

# Investigation on Mechanical Properties of CMSLDS/ Acrylate Copolymeric Blending Films for Warp Sizing

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**Abstract:** Carboxymethyl starch with lower degree of substitution was blended with acrylate copolymer for revealing the relation between mechanical properties and chemical structure of blending film. Effects of carboxymethylation of starch, acrylate constituent units of acrylate copolymers, and copolymer content of the film on the properties were investigated. The mechanical properties were evaluated in terms of tensile strength, breaking elongation, abrasion resistance, and flex-fatigue resistance. Film morphology was examined with X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscope (AFM). It was found that the properties depended on the degree of substitution of carboxymethyl starch, chemical structure of acrylate units, and content of acrylate copolymer. Phase-separation of the two ingredients occurred within film matrix and the separation was decreased after starch carboxymethylation. Breaking elongation and flex-fatigue resistance of the film reached maximums when acrylate copolymer content was 50%. Excessively increasing the content of acrylate copolymer reduced the film properties.

**Key words:** carboxymethyl starch; acrylate copolymer; blending film; mechanical properties; degree of substitution

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## Introduction

In past 2 - 3 decades, carboxymethyl starch used in warp sizing procedure was produced in organic solvents and had a degree of substitution (DS) about 0.2. The product was widely used as compatibilizer for warp sizing. However, it is high in cost and unfriendly in environmental protection because of high DS value and being produced in organic solvents. Moreover, with the development of starch modification, compatibility between starches and other sizing ingredients has been greatly improved. As a

result, the carboxymethyl starch used as compatibilizer is being reduced both in China and abroad.

In recent years, some new starch-based sizing agents have been developed to improve the quality of sized warp yarns. The agents are available from a slight carboxymethylation of starch in water through a reaction of starch with monochloroacetic acid in presence of sodium hydroxide<sup>[1, 2]</sup>. It has been elucidated that the carboxymethylation of starch with lower DS value evidently enhances the adhesion to fibers<sup>[3]</sup> and substantially reduces the amount of PVA component required in a size formulation<sup>[4]</sup>. Up to now, great efforts have been made to confirm their effectiveness through industrial trials. It has been confirmed that the carboxymethyl starch with lower degree of substitution (CMSLDS) shows good performances for warp sizing<sup>[5]</sup>. However, industrial trials reveal that CMSLDS leads to increased flaking of size.

As is well known, in sizing procedure, part of sizing paste is converted to sizing film around sized yarns. The film protects the yarns from various abrasions and increases their abrasion resistance. Generally, the film should possess such properties as sufficient breaking elongation, appropriate strength, excellent flex-fatigue resistance, and good abrasion resistance. However, starch films are usually brittle and rigid<sup>[6]</sup>, thereby arising the question like flaking of size. The flaking is a serious threat to quality of sized yarns. Therefore, it is an urgent need to reduce the flaking and improve the mechanical properties of CMSLDS film.

Industrial concern on qualities of sized yarns has now resulted in a research interesting in finding a suitable way to reduce brittleness of starch film around sized yarns. An important way to eliminate the defect of starch films is to incorporate suitable synthetic polymers<sup>[7, 8]</sup>. As is well known, acrylate copolymers can be used with starch-based sizing agents to size a large quantity of warp yarns. Therefore, we incorporate acrylate copolymers within CMSLDS and explore the impact of the incorporation on mechanical properties of CMSLDS/acrylate copolymer blending films. Obviously, acrylate constituent units in the copolymers, DS value of CMSLDS, and copolymer content exert significant effects on

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the properties of the film. Therefore, the factors mentioned above are considered in this investigation.

## 1 Experimental

### 1.1 Materials

Commercial cornstarch with a paste viscosity of 42 mPa·s was obtained from Yixing Starch Co., Ltd. The starch was purified before use in accordance with a previous study<sup>[9]</sup>. Methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), acrylic acid (AA), and benzoyl peroxide (BPO) were of analytical grade.

