

Toughened cyanoethyl starch by blending with poly(methyl acrylate-co-acrylic acid-co-acrylonitrile) latex for warp sizing

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The effect of an emulsion-copolymerized poly(methyl acrylate-co-acrylic acid-co-acrylonitrile) latex on the toughening of cyanoethyl starch (CES) has been studied through blending to reduce the brittleness of CES film for warp sizing. The toughening has been accessed in terms of breaking elongation, tensile strength, work-at-break, and bending endurance of CES film. Also, the influences of the latex on the adhesion-to-fibre, desizability, and aerobic biodegradation of CES have been examined. The results show that the latex is able to toughen CES film and this action depends strongly on its blending ratio. With the increases in ratio, the breaking elongation, work-at-break, and bending endurance of the film increase gradually, whereas tensile strength of the film decreases slowly. In addition, blending the latex with CES favors the adhesion of CES to cotton and polyester fibres. It has also been found that the latex/CES blends are desizable and aerobic degradable. Suitable blending ratio in warp sizing is found in a range of 12-16 % by weight.

Keywords: Acrylic latex, Cyanoethyl starch, Starch film, Toughness, Warp sizing

1 Introduction

The cyanoethyl starch (CES) with low degree of substitution (DS, usually less than 0.1) has been considered as a low-cost alternative in warp sizing because it shows good properties¹. This is mainly attributed to the ability of cyano functions to form donor-acceptor bonds with contacting phase². Cyanoethylation of starch can be performed by reacting starch with acrylonitrile using Michael addition¹. However, the nitrile groups in cyanoethyl substituents introduced onto starch chains are strong in polarity and raise intermolecular forces between starch chains, thereby aggravating the brittleness of starch film on surface of sized yarns. Undoubtedly, a brittle film will not support large deformations and fracture without appreciable yielding. The brittleness induces the rupture of starch film on surface of sized yarns and results in size shedding. The shedding damages sizing film integrity, reduces protection to warp yarns, enhances friction of warp yarns, and increases hairiness of sized yarns³. Another major shortfall of the brittleness in warp sizing is a reduction in the adhesion to fibres⁴. As a result, these adverse effects of starch cyanoethylation aggravate some

drawbacks of starch during warp sizing. Therefore, there is an urgent need to reduce the brittleness of CES.

Blending some synthetic polymers with starch is a traditional and efficient way to toughen starch film. Previous studies demonstrated that blending water-based polyesters⁵, polyurethane⁶, polyvinyl alcohol (PVA)⁷, and solvent-copolymerized poly(butyl acrylate-co-acrylic acid)⁸ with starch respectively, could reduce starch brittleness. So far, the worse biodegradability of PAV and the solvent in the copolymer have limited their application in warp sizing. In addition, brittle starch films can also be plasticized with small molecular weight plasticizers like glycerol⁹. However, the plasticizers often have an undesirable shortcoming, such as lack of permanence due to volatility, exudation, migration, and extractability¹⁰. On the other hand, various acrylic latices with shorter alkyl esters have been developed via emulsion copolymerization. The latices have grown enormously in recent times, as driven by the need to find alternatives for solvent-based materials. Although microcosmic insights of these latices can be easily observed by the use of modern instrumental techniques, the actual effect on plasticization of starch films is still a subject of being less debated. It is as well to emphasize that the failure strain of some

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latices may be hundred times greater than that of starch. Therefore, they may be able to toughen CES film via blending for reducing its brittleness during warp sizing.

Accordingly, the present study was aimed at examining whether emulsion-copolymerized acrylic latex can be applied to toughen CES film for warp sizing. Another objective was to reveal the influence of latex on the adhesion-to-textile fibres, desizability, and aerobic biodegradation of CES. It has been demonstrated that an emulsion-copolymerized poly(methyl acrylate-co-acrylic acid-co-acrylonitrile) (P(MA/AA/AN)) latex has very great failure strain and exhibits excellent properties required for sizing warp yarns¹¹. Therefore, this latex was prepared for toughening CES film. The experiment was arranged in such a way that the measurements were performed not only on CES/P(MA/AA/AN) blends, but also on CES. Such arrangement enabled us to extract the effect of P(MA/AA/AN) itself from experimental data.

