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# Preparation and Properties of β-Cyclodextrin / Modified Cellulose Membrane Composites

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**Abstract:** At present, the oil is not represented as the depletion of renewable resources, to find new renewable resources and its effective development and utilization is imperative. Natural cellulose is widely found in the natural biological macromolecules, with cheap, easy to get, environmentally friendly and many other advantages. But the solubility of cellulose to a certain extent affected the cellulose reactivity, for this modified cellulose, making the cellulose material came into being. In this study, β-cyclodextrin (β-CD) modified cellulose composite membrane was prepared under basic conditions using β-CD and sodium carboxymethyl cellulose as raw materials. The results showed that the introduction of β-CD reduces the deformation rate of the film and enhances the tensile strength of the composite membrane by infrared spectroscopy and mechanical properties. β-CD modified cellulose-based crosslinking to β-CD, sodium carboxymethyl cellulose original infrared characteristics of the peak, cross-linked at 1650 $cm^{-1}$ produced a new of the double peak, at 1450 $cm^{-1}$ produced a new single peak.
**Keywords:** Modified Cellulose; β-Cyclodextrin; Membrane Composites.

## INTRODUCTION

"Accelerating the construction of a resource-conserving and environment-friendly society" is a major decision made in the light of China's national conditions. With the depletion of non-renewable resources represented by petroleum, the use of natural polymer materials instead of petroleum and other non-renewable resources to prepare membrane materials has aroused great attention of scientists in the film industry [1]. It is imperative to find new renewable resources and effectively develop and utilize them. Environmentally friendly chemistry should be the preferred method for every researcher.

Cellulose is the natural macromolecular compound with the largest reserve in nature and has a wide range of sources, which is considered as the main source of energy and chemical industry in the future [2]. At present, environmental problems and energy problems are becoming more and more prominent in China, and environment-friendly materials have become the unremitting pursuit of researchers in various fields in China. Cellulose has many advantages, such as cheap, easy to obtain, non-toxic, good reproducibility and environmental friendliness [2]. It plays an important role in solving environmental and energy problems and has been widely concerned. Therefore, the key to the development and utilization of these natural macromolecular compounds is to explore the new "green" solvent for cellulose and other macromolecular dissolution and the "green" process for building materials [3]. However, the solubility of cellulose affects the reactivity of cellulose to a certain extent. The low solubility leads to the decrease of reactivity of cellulose, which is an obstacle to the wide application of cellulose. Therefore, modified cellulose emerges at the right moment.

Carboxymethyl cellulose (CMC), also known as modified cellulose is most dosage in the raw material of cellulose and the widest range, low cost, non-toxic, has a good biocompatibility, degradability and hygroscopicity of derivatives, its morphology is a white fibrous or granular powder, odourless tasteless, has the water absorbability, insoluble in organic solvents, soluble in hot water to form a transparent solution. CMC has the properties of stabilizer, dispersant, binder, emulsifier, thickener, suspension agent, sizing agent,

etc., so it has been widely used in the production of food, medicine, daily chemical, petroleum, papermaking, textile, construction and other fields. Sodium carboxymethyl cellulose (CMC-Na) is a modified product of cellulose. In addition to the advantages of wide source and low price, the most important is that it has excellent film-forming and biodegradability and other advantages, and is widely used [4]. Lan *et al*.[5] showed in the research progress of preparation technology of cellulose composite film that there were various types of materials that could be combined with cellulose, and the composition of other materials could not reach the excellent characteristics of plastic film except CS and polyvinyl alcohol, which were relatively abundant. Therefore, further studies on cellulose composite membranes should be carried out.

β-cyclodextrin (β-CD) is the crystallization of cyclodextrin oligosaccharides produced by starch under the action of cyclodextrin glucosyltransferase produced by bacillus cereus [6]. According to the previous research results, beta cyclodextrin has a "truncated conical" cavity structure, the outer wall has a strong hydrophilic property, and the inner cavity has a strong hydrophobic function, so it can play a role in stabilizing/protecting the guest molecules or controlling/delaying the release of the guest molecules [7]. Beta cyclodextrin belongs to a polyhydroxyl structure; the hydroxyl group in the molecular structure makes it easier to participate in chemical reactions. At the same time, compared with alpha-cyclodextrin and gamma-cyclodextrin, β-CD has higher selectivity, higher capacity, and better compatibility with biological systems when binding hydrophobic molecules, which has been proved non-toxic by safety evaluation and low price [7]. Therefore, β-CD has higher application value in various fields.