### 1.2 Preparation and characterization of CMSLDS

Before carboxymethylation, cornstarch was acid-modified in order to decrease paste viscosity. Apparent viscosity and its stability of the acidified starch were 16 mPa·s and 88%, respectively. The acid-modified starch (100 g, dry base) was dispersed in 250 mL distilled water, and the dispersion was transferred into a 500 mL flask. After monochloroacetic acid and sodium hydroxide were added into the flask, the reactants were reacted under continuous stirring at 50 °C for 6 h. By changing the amounts of monochloroacetic acid and sodium hydroxide, a series of CMSLDSes with different DS value was obtained. The products were neutralized with 1 mol/L HCl, filtered, washed with distilled water for 6 times. Finally, the modified starch was dried at 40 °C.

Apparent viscosity and its stability of CMSLDS were determined with the method described in Ref. [9]. DS value of CMSLDS was calculated from Eq. (1) through carboxyl content:

$$DS = \frac{162M}{4500 - 58M} \quad (1)$$

where M was carboxyl mass content (%) of CMSLDS. The content was measured according to Ref. [10].

### 1.3 Synthesis and determination of acrylate copolymer

The copolymer was synthesized through a copolymerization of acrylates with acrylic acid. The copolymerization was indicated in Ref. [11].

Conversion of monomer to polymer, solid content, and

apparent viscosity of the acrylate copolymers were determined as the methods indicated in Ref. [11]. Molecular weight and its distribution were measured with a high pressure liquid chromatograph (HPLC, 1515, Waters Company, USA).

### 1.4 Preparation and measurement of the films

CMSLDS and acrylate copolymer were diluted with distilled water to form 6% dispersion. The dispersion was heated to 95 °C under continuous stirring and maintained at the temperature for 1 h. The blended paste was poured onto a 650 mm × 400 mm polyethylene film spread on a glass plate with the same size, and dried under 65% relative humidity at 20 °C. Then, the films were collected and tailored into strips with required sizes (200 mm × 10 mm for the tests of tensile and abrasion resistance, and 50 mm × 5 mm for the flex-fatigue resistance measurement). After the stripped films had been stood under the above condition for 24 h, their tensile strength, breaking elongation, wear loss, and flex-fatigue resistance were measured in accordance with Ref. [9].

Crystallinity of the film was measured using XD/max-2500XRD device (Japan). The radiation source was 30 kV, 20 mA,  $\lambda = 0.154$  nm, and scan area was 5°-60°. Surface morphology of the films was surveyed by an SEM (Quanta-200, Holland FEI Company) at a magnification of 2400. AFM (CSPM-4000, Guangzhou Benyuan Company) was employed to image surface morphology of the films.

## 2 Results and Discussion

CMSLDS and acrylate copolymers prepared are characterized in Tables 1 and 2, respectively.

**Table 1** Characterization of CMSLDS

DS	Apparent viscosity/ mPa·s	Viscosity stability/ %
0.000	16	88
0.004	13	85
0.009	15	87
0.017	16	92
0.026	17	94
0.036	18	94

**Table 2** Characterization of acrylate copolymers

Acrylate copolymers	Molar content of acrylate units in copolymers		Conversion of monomer / %	Solid content / %	Apparent viscosity / mPa·s	$\bar{M}_n$ ( $\times 10^4$ )	$\bar{M}_w$ ( $\times 10^5$ )	$\bar{M}_w / \bar{M}_n$
	Monomer fed/ %	Measured/ %						
P(MA/AA)	80	83.0	99.02	24.98	5.0	10.00	1.38	1.38
	70	73.8	98.61	24.72	5.5	9.90	1.40	1.41
	60	65.4	97.55	23.78	8.8	9.42	1.34	1.42
P(EA/AA)	70	72.6	96.16	24.28	2.8	7.50	1.07	1.43
P(BA/AA)	70	71.9	97.34	23.29	2.4	9.17	1.41	1.54

## 2.1 Effect of starch carboxymethylation

Table 3 demonstrates the influence of starch carboxymethylation on mechanical properties of CMSLDS/polyacrylate blending films. Breaking elongation and flex-fatigue resistance of the film increase initially with the increase of DS value, reach maximum simultaneously at a DS value of 0.026, and then decrease. As the DS value increases, tensile strength decreases, whereas wear loss increases continuously.

