacrylate²⁶. Consequently, the tensile strength of the film of the starch grafted with the acrylate decreases. The contribution of the weakened plasticization could be compensated by the negative influence of the longer carbon chain on the tensile strength of the film. If the carbon chain is excessively long, the negative influence on the tensile strength will turn predominant. Thus, the tensile strength of the starch-*g*-poly(AA-co-EHA) film "is decreased substantially.

Abrasion resistance of sizing film is determined comprehensively by its tenacity and elongation. With the increase in the carbon chain length of the acrylate, the tenacity and elongation of the film are reached at the top when EA and MA are chosen as acrylate monomers respectively. Therefore, wear loss of the film of the allyl starch grafted with MA or EA becomes the lowest. In other words, abrasion

resistance of the films of starch-*g*-poly(AA-co-MA) and starch-*g*-poly(AA-co-EA) is found to the best among the grafted samples tested and shows no significant differences.

3.2.4 Effect on Adhesion

Sizing operation demonstrates that the performance of a sizing agent is closely related to the adhesion to fibres^{27,28}. Adhesion could enhance the strength of sized yarns by binding fibres together, reduce the amount of yarn hairiness and strengthen the connection between sizing film and yarn body. It is important to develop a sizing agent to possess good adhesion to polyester fibres, to which common starch sizes have weak adhesion¹⁷. Figure 4 shows that the adhesion of the allyl starch-*g*-poly(AA-co-acrylate) to polyester fibres is better than that of the non-grafted starch. In addition, the contact angle of the allyl starch-*g*-poly(AA-co-acrylate) on the polyester fabric is smaller than that of the non-grafted starch. As far as the grafted samples are concerned, with the increase in the carbon chain length of the acrylate, the adhesion and wettability initially show no substantial change and begin to decrease when BA is used as acrylate monomers.

After grafting, active hydrogen atoms of hydroxyls of starch are abstracted, and grafted branches (e.g. PMA, PEA and PBA) are connected with the starch backbone. Starch macromolecules are chemically modified and their polarity is reduced. Generally, as for the same polymer, decreasing its polarity favors the decrease in the surface tension of the polymer solution²⁹. Therefore, contact angle of the grafted starch paste is smaller than that of the non-grafted

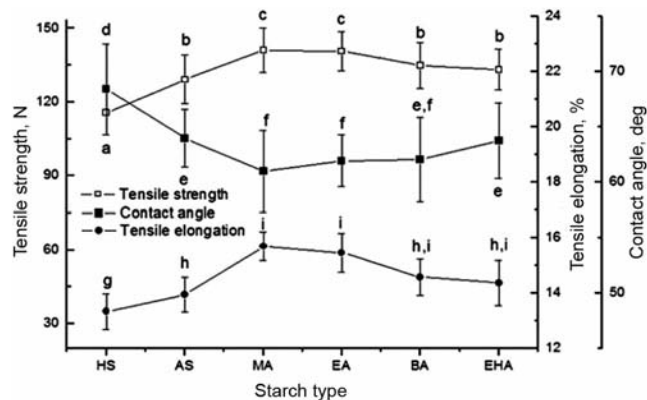


Fig. 4—Effects of monomer structure on the adhesion of the starch to polyester fibres and contact angle of the starch paste on polyester fabric [HS - hydrolyzed starch; AS - allyl starch; MA, EA, BA, and EHA - the allyl starch grafted with MA, EA, BA, and EHA as acrylate monomers respectively]

starch ones. Moreover, for the same series of polymers (e.g. polyacrylates), the higher the molecular weight, the larger is the surface tension of the corresponding polymer solution²⁹. As a result, contact angle of the grafted pastes on the polyester fabric is gradually turned larger with the increase in carbon chain length of the acrylate.

Starch molecules have strong polarity but polyester fibres exhibit non-polarity. A strong bonding can be obtained when adhesive and fibre are either polar or nonpolar. Thus, a polar–nonpolar pair can never form strong adhesion¹⁷. After grafting, non-polar polyacrylate branches are introduced onto the molecular chains of the starch and then the polarity of the starch is decreased. Therefore, both the affinity of the starch to polyester fibres and the wettability of the starch paste on polyester fabric improve. Moreover, crosslinking might occur between the starch molecules in the graft copolymerization and can increase the molecular weight of the grafted starch. The cohesion of the starch layer among fibres is increased. In addition, contact angle of the grafted starch paste on the polyester fabric is lower than that of the non-grafted starch paste (Fig. 4). A lower contact angle indicates better wetting of the grafted starch and hence formation of a better interface between the polyester and grafted starch. As a result, the three main factors determine that the allyl starch-*g*-poly(AA-co-acrylate) has better adhesion to polyester fibres than the non-grafted starch.