In this experiment, CMC/β-CD membrane composites were prepared by using green and non-polluting raw materials, sodium carboxymethyl cellulose and β-CD as raw materials. The influence of different cyclodextrin contents on the composite membrane was explored, and the optimized composite membrane design scheme was finally obtained. It provides some theoretical reference for the preparation of environment-friendly green composites.

## EXPERIMENTAL METHODS

### Preparation of modified cellulose matrix

Based on the hydrogen bond interaction between $SiO_2$ and water and cellulose, $SiO_2$ nanoparticles were successfully introduced into cellulose matrix in pre-cooled LiOH/urea aqueous solvent system, and inorganic/organic nanocomposite films were formed after solidification and regeneration [3]. Therefore, the corresponding raw materials were weighed according to the proportion of $H_2O$: NaOH: urea =200:15.1:8, and the three ingredients were placed in a 250 ml beaker to prepare 11 wt.% NaOH/4 wt.% urea aqueous solution. A certain amount of $SiO_2$ was placed in the alkaline system. After several hours of intense stirring at room temperature, $SiO_2$ was placed in the ultrasonic cleaning instrument for 0.5 hours to disperse evenly. Then mix the solution (5℃) for 5 h in the refrigerator frozen or at room temperature. Then a certain amount of sodium carboxymethyl cellulose was slowly added into the mixture system, and the mixture was set aside overnight. Sodium carboxymethyl cellulose is labeled as CMC-x.

**Table-1: The ratio of each sample matrix**

| No. | CMC (wt. %) | Water (g) | NaOH (g) | Urea (g) | $SiO_2$ (g) | Time(h) | Ultrasound (h) | Freezed or not |
|---|---|---|---|---|---|---|---|---|
| CMC-1 | 3 | 200.33 | 15.16 | 8.04 | 0.19 | 3 | 0.5 | Y |
| CMC-2 | 3 | 200.59 | 15.19 | 8.12 | 0.21 | 6 | 0.5 | N |
| CMC-3 | 3 | 200.16 | 15.18 | 8.10 | 0.2 | 12 | 0.5 | Y |
| CMC-4 | 3 | 401.73 | 30.31 | 16.41 | 0.43 | 6 | 0.5 | N |
| CMC-4(1) | 1.5 | 224.22 | - | - | - | - | - | - |
| CMC-4(2) | 0.5 | 219.96 | - | - | - | - | - | - |
| CMC-5 | 1.5 | 404.41 | 30.32 | 16.51 | 0.41 | 3 | 0.5 | N |
| CMC-5(1) | 1.5 | 223.45 | - | - | - | - | - | - |
| CMC-5(2) | 0.5 | 225.41 | - | - | - | - | - | - |
| CMC-6 | 3wt% | 402.78 | 30.25 | 16.07 | 0.41 | 12 | 0.5 | N |
| CMC-6(1) | 3wt% | 223.68 | - | - | - | - | - | - |
| CMC-6(2) | 3wt% | 223.76 | - | - | - | - | - | - |
| CMC-7 | 3wt% | 200.09 | 15.11 | 8.01 | 0 | 6 | 0.5 | Y |
| CMC-8 | 3wt% | 200.03 | 15.18 | 8.00 | 0.40 | 6 | 0.5 | Y |

### Preparation of modified composites

Apply adequate amount to the preparation method of modified cellulose matrix on the glass, use the method of tape casting on the glass, then put in dryer at the constant temperature of 50 ℃, tag was the same as the pure sodium carboxymethyl cellulose tag.

**Preparation of membrane composites with different contents of β-CD**

20.0g water was in a beaker of 100 ml, weighed the appropriate amount of β- cyclodextrin and mixed with water, putted the beaker in a water bath to dissolved β-CD completely, weighed 22.5 g modified cellulose matrix in the beaker. Putted the magnetic rotor into the beaker and placed the beaker on the magnetic stirrer to stir for 2 hours. Through trial and error, the film and glass glue were too tight, finally took the glass with a layer of transparent adhesive tape method to reduce the resistance between the film and glass, and was advantageous for the composite membrane stripped. Upon the stirring, sodium carboxymethyl cellulose/β-CD mixed spread on the glass substrate would the method of tape casting, then putted glass at 50 ℃ constant temperatures in drying oven. After drying completely, we removed the composite film and placed it in the fresh sealing bag for preservation and marking as showed in Table 2.