**Table 3** Influence of DS value on mechanical properties of the film

DS of CMSLDS	Tensile strength / (N · mm <sup>-2</sup> )	Breaking elongation / %	Wear loss / (mg · cm <sup>-2</sup> )	Flex-fatigue resistance / times
0.000	13.14	21.08	0.67	1 690
0.004	12.91	21.56	0.71	1 784
0.009	12.39	22.47	0.73	1 850
0.017	12.05	23.50	0.81	2 062
0.026	11.71	25.87	0.90	2 405
0.036	3.80	3.37	1.04	942

Notes: Weight ratio of P(MA/AA) to CMSLDS was 50 : 50; molar ratio of MA fed to the monomers charged was 70 %.

Carboxymethyl groups introduced onto starch backbones prevent formation of hydrogen bonds and interfere with intermolecular association of starch molecules due to their steric effect. The prevention and interference lead to reduced orientation in starch arrangement and result in decreased crystallinity of starch film. This can be confirmed through XRD analysis for the starch film cast before and after starch carboxymethylation as shown in Fig. 1.

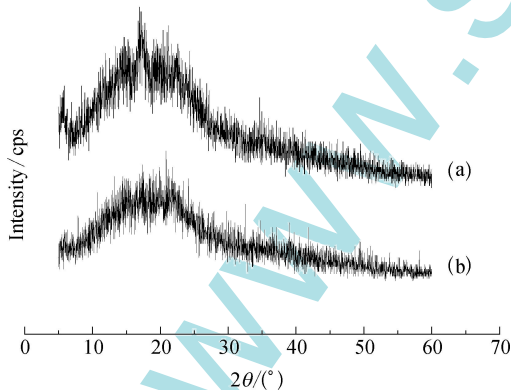
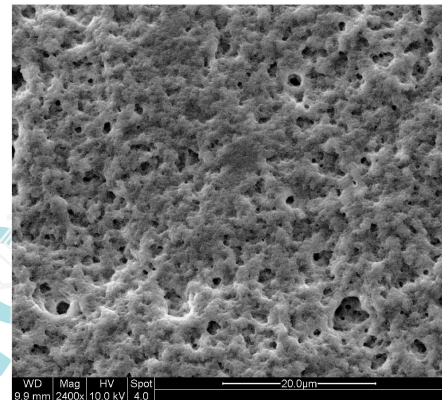


Fig. 1 XRD patterns of the blending films (a) native starch, (b) CMSLDS with a DS value of 0.017

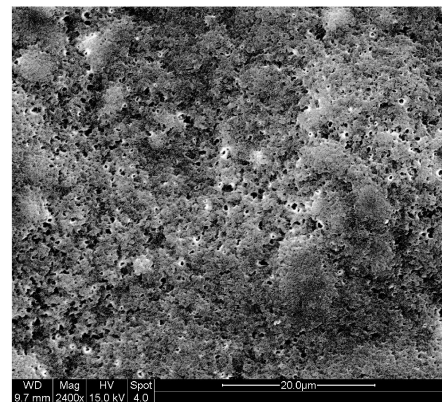
In addition, the groups are hydrophilic and capable of absorbing water. The steric effect of the groups and the water absorbed play a plasticization action to starch films and enhance their elasticity. As a result, film brittleness reduces, and its breaking elongation and flex-fatigue resistance increase. Moreover, the groups introduced and water absorbed increase the distance of starch molecules, which results in decreased van der Waals forces among starch

molecules. Therefore, the strength decreases with the increase of DS value from 0 to 0.026. When the DS exceeds 0.026, however, breaking elongation and flex-fatigue resistance of the film decrease. It has been observed that starch filtration becomes difficult. Apparently, the decrease is caused by part gelatinization of carboxymethyl starch in preparation. Therefore, it is proposed that the modification level of CMSLDS prepared in water should be limited to about 0.026.