It is noteworthy that the viscosity of CES is too large to be satisfactorily used in warp sizing if native corn starch is employed as raw material for the preparation of CES. Therefore, controlled acid-degradation on starch was done before cyanoethylation was conducted to degrade starch to a desired extent. Also, it is very important to keep granular form of starch during cyanoethylation. This form of starch makes the cyanoethylation and purification easy by the use of traditional equipments and water. Accordingly, we only employ the techniques that can keep starch granules during cyanoethylation.

2 Materials and Methods

2.1 Materials and Reagents

Granular native cornstarch used in this work was commercially obtained from Zaozhuang Starch Factory (Shandong, China). Moisture content and apparent viscosity were 13.0 % (by wt) and 49 mPa·s respectively. The starch was refined to remove protein and acid-thinned for lowering its excessive viscosity before being used for the cyanoethylation¹². Methyl acrylate (MA), acrylonitrile (AN), and acrylic acid (AA), were chemically pure reagent grades and used without purification. Sodium dodecyl sulfate, ammonia persulfate, and sodium hydroxide were reagent grades and used as received.

Polyester roving (446 tex linear density and 57 twist factor), used for the measurement of adhesion

to fibres, was obtained from Yizheng Chemical Fibre Co., Ltd. (Jiangsu, China). Cotton roving (460 tex linear density and 112 twist factor) was supplied by Wuxi Talak Cotton Factory (Jiangsu, China). Fibre length and linear density were 38 mm and 1.73 dtex for the polyesters in polyester roving, and 29 mm and 1.67 dtex for the cotton in cotton roving respectively.

2.2 Synthesis of Latex and CES

Starch cyanoethylation was in accordance with the methods described in our previous publication¹³. The emulsion copolymerization of MA, AN, and AA was carried out in a 1000-mL flask. Sodium dodecyl sulfate (1.25 g) was dissolved in 560 mL of distilled water, and the solution transferred into the flask and heated to 72 °C. Afterwards, MA (92.3 mL), AN (7.3 mL), and AA (9.2 mL) were mixed while ammonia persulfate (0.25 g) was dissolved into 40 mL of distilled water at room temperature. One third of the monomer mixture and half of the initiator solution were charged into the flask and copolymerized under mechanical stirring. Forty minutes later, the remaining monomer mixture and initiator solution were added continuously in 1 h. One hour later, an additional amount of initiator (0.1 g, dissolved in 5 mL of distilled water) was refilled into the flask. The copolymerization was carried out under continuous stirring at 72–76 °C for 3 h. The product was cooled down to 60 °C and neutralized with 15 % aqueous sodium hydroxide.

2.3 Characterization of Latex and CES

The DS value of CES was determined as per the study reported¹³. Apparent viscosity of CES was measured by a NDJ-79 rotary viscometer with a shear rate of 2028 s⁻¹ under a paste concentration of 6 % (by wt) at 95 °C. Reaction efficiency (E_r , %) of starch cyanoethylation was calculated based on the following equation:

$$E(\%) = \frac{DS}{M_1 / M_2} \times 100 \quad \dots(1)$$

where M_1 and M_2 are the molar qualities of AN and starch charged during the cyanoethylation respectively. The DS value, viscosity, and reaction efficiency were 0.045, 11 mPa·s and 23.5 % respectively.

The FTIR spectra of CES and native starch were recorded over a wave number range between 500 cm⁻¹ and 4000 cm⁻¹ on a Nicolet Nexus 470 Spectrometer (Thermo Nicolet Co., Ltd. UAS). Starch product was

washed with ethanol-distilled water (50/50, by volume) thoroughly, dried, powdered by grinding the dried starches with KBr, and then pressed into discs. The discs were dried in electric oven at 105 °C for 12 h before analysis.

Conversion of monomer to polymer of aqueous P(MA/AA/AN) was measured by a titration using 0.1 mol/L standard sodium hyposulfite¹⁴. Apparent viscosity of P(MA/AA/AN) was determined using an NDJ-79 rotary viscometer under a concentration of 4 % (w/w) at 20 °C¹⁵. Solid content of P(MA/AA/AN) was determined based on a weight method¹⁴. The conversion, viscosity, and solid content of the latex were 99.5 %, 3.2 mPa·s, and 13.94 % respectively.