**Table-2: Preparation of membrane composites with different contents of β-CD**

| No. | Water (g) | β-CD (g) | CMC-2 (g) | Dry film before(g) | Dry film (g) |
|---|---|---|---|---|---|
| Control | 20 | some | 22.5 | - | - |
| CD-0 | 20.06 | 0 | 22.43 | 24.18 | 3.12 |
| CD-1 | 20.32 | 0.13 | 22.64 | 33.49 | 4.77 |
| CD-2 | 20.11 | 0.22 | 22.67 | 33.75 | 4.81 |
| CD-3 | 19.98 | 0.32 | 22.44 | 18.80 | 3.54 |
| CD-4 | 20.11 | 0.42 | 22.69 | 35.32 | 5.20 |
| CD-5 | 20.08 | 0.50 | 22.77 | 29.53 | 4.62 |
| CD-6 | 20.23 | 0.60 | 22.61 | 33.59 | 5.03 |
| CD-8 | 20.36 | 0.70 | 22.78 | 29.66 | 4.84 |
| CD-9 | 20.30 | 0.81 | 22.64 | 34.36 | 5.21 |
| CD-10 | 20.16 | 0.90 | 22.68 | 32.41 | 4.51 |
| CD-11 | 20.04 | 1.07 | 22.54 | 31.43 | 4.66 |
| CD-12 | 20.43 | 1.54 | 22.64 | 31.15 | - |
| CD-13 | 20.39 | 2.01 | 22.61 | 35.74 | - |
| CD-14 | 20.02 | 2.52 | 22.51 | 28.84 | - |
| CD-15 | 20.07 | 3.03 | 22.60 | 34.25 | - |

Note: the quality of the film is calculated according to the area of the glass plate.

2.2.2 Preparation of composite membranes under different matrix conditions

20.0g water was in a 100ml beaker, weighed and dissolved 0.5g β-CD with water, putted the beaker in a water bath to dissolve β-CD completely, and weighed and took 22.5g modified cellulose matrix under different conditions. Because CMC-4 and CMC-5 did not get the formed membrane in the membrane laying process of pure matrix, they were dropped in this step. In a beaker. Put the magnetic rotor into the beaker and place the beaker on the magnetic stirrer to stir for 2 hours. Following the method of 2.3.1, stirring, after the completion of the sodium carboxymethyl cellulose/beta - cyclodextrin mixed spread on the glass substrate will film roll out, then put glass at 50 ℃ constant temperature in drying oven drying. After drying completely, we removed the composite film and placed it in the fresh sealing bag for preservation and marking (Table 3).

**Table-3: Preparation of composite membranes under different matrix conditions**

| No. | Water (g) | β-CD (g) | Matrix(g) | Dry film before(g) | Dry film (g) |
|---|---|---|---|---|---|
| Control | 20 | 0.5 | 22.5 | - | - |
| A | 20.18 | 0.51 | CMC-1:22.51 | 36.33 | 4.88 |
| B | 20.07 | 0.51 | CMC-2:22.58 | 22.54 | 2.69 |
| C | 20.07 | 0.51 | CMC-3:22.68 | 26.15 | 3.21 |
| D | 20.28 | 0.51 | CMC-6:22.61 | 29.89 | 3.83 |
| E | 20.15 | 0.51 | CMC-7:22.64 | 36.20 | 4.38 |
| F | 20.07 | 0.54 | CMC-8:22.43 | 31.89 | 4.16 |

**Performance test**

**Mechanical test**

The tensile strength and elongation at break of modified cellulose film and sodium carboxymethyl cellulose/beta-cyclodextrin film were tested by the intelligent electronic tensile testing machine of Jinan Languang electromechanical technology co., LTD. It is required that the sample should be kept as smooth as possible without wear, fracture or damage. According to ASTMD 882-02 standard [8], the sample was cut into squares, 150 mm long and 15 mm wide. During the test, the clamping distance was 10 mm and the tensile rate was 25 mm/min. Experimental data requires no less than 5 parallel measurements [9].