Film morphology is shown in Figs. 2 and 3. The pictures depict that phase separation occurs within the film no matter whether the starch is carboxymethylated. It should be noted, however, that the separation extent is reduced after starch carboxymethylation.

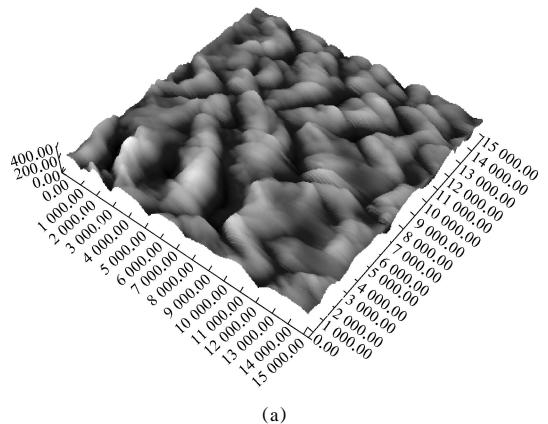


(a)

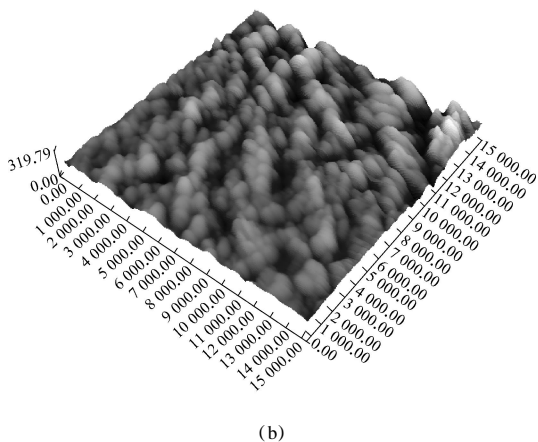


(b)

Fig. 2 SEM pictures of blending films (a) native starch, (b) CMSLDS with a DS value of 0.017



(a)



ig.3 AFM pictures of blending films (a) native starch ,  
(b) CMSLDS with a DS value of 0.017  
(scanning scale: 15 000 nm  $\times$ 15 000 nm)

## 2.2 Effect of acrylate units

It is obvious that mechanical properties of the blending

**Table 4** Influence of acrylate constituent units on the mechanical properties

Acrylate copolymers	Molar content of acrylate units in copolymers		Tensile strength / (N $\cdot$ mm <sup>-2</sup> )	Breaking elongation / %	Wear loss / (mg $\cdot$ cm <sup>-2</sup> )	Flex-fatigue resistance / times
	Monomer fed/ %	Measured/ %				
P(MA/ AA)	80	83.0	9.85	25.83	0.96	2 684
	70	73.8	12.06	23.50	0.81	2 062
	60	65.4	13.49	13.57	0.71	876
P(EA/ AA)	70	72.6	8.40	25.23	1.05	2 655
P(BA/ AA)	70	71.9	5.60	28.64	1.22	3 923

Notes: Weight ratio of acrylate copolymer to CMSLDS was 50 : 50; DS value of CMSLDS was 0.017.

With the increase of the atom number, cohesive force among acrylate copolymer molecules reduces and glass transition temperature of acrylate copolymers decreases. This leads to an increased flexibility and movability for copolymer molecules. Therefore, the breaking elongation and flex-fatigue resistance of the films enhance. Apparently, reduced cohesive force leads to a decreased strength. Furthermore, as molar content of MA units decreases, glass transition temperature of acrylate copolymer increases, and movability of the copolymeric chains decreases. Thus, breaking elongation and flex-fatigue resistance of the films decrease while tensile strength increases.