2.4 Cast and Measurements of Starch Film

Starch film was cast from aqueous CES/P(MA/AA/AN) paste. Twenty four grams of the latex and CES (blending ratio indicated in Table 1) was dispersed in distilled water to form 400 g of dispersion. The dispersion was heated to 95 °C and mechanically stirred for 1 h. Then, the paste was cooled down to 60 °C and completely poured onto a 650 mm × 400 mm polyester film spread on a well-leveled glass plate and dried at a controlled ambient condition (65 % relative humidity and 20 °C). The film obtained from the paste was carefully peeled off, tailored into strips (200 mm × 10 mm, 100 mm × 20 mm, and 100 mm × 5 mm), and kept under above ambient condition for 24 h before being tested.

By using 200 mm × 10 mm strips, tensile strength, breaking elongation, and work-at-break of the film were determined on a BZ2.5/TNIS Zwick Material Tester (Zwick, Ulm, Germany) with an initial chuck-distance of 100 mm and a drawing speed of 50 mm/min in accordance with our previous work¹⁶.

Twenty samples were measured for each case, and their average and coefficient of variation were reported.

Bending endurance of the film was determined in term of the time required for bending the film to break. The determination was conducted on a Y 731 machine (Changzhou Textile Instrument Plant, Jiangsu, China) using the strips (using 100 mm × 5 mm strips). The machine bent the strips repeatedly to an angle of 120° under a tension of 4900 dynes until it broke. The average times reported were 10 successful tests with which the abnormal values were rejected by statistical analysis.

Thickness of the strip was gauged with an YG141 measuring tool (Changzhou Textile Electronic Tester Co. Ltd., China). For each individual strip, three values were measured (one was in the middle position of the strip and others at its two ends). Twenty samples were measured for each case and their average was reported. Moisture regain of the film was surveyed by a weight method¹⁶.

The time required for breaking the strip in water was measured by saturating the strip (100 mm × 20 mm) in excessive water. One end of the strip was gripped over water bath, and another end of the strip was put into water at 80 °C under a tension of 490 dynes (by fixing a 0.5 g metal load on the end immersed into water). The time measured was a period beginning from the time when one end of the strip was put into water and ending at the time when the strip was broken. Ten samples were determined for obtaining mean value and coefficient of variation.

2.5 Adhesion-to-Fibres

The adhesion-to-fibres was measured by using roving as fibre substrate on the basis of FZ/T 15001-2008. Briefly, the roving carefully wound onto a frame was impregnated with a 1 %

Table 1—Effect of P(MA/AA/AN) on tensile properties of CES film^a

Blending ratio of P(MA/AA/AN) % (by wt)	Tensile strength		Breaking elongation		Work-to-break	
	Average MPa	CV %	Average %	CV %	Average mJ	CV %
0	35.4	13.41	1.94	9.28	37.1	28.15
3	34.9	15.80	2.31	15.17	46.9	27.80
6	33.3	9.26	3.18	9.35	62.3	9.26
9	31.1	5.33	3.38	9.81	66.2	13.68
12	31.1	12.03	4.02	17.25	78.9	18.47
16	30.1	5.81	4.63	13.50	89.8	14.65
20	30.5	4.85	6.56	15.38	139.1	4.85

^a Measured under the atmospheres of RH 65 % and 20 °C with a drawing speed of 50 mm/s.

CES/P(MA/AA/AN) paste and dried in air. Then, the sized roving was subjected to a drawing test to failure. It was the failure force that was used to evaluate the adhesion of the blends to fibres. Generally, greater value of the force of sized roving implied stronger adhesion to fibre. The measurement of the force was described in our former work¹⁶.

2.6 Determination on BOD₅ and COD

Aerobic biodegradation were evaluated by chemical oxygen demand (COD) and biological oxygen demand within 5 days (BOD₅) via a standard method¹⁷. The COD test determines the organic content in terms of both biodegradable and non-biodegradable compounds, whereas the BOD₅ evaluates the biodegradable fraction¹⁸. The data of COD and BOD₅ reported were the averages of triplicate individual tests for aqueous paste (0.1 g/L). The ratio of BOD₅ to COD was adopted to reflect aerobic degradability according to a criterion¹⁹.

3 Results and Discussion

Infrared spectra of CES (a) and native starch (b) were taken for examining the change in the chemical structure of starch before and after the cyanoethylation, as shown in Fig. 1. As is expected, a new adsorption peak is observed at 2225 cm⁻¹ besides the characteristic absorption peaks of native starch. The new peak corresponds to the characteristic absorption peak of nitrile in the cyanoethyls introduced onto starch chains. This new peak proves the existence of cyanoethyls introduced.