As shown in Fig. 2, the grafting ratio of allyl starch-*g*-poly(AA-co-MA) is higher than that of allyl starch-*g*-poly(AA-co-EA). The molecular weight of MA is lower than that of EA. As a result, the molar amount of ester groups of the starch-*g*-poly(AA-co-MA) is more than that of the starch-*g*-poly(AA-co-EA). Therefore, the affinity of the starch-*g*-poly(AA-co-MA) towards polyester fibres should be higher than that of the starch-*g*-poly(AA-co-EA), but the adhesion of the two grafted starch is found quite similar actually. It should be noted that the adhesive strength is determined by both the affinity of the adhesive to the fibres and the cohesive strength of the adhesive layer among the fibres. However, it is impossible to strip the adhesive layer among fibres to test their mechanical properties. Fortunately, Zhu²⁰ reported a simple method to evaluate the mechanical properties approximately. They cast a polymeric film using the same sizing agent for drawing test to failure and recording the failure load of a sizing film e.g.

starch film. It is the failure load which is adopted to assess the mechanical properties of the cohesive failure. It could be observed from Fig. 3 that the tensile strength of the starch-*g*-poly(AA-co-EA) film is higher than that of the starch-*g*-poly(AA-co-MA) film while the tensile elongation of the former is lower than that of the latter. Thus, the starch-*g*-poly(AA-co-EA) has higher cohesive strength but slightly lower elongation than the starch-*g*-poly(AA-co-MA). In addition, contact angle of the starch-*g*-poly(AA-co-MA) paste on the polyester fabric is found nearly equal to that of the starch-*g*-poly(AA-co-EA) paste. It denotes that the wetting abilities of the two kinds of grafted starch pastes on polyester fabric are similar. As a result, the tensile strengths of polyester fibres sized by starch-*g*-poly(AA-co-EA) and starch-*g*-poly(AA-co-MA) are quite similar and the tensile elongation of the fibres sized by the former is a little lower. Moreover, the affinity of the starch-*g*-poly(AA-co-EA) to polyester fibres and the cohesive strength are higher than those of the starch-*g*-poly(AA-co-BA) and starch-*g*-poly(AA-co-EHA). The contact angle of the starch-*g*-poly(AA-co-EA) paste on the polyester fabric is also found lower than that of the starch-*g*-poly(AA-co-BA) and starch-*g*-poly(AA-co-EHA) pastes. Consequently, the adhesion of the starch-*g*-poly(AA-co-EA) to polyester fibres is better than that of the starch grafted with BA or EHA.

4 Conclusion

The molecular structure of acrylate monomers has substantial influence on the grafting parameters and the performance of allyl starch-*g*-poly(AA-co-acrylate) for warp sizing. Grafting parameters, apparent viscosity and its stability, mechanical properties of sizing film, and adhesion-to-fibres of the allyl starch-*g*-poly(AA-co-acrylate) depend directly on the molecular structure of acrylate monomers. The allyl starch exhibits better sizing performance after grafting with the acrylate having appropriate carbon chain length.

With the increase in carbon chain length of the acrylate, all the monomer conversions are above 95% and show changes which are statistically not significant. The grafting ratio and grafting efficiency decrease therewith. The preferred allyl starch-*g*-poly(AA-co-acrylate) can be prepared through a two-step reaction method, i.e. allyl etherification and graft copolymerization. It is necessary to conduct the graft copolymerization using $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2/\text{H}_2\text{O}_2$ as

initiators under the protection of nitrogen gas. Both MA and EA are chosen as the appropriate acrylate monomers. The allyl starch-g-poly(AA-co-MA) and allyl starch-g-poly(AA-co-EA) thus produced show different favorable sizing performance. The allyl starch-g-poly(AA-co-MA) possesses higher parameters of 30 mPa·s, 94.0% and 3.95% in paste viscosity, viscosity stability, and tensile elongation of the sizing film respectively. The allyl starch-g-poly(AA-co-MA) has better adhesion to polyester fibres. The tensile strength and elongation of the polyester rovings sized by the grafted starch are found to be 141.1 N and 15.69% respectively. The wear loss of the allyl starch-g-poly(AA-co-MA) film and the contact angle of its paste on polyester fabric are 0.36 mg/cm² and 61° respectively, nearly equal to those of the allyl starch-g-poly(AA-co-EA). The two low values of the allyl starches grafted with MA and EA show higher abrasion resistance and better wettability. As for the allyl starch-g-poly(AA-co-EA), it exhibits higher tensile strength of the sizing film and the strength reaches 38.7 N·mm⁻². The two kinds of modified allyl starch, which are grafted with MA and EA respectively, are expected to meet various requirements in sizing process.

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