## 2.3 Effect of copolymer content

Effect of the copolymer content on mechanical properties of the film is shown in Table 5. Tensile strength of the films decreases continuously as the content increases. Breaking elongation, wear loss, and flex-fatigue resistance of the films increase progressively with the increase of the content, reach their maximal values simultaneously at 50 %, and then decrease.

films are not only directly related to the CMSLDS ingredient, but also depending on the acrylate copolymers blended. Therefore, the influence of acrylate copolymers upon the properties should be evaluated. There are two parameters that decide chemical structure of the copolymers: one is carbon atom number of alkyl ester in acrylate constituent units of acrylate copolymer, the other is molar content of acrylate units in acrylate copolymer.

Effects of carbon atom number and molar content on mechanical properties of the blending films are shown in Table 4. Breaking elongation, wear loss, and flex-fatigue resistance of the films increase with the atom number increasing, while tensile strength decreases. Furthermore, as molar content of MA units decreases from 80 % to 60 %, the strength increases, whereas the breaking elongation, wear loss, and flex-fatigue resistance decrease.

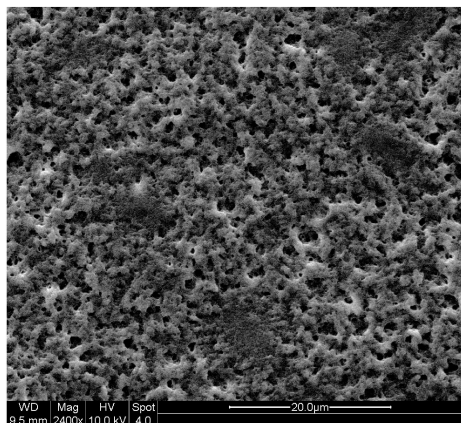
**Table 5** Influence of acrylate copolymer content on mechanical properties of blending films

P(MA - AA) content / %	Tensile strength / (N $\cdot$ mm <sup>-2</sup> )	Breaking elongation / %	Wear loss / (mg $\cdot$ cm <sup>-2</sup> )	Flex-fatigue resistance / times
0	32.33	3.02	0.40	1 082
10	24.95	2.29	0.57	564
30	19.35	4.42	0.75	1 236
50	12.06	23.50	0.81	2 062
70	2.69	5.81	0.95	1 740

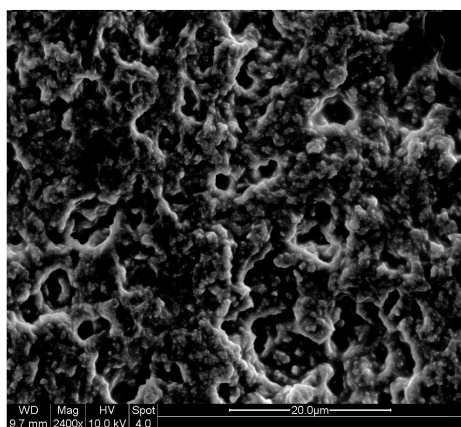
Notes: DS value of CMSLDS was 0.017; molar content of MA fed to the monomers charged was 70 %.

It is well known that tensile strength of acrylate copolymer is far lower than that of starch, whereas breaking elongation is much greater. Therefore, increasing the content leads to the decrease of tensile strength and results in the increase of breaking elongation. SEM pictures in Fig.4 show variation of film morphology. The pictures reveal that the content exerts a significant effect on the morphology. When the content reaches 70 %, starch is converted into separation phase. Therefore, the properties of the film are mainly dependent on acrylate copolymer

ingredient, which makes tensile strength decrease. It is beneficial to enhance the elongation and flex-fatigue resistance when the content is 50 %.



(a)



(b)

Fig.4 SEM pictures of the films : acrylate copolymer content (a) 50 % , (b) 70 %

### 3 Conclusions

Incorporation of acrylate copolymer into CMSLDS/ acrylate copolymer blends is an effective method to enhance elasticity for the blending film. Mechanical properties of the film strongly depend on the DS value of CMSLDS, carbon atom number of alkyl ester in acrylate constituent units of acrylate copolymer, molar content of acrylate constituent units in acrylate copolymer, and content of acrylate copolymer in the film.