3.1 Effect on CES Film

Table 1 shows the effect of P(MA/AA/AN) latex on the tensile strength, breaking elongation, and work-at-break of CES films. It can be observed that

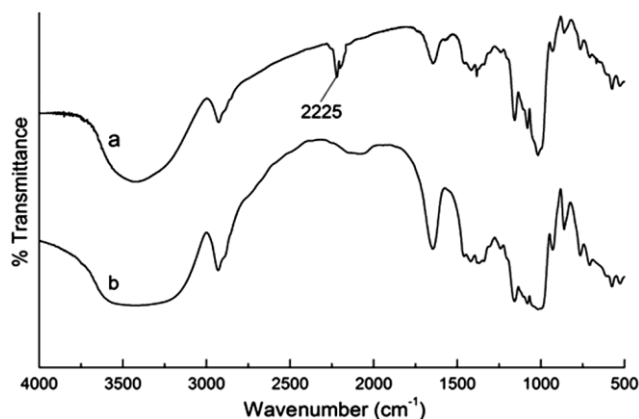


Fig. 1—FTIR spectra of CES (a) and native starch (b)

the elongations and works of CES/P(MA/AA/AN) films are significantly greater than those of pure CES one, whereas the strengths of the blending films decrease. In addition, the tensile properties depend on the amount of the latex blended with CES. With the increase in the amount of latex, breaking elongation and work-at-break increase. The maximum elongation and work of CES/P(MA/AA/AN) film are found to be 6.58 % and 139.1 mJ respectively, and are observed at 20 % (by wt) of the latex. This elongation of CES/P(MA/AA/AN) film is 2.38 times greater than that of pure CES film, whereas its maximum work is 2.75 times greater than the work of pure CES film. The result implies that the latex produces significant toughening to CES film. An increase in the amount of the latex favors the reduction in film brittleness. This finding is found similar to the result observed by Zhang *et al.*⁶, who toughened starch with polyurethane prepolymers for thermoplasticity. They reported that almost 100 % of polyurethane particles were cross-linked to starch matrix. However, excessive cross-linking is seriously deleterious to the removal of starch from sized yarns¹⁶. Accordingly, the technique cannot be adopted during sizing operation.

To examine the effect of this latex on the toughening of CES film, stress-strain curves of CES and CES/P(MA/AA/AN) films have been taken (Fig. 2). Generally, the shape of stress-strain curve and the area under the curve can be used to distinguish the brittleness or toughness of a polymeric material²⁰. The curve clearly indicates that the strength of CES film rises rapidly until it reaches failure point with a small extension, reflecting that CES film is brittle and rigid. On the other hand, however, the curves of CES/P(MA/AA/AN) film present significantly larger

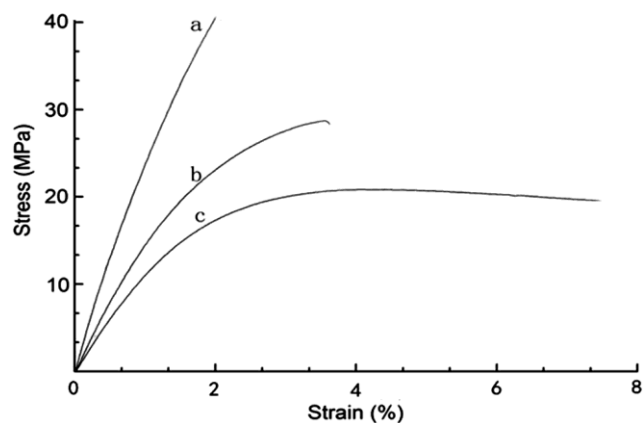


Fig. 2—A typical stress-strain curves of pure CES film (a), CES film toughened with 9 % P(MA/AA/AN) (b), and CES film toughened with 20 % P(MA/AA/AN) (c)

deformation than that of CES one. The failure strains of CES/P(MA/AA/AN) films are about 1-3 times higher than the strain of CES one. Moreover, the area under the curve represents the energy required for breaking a specimen and is often used to reflect the toughness of a polymer material. The areas of stress-strain curves of the blending films are markedly larger than that of CES one. The observations confirm that the latex reduces the brittleness of CES film.

The improvement in the toughness of CES film is mainly due to the fact that the latex is a soft, flexible, and uncrystallized polymer, whereas starch is recognized as a brittle and rigid one. The segments of the latex molecules are mobile, which is able to generate larger deformation for the blending film. Undoubtedly, the deformability of the latex is much greater than that of starch, while its tensile strength is far weaker. Therefore, the elongation of the blending film inclines and the tensile strength declines after the latex is blended with CES.