**Fourier transforms infrared spectroscopy (FTIR)**

A certain amount of the freeze-dried hydrogel sample and KBr powder were placed in an agate mortar, mixed and ground, and then compressed, and subjected to FTIR infrared spectrum scanning to obtain an infrared spectrum of the sample [10, 11]. The scanning wavelength range is 500~4000 $cm^{-1}$.

**RESULTS AND DISCUSSION**

**Effect of different matrix conditions on the mechanical properties of composites**

The mechanical test results of sodium carboxymethyl cellulose matrix were prepared under different conditions by flow ductility method (Fig. 1a-c). As shown in Fig. 1a, the deformation rate of CMC-2 and the tensile strength of CMC-3 were the best when other conditions are the same and the mixing time is different. It could be concluded that the deformation rate of CMC-2 and the tensile strength of CMC-3 were the best when other conditions were the same and the mixing time was different. As shown in Fig. 1b, $SiO_2$ increases or decreases exponentially with the same other conditions. $SiO_2$ has the largest deformation rate and the weakest tensile strength once it is doubled. As shown in Fig.1c, other conditions were the same and the temperature was different. The deformation rate of CMC-2 and CMC-6 was similar to the tensile strength, but cellulose was dissolved quickly under freezing condition. In general, CMC-2 with 3 wt.% CMC, double $SiO_2$, was stirred for 6 h had better performance.

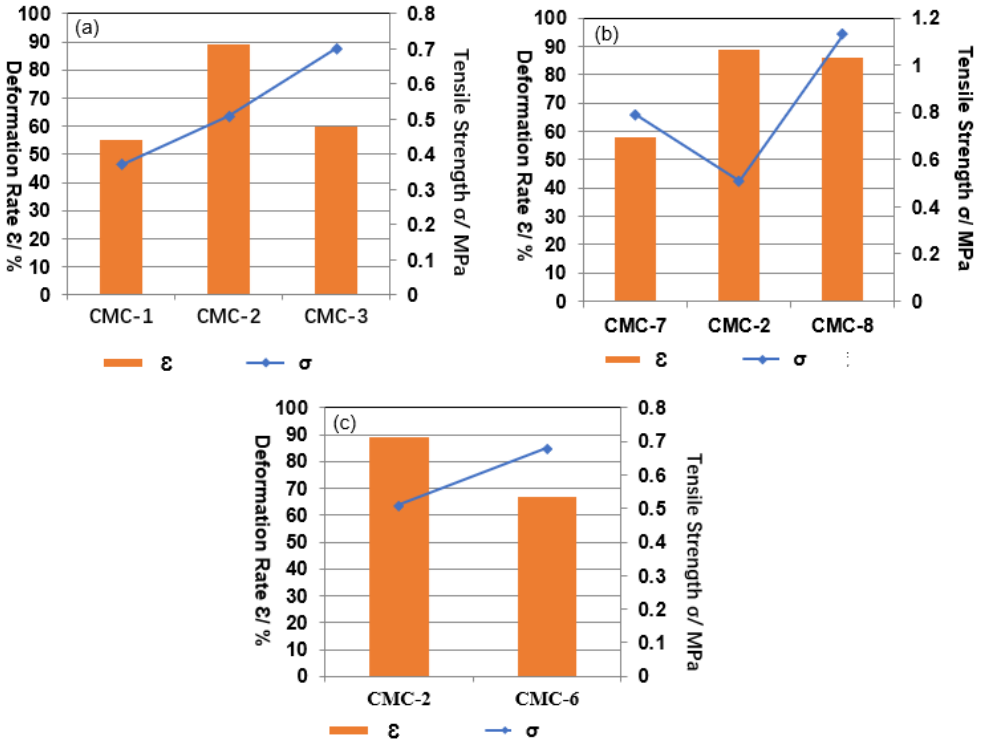


**Fig-1: The mechanical properties of composites under different matrix conditions (a: the mixing time; b: the content of $SiO_2$; c: frozen or not)**

**Effect of different β-CD content on the mechanical properties of composites**

Fig. 2 shows the test results of mechanical properties of the same modified cellulose matrix (CMC-2), β-CD, increased by 0.1 g gradient. By observation, the deformation rate increased first and then decreases with the increase of β-CD, which was the largest when the β-CD was 0.5g. Tensile strength tends to increased

and then decreased with the increase of β-CD, and was strongest at 0.9 g of β-CD. Taken together, the performance appeard to be better at 0.5 g of β-CD.