Carboxymethylation of starch in water is only capable of introducing a small amount of carboxymethyl groups onto starch backbones if starch granules are intended to stand granules so as to facilitate separation in preparation of CMSLDS. In spite of being low-modified, CMSLDS gives substantial variations in tensile strength, breaking elongation, wear loss, and flex-fatigue resistance of the blending film. The modification introduces elasticity to the blending film. Maximal effect can be achieved at a DS

value of 0.026. Further increasing modification level of CMSLDS makes starch granules partly gelatinized in preparation. Therefore, the DS level of CMSLDS prepared in water should be limited to about 0.026. Phase-separation extent within the film reduces after the carboxymethylation.

Excessively increasing the content of either acrylate copolymer or CMSLDS ingredient decreases the properties of the film. By incorporating 50 % acrylate copolymer into CMSLDS, a notable improvement on the elasticity can be achieved. A preferred acrylate copolymer for enhancing the mechanical properties can be obtained from a copolymerization of butyl acrylate and acrylic acid at a molar ratio of 70 : 30 through free radical polymerization. The results provide a base to enhance the elasticity of the film and eliminate the flaking of size when CMSLDS is used as sizing agent.

### References

- [ 1 ] Khalil M I, Hashem A, Hebeish A. Carboxymethylation of Maize Starch [J]. *Starch/ Stärke*, 1990, **42**(2) : 60 - 63.
- [ 2 ] Stojanović Ž, Jeremić K, Jovanović S. Synthesis of Carboxymethyl Starch [J]. *Starch/ Stärke*, 2000, **52**(11) : 413 - 419.
- [ 3 ] Zhu Z F, Gu G X, Kang C Z. Effect of Carboxymethyl Starch with Low Degree of Substitution on the Adhesion Behavior to Textile Fibers [J]. *Polymer Materials Science & Engineering*, 2003, **19**(4) : 106 - 109. (in Chinese)
- [ 4 ] Zhang L X, Wang Y X, Zhu Z F. Research on the Properties of Low-Substituted Carboxymethyl Starch [J]. *Yarn & Fabric Forming Technology*, 2008, (2) : 49 - 52. (in Chinese)
- [ 5 ] Mostafa K M, El-Sanabary A A. Carboxyl-Containing Starch and Hydrolyzed Starch Derivatives as Size Base Materials for Cotton Textiles [J]. *Polymer Degradation and Stability*, 1997, **55**(2) : 181 - 184.
- [ 6 ] Wurzburg O B. *Modified Starches: Properties and Uses* [M]. Florida : CRC Press, 1986 : 1 - 16.
- [ 7 ] Jiang W B, Qiao X Y, Kang S. Mechanical and Thermal Properties of Thermoplastic Acetylated Starch/ Poly (ethylene-co-vinyl alcohol) Blends [J]. *Carbohydrate Polymer*, 2006, **65**(2) : 139 - 143.
- [ 8 ] Wu C S. Physical Properties and Biodegradability of Maleated-Polycaprolactone/Starch Composite [J]. *Polymer Degradation and Stability*, 2003, **80**(1) : 127 - 134.
- [ 9 ] Zhu Z F, Chen P H. Carbamoyl Ethylation of Starch for Enhancing the Adhesion Capacity to Fibers [J]. *Journal of Applied Polymer Science*, 2007, **106**(4) : 2763 - 2768.
- [ 10 ] Daul G C, Reinhardt R M, David R J. Preparation of Soluble Yarns by the Carboxymethylation of Cotton [J]. *Textile Research Journal*, 1953, **23**(10) : 719 - 726.
- [ 11 ] Zhu Z F, Qiao Z Y, Kang C Z, et al. Effect of Acrylate Constituent Units on the Adhesion of Polyacrylate Sizes to Fiber Substrates [J]. *Journal of Applied Polymer Science*, 2004, **91**(5) : 3016 - 3022.