During weaving operation, sized yarns have to withstand repeated and extensive bending³. Therefore, the impact of the latex on bending endurance must be accessed. Figure 3 demonstrates the effect of the latex blended with CES on bending endurance of the film. The Figure indicates that the latex improves the endurance and the improvement depends on its blending ratio. With the rise in the ratio, the endurance increases initially, reaches a maximal value at 16 % (by wt) of the latex, and then decreases again. This result is obviously attributed to the reduced brittleness or toughening arisen by the blending. However, excessively increasing the amount of the latex blended with CES leads to a substantial decrement in tensile strength of the film, and thus lowering bending endurance.

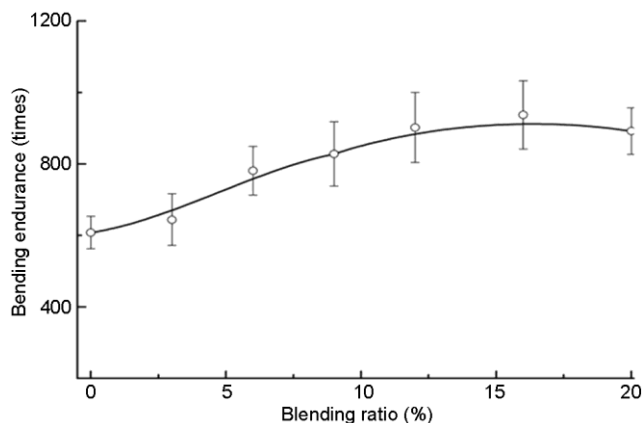


Fig. 3—Effect of P(MA/AA/AN) on bending endurance of the blending film

3.2 Effect on Adhesion

The influence of the latex blended with CES on the adhesions of CES to cotton and polyester fibres is shown in Table 2. It can be observed that the latex is able to improve the adhesions of CES to the two kinds of fibres. Blending ratio of the latex plays an important role on the adhesion. With the increase in the ratio, the adhesion increases, reaches a maximal value at 12-16 % (by wt), and then declines slightly.

Adhesion failure is usually divided into cohesive and interfacial failures, according to failure position. The former refers to a failure that occurs wholly within the bulk phase of an adhesive layer, whereas the latter denotes a failure that occurs exactly at the interface between the adherent and adhesive layer. It is as well important to emphasize that the shrinkage of adhesive layers on drying due to water loss of starch paste generates internal stresses both on the interfaces and within the bulk phase of adhesive layers since adhesive layer/fibre interfaces are constrained by adhesive bonding. The stresses thus developed are deleterious to bonding strength, particularly for brittle adhesives like starch. However, the stresses will relax if an adhesive is toughened. Due to the blending of this flexible latex, sufficient deformation is likely to reduce the stresses and thus enhances the adhesion therewith. On the other hand, however, cohesive failure must also be considered. The strength of CES/P(MA/AA/AN) film decreases as blending ratio increases (Table 1). This can be interpreted as a decreased cohesive force of the adhesive layers among fibres. Therefore, cohesive failure may occur at lower applied force when the latex is blended excessively. Therefore, excessive increase in the ratio reduces the adhesion.

Table 2—Effect of P(MA/AA/AN) on the adhesion to fibres

Blending ratio of P(MA/AA/AN) % (by wt)	Cotton		Polyester	
	Bonding strength cN/tex	CV %	Bonding strength cN/tex	CV %
0	17.9	3.92	27.8	6.22
3	18.4	5.19	28.8	6.79
6	18.9	4.34	29.8	7.47
9	18.8	4.99	29.4	3.48
12	19.6	3.99	31.7	7.16
16	19.4	3.66	31.8	2.47
20	19.0	4.12	31.3	5.72

3.3 Effect on Desizeability

The starch sized onto warp yarns must be removed from the yarns after weaving and before dyeing, printing, and finishing. Insufficient removal of the starch induces fabric with a hard handle, and causes stains compromising fabric appearance and subsequent processing²¹. As a result, easy desizing is one of the essential requirements for any kind of warp sizes. Therefore, desizability of the blends is accessed. Currently, a time required for breaking starch film in hot water is often used to evaluate the desizability of a sizing agent¹⁶. A shorter time often means an easier desizing.