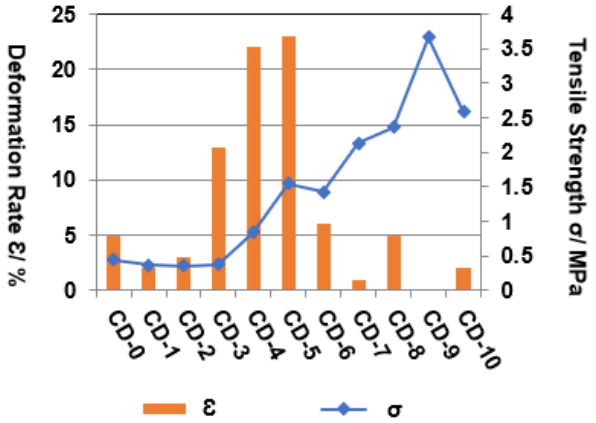


**Fig-2: The mechanical properties of composites under different β-CD content**

**Effect of different matrix conditions on the mechanical properties of composites with β-CD introduction**

Fig. 3a-c showed the deformation rate and tensile strength of the membrane composites formed by crosslinking the modified cellulose matrix with β-CD under different conditions, corresponding to figures 1a-c, with the difference of adding 0.5g β-CD. Corresponding observations showed that the introduction of β-CD reduced the deformation rate and enhanced the tensile strength of the membrane. As shown in Fig. 3b, after adding 0.5g β-CD, the deformation rate of the membrane decreases with the increase of $SiO_2$, and the tensile strength decreased first and then increased. When adding twice $SiO_2$, the tensile strength was relatively weak. As shown in Fig. 3c, after adding 0.5g of β-CD, the modified cellulose matrix without freezing showed higher deformation rate and weaker tensile strength than the modified cellulose matrix under freezing conditions.

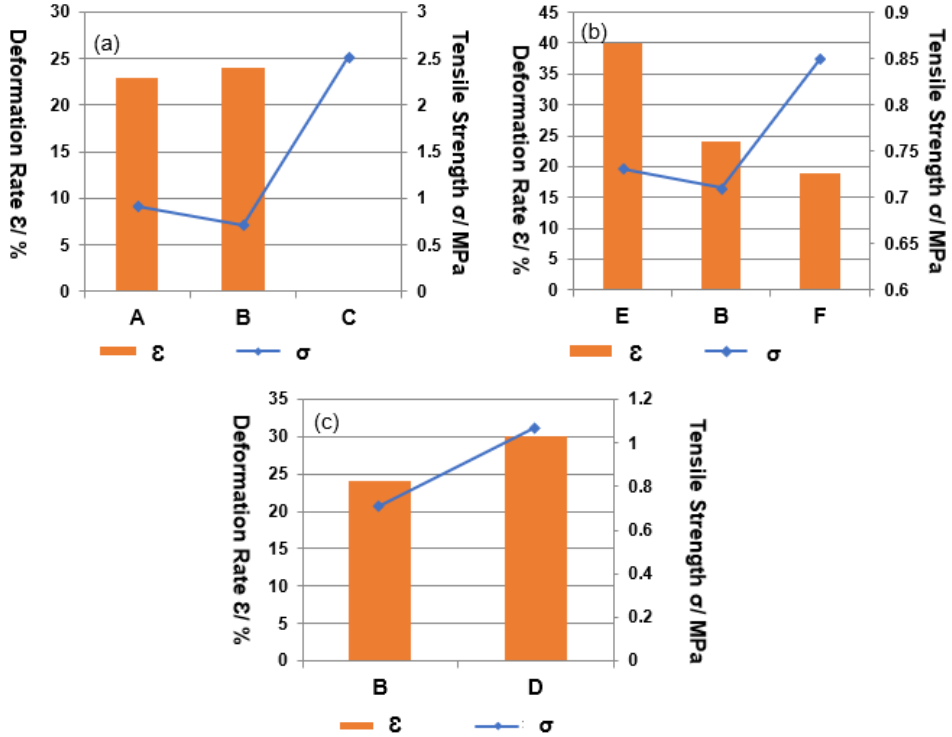


**Fig-3: The mechanical properties of composites with 0.5g β-CD added under different matrix conditions (a: the mixing time; b: the content of $SiO_2$; c: frozen or not)**