The influence of the latex on the time required for breaking starch film in water is shown in Table 3. It can be observed that the latex has substantial impact on the time. The time is directly dependent on the blending ratio of the latex. The greater the ratio, the shorter is the time. This suggests that the blending of the latex favors the removal of CES from sized yarns. The reason is obviously due to water solubility of the latex in water. Moreover, the increased moisture regain of the film is also helpful in the removal.

During the formation of starch film from cooked starch paste, linear amylose in the paste aligns them to form three-dimensional arrays²¹ through hydrogen bonding. The film with this peculiar structure is difficult to break apart in water. Accordingly, starch film is water-insoluble and the desizing of starch with water is usually a time-consuming process. Consequently, the starch sized onto warp yarns cannot be simply washed away by water and specific processes such as enzymatic, oxidative, and alkaline desizing^{22,23} are required. However, the emulsion-copolymerized P(MA/AA/AN) is hydrophilic and water dispersible. After being blended with CES, it forms uncrystallized

Table 3—Effect of P(MA/AA/AN) on the desizability of CES

Blending ratio of P(MA/AA/AN) % (by wt)	Thickness μm	Moisture regain %	Time required to break the film in water	
			Average s	CV %
0	98	10.57	685	7.28
3	102	11.13	379	5.54
6	98	11.95	284	4.11
9	107	11.82	107	11.8
12	93	12.03	31.6	6.95
16	97	13.13	28.7	12.5
20	92	14.35	23.4	8.62

and water-soluble domains dispersed in continuous starch phase during film formation. When the blending film is placed in contact with water, it converts into swollen substances via absorbing water, leading to increased latex domains dispersed in starch matrix. Undoubtedly, the latex domains dispersed in starch film swell more heavily than starch matrix. However, the domains can only swell to some equilibrium state at which the retractive forces of continuous starch matrix balance the swelling force of latex domains since they are combined to form an integrated film. It is likely that the swelling force of the latex domains accelerates disintegration of the film and shortens the time.

3.4 Effect on Aerobic Biodegradation

To reveal the influence of the latex on aerobic biodegradation of desizing water, BOD₅ and COD of the blends have been measured and their ratios are used to evaluate the biodegradation (Table 4). It can be seen that BOD₅/COD ratio of CES is lower than that of native starch. This is attributed to the cyanoethyls introduced onto starch chains, as these substituents give starch a resistance to biodegradation². For the blends, their ratios are little lower than the ratio of CES, and show a certain extent of sensitivity to the amount of the latex blended. The ratios of the blends decrease as the amount of the latex increases. Obviously, P(MA/AA/AN) latex is a synthetic polymer and cannot be competitive with starch on biodegradation. Therefore, the ratios of the blends are lower than those of the two kinds of starches considered. However, the ratios of the blends are all over 0.2, indicating that the blends are also biodegradable¹⁵.

Table 4—Effects of P(MA/AA/AN) on the COD, BOD₅, and BOD₅/COD ratio of the blends

Types of sizes	Blending ratio of P(MA/AA/AN) % (by wt)	BOD ₅ mg O ₂ /L	COD mg O ₂ /L	BOD ₅ /COD
Native starch	-	36.6	96.6	0.379
CES	-	31.7	102.5	0.309
CES/ACL blends	3	31.2	103.2	0.302
	6	30.8	105.1	0.293
	9	30.5	107.9	0.283
	12	29.7	110.8	0.268
	16	28.9	114.2	0.253
	20	28.1	120.5	0.233

4 Conclusion

It has been found that the emulsion-copolymerized P(MA/AA/AN) latex is an efficient toughening agent for alleviating the brittleness of CES film through mechanical blending for warp sizing. The latex blended with CES produces significant effect on the properties such as tensile strength, breaking elongation, work-at-break, and bending endurance of CES film. In addition, it is able to improve the adhesions of the starch to cotton and polyester fibres. Furthermore, the trials of desizing and aerobic biodegradation display that P(MA/AA/AN)/CES blends are desizable and aerobic biodegradable. The blending ratio of P(MA/AA/AN) latex is one of the most important parameters that determine the performances of the blends. Properly increasing amount of the latex is able to improve the performances required for warp sizing. However, excessive increase in the ratio leads to some problems such as significant reduction in tensile strength of starch film and notable retardation in aerobic biodegradation of desizing wastes. Based on the film properties, adhesion, desizability, and aerobic biodegradability, the blending ratio of the latex is recommended in a range of 12-16 % (by wt) for warp sizing.

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