**Infrared test analysis**

Fig.4 showed the infrared spectra of sodium carboxymethyl cellulose, β-CD, and β-CD /modified cellulose matrix membrane composites. Through the β-CD /modified cellulose composite membrane and sodium carboxymethyl cellulose, β-CD, changes can be found as follows: (1) β-CD /modified cellulose composite membrane in 3500 $cm^{-1}$ of -H stretching vibration (O) produced from sodium carboxy methyl cellulose, β-CD strong infrared characteristic peaks; (2) β-CD /modified cellulose composite membrane at 1650 $cm^{-1}$ was new twin peaks, at 1450 $cm^{-1}$ created a new unimodal, may be caused by the crosslinking chemical structure changes, a new chemical bonds. This indicated that β-CD could cross-link with functional groups such as hydroxyl group on the surface of cellulose under certain conditions to form relatively stable chemical bonds, promoted the formation of composite membrane material, and further enhanced the overall performance of the material.

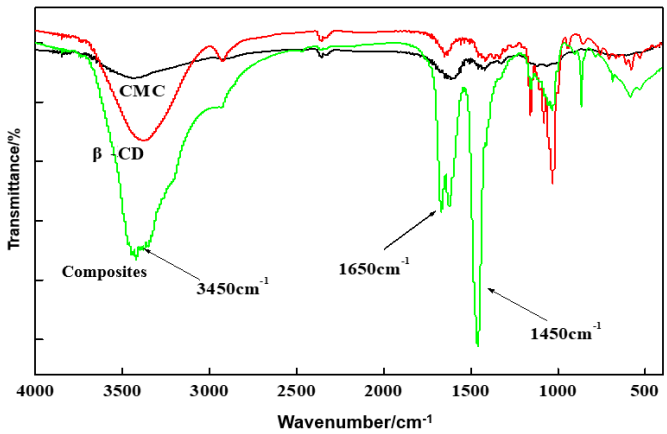


**Fig-4: The FTIR spectrogram of CMC, β-CD, and β-CD/CMC membrane composites**

Fig. 5 showed the infrared spectra of the modified cellulose matrix prepared under different conditions. As shown in Fig. 5, changes in the preparation conditions of the matrix did not lead to new chemical bonds in the composite membrane, but caused changes in the characteristic peak strength, which may be that the strength of chemical bonds affects the tensile strength of the membrane material.

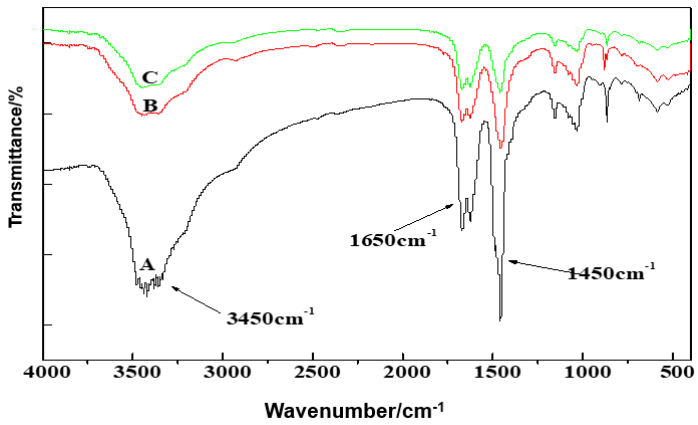


**Fig-5: The FTIR spectrogram of composite membranes under different matrix conditions (A: CMC-1; B: CMC-2; C: CMC-3)**

## CONCLUSION

In this paper, carboxymethyl cellulose sodium and β-CD were used as raw materials to synthesize β-CD/modified cellulose matrix composite membrane under alkaline conditions. Different composite films were obtained by changing experimental conditions, and mechanical and infrared tests were carried out. In the preparation of pure modified matrix membrane, other conditions remain the same; stirring time is different, stirring at the maximum deformation rate for 6 h, tensile strength increased in prolonging the mixing time. Other conditions being the same, $SiO_2$ increases or decreases exponentially. When $SiO_2$ added twice, the deformation rate was the largest and the tensile strength was the weakest. The freezing treatment had little effect on the mechanical properties of the film.

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