

The Application Research of Carboxymethyl Cellulose in Paper Printing & Packaging Materials

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Abstract: Cellulose is one of the most important renewable resources in the nature. Carboxymethyl cellulose, one of the most important cellulose modified products, has been widely used in paper printing and packaging materials. For example, it can be used as the additives such as retainer when producing the paper, the functional additives such as sizing agent and strengthening agent, and the adhesive of the paper coating such as water retaining agent, and it can also affect the property of the paper packaging materials significantly. The best process condition of high viscosity carboxymethyl cellulose was obtained by single factor experiment, and then, the effect of CMC made by the best process condition on the coated paper was also evaluated.

Keywords: Carboxymethyl Cellulose (CMC); process condition; strengthening agent

Carboxymethyl Cellulose (CMC), which is also called sodium carboxymethyl cellulose, is obtained by the alkalization and etherification reaction of cellulose; it is a kind of anionic, straight chain, water soluble cellulose ether^[1]. It can change the viscosity of most of the aqueous solution^[2]; it can dissolve in cold or hot water and form a kind of neutral of alkalescent transparent solution with certain viscosity; it can not dissolve in some kind of organic solvent such as ethanol, ether, isopropanol, acetone^[3]. Carboxymethyl Cellulose is one of most the important cellulose modified products and has been used widely in printing and packaging materials, for example, it can be used as the retention agent, sizing agent, strengthening agent and the water retaining agent of the coating^[4] and it has significant effects on the property of paper packaging material.

There are many kinds of raw materials which can be used to prepare CMC, in some reports, some people use agricultural wastes such as sugar meal waste, cotton stem, sawdust, corn stalk, bamboo leftover^[5-11] and so on to prepare CMC and get ideal products. These methods can improve utilization efficiency of agricultural products, reduce the producing cost of CMC and have a bright future.

The preparation methods of CMC in industry can be divided into hydrophily method and solvent method by etherifying medium. Hydrophily method is a kind of method which take water as its reaction medium during the process of alkalization and etherification reaction and it is usually used to produce low-end CMC. Solvent method is a kind of method which take organic solvent as its reaction medium during the process of alkalization and etherification reaction and it can be used to produce high-end CMC^[12].

Currently, the international research and development on CMC is tend to update and upgrade and is developing toward high purity, high degree of substitution, high viscosity and homogeneous degree of substitution. Besides, CMC with high degree of substitution has many excellent performances, so researches on these problems are very active. The CMC was made by traditional hydrophily method and the best processing conditions of alkali dosage, alkalization temperature, alkalization time, ether dosage and etherification temperature were obtained. The paper was coated by the CMC made according these best processing condition. The effect of the CMC made according these best processing condition on the properties of paper was also researched.

1 Experiment

1.1 Materials and apparatus

Paper pulp, bleached paper pulp plate, the seventh factory of Beijing papermaking factory; chloroacetic acid, analytically pure, Beijing Chemical Plant; ethanol, analytically pure, Beijing Chemical Plant; NaOH, analytically pure, Beijing Chemical Plant; H₂O₂ solution (30%), analytically pure, Beijing Chemical Plant; paper sheet, A4 copy paper, UPM-Kymmene (Changshu) Paper Industry Co., Ltd..

Cycle water typed multi-use vacuum pump, SHB-B95, Zhengzhou Changcheng division industry and trade Co., Ltd.,; electric mixer, D2004W, Shanghai Tongle apparatus Co., Ltd.; electrothermal constant temperature water bath pot, DKS-12, Hangzhou Lantian chemical examination instrument factory; viscometer, DV-II+PRD, America Brookfield company; micro control tensile machine, KZW-300, Changchun paper experimental machine factory; electric paper folding resistant tester, ZZD-025C, Changchun paper experimental machine factory.



1.2 CMC preparation technology

Take a piece of paper and tear it to pieces by hand, soak it in a large beaker by water for 24 hours, remove the impurities. Add 50g NaOH into 1000ml water to get 5% aqueous solution, soak the paper pulp obtained above in it for 2 hours and then remove the solution. Adjust the water bath to 90°C, add 100g NaOH to 1000ml water and place the 10% water solution in a large beaker, soak the water pulp into the solution and cook it for 4 hours, cool and air pump filtrate it. Adjust the water bath to 30°C, take certain amount of H_2O_2 and soak the water pulp obtained above in it, bleach and air pump filtrate, then wash it by water for 2 times, dry it in dry box for 10 hours and get the paper pulp material.

Add 10.0g paper pulp material and 200ml 85% ethanol aqueous in mikuchi bottle which with stirring apparatus, mix it until it is uniform and then add certain amount of NaOH into it, stir it under a certain temperature for certain time and get the alkaline cellulose. Add 50ml ethanol aqueous which contain certain amount of chloroacetic acid to the alkaline cellulose obtained above, adjust the water bath to 70°C and wait for a certain time, add alkaline catalyst solution which is obtained by mixing 1g NaOH and 50ml ethanol together drop by drop and stir it for 150min under the temperature is 75°C. neutralize it by hydrochloride and wash it by 75% ethanol for 2 times, and then wash it by 95% ethanol and air pump filtrate it. At last, dry it to get the CMC product.

1.3 Paper coating

Compound CMC into 2% solution, stir it until it is uniform, coat it onto A4 copy paper by coating bar, dry it and test its properties.

1.4 Testing

Compound CMC into 2% solution, test its viscosity by viscometer under the temperature of 25° C.

The smoothness, glossiness, whiteness, tensile strength and folding endurance are tested according to national standard test procedure.

2 Results and discussions

2.1 Effect of alkali dosage on viscosity of CMC

Keep other factors such as alkalization temperature 35 $^{\circ}$ C, alkalization time 90min, etherifying agent dosage 1.2g/g, etherifying temperature 75 $^{\circ}$ C and etherifying time 150min stable, research the effect of alkali dosage on the viscosity, the result can be seen in Table 1.

Table 1. Effect of alkali dosage on viscosity of CMC

alkali dosage (g/g)	0.6	0.7	0.8	0.9	1.0
viscosity (cP)	550	1800	2250	3200	550

Note: alkali dosage (g/g) means alkali dosage/paper pulp consumption From Table 1, it can be found that as the alkali dosage increase, the viscosity of CMC increase at first and then decrease. When the alkali dosage is 0.9g/g, the viscosity of the product reach the highest value. When the alkali dosage is small, the expansion degree of cellulose is relatively low, and the alkalization is not enough, it is not enough to form the alkali cellulose and neutralize the etherifying agent, the viscosity and the purity of the product are relatively low; when the dosage of NaOH is too large, the content of free alkali is high, reaction will occur between excess alkali and chloroacetic acid, it can consume the etherifying agent and decrease the etherifying degree and viscosity of the product. So, the best dosage is 0.9g/g.

2.2 Effect of alkalization temperature on viscosity of CMC $\,$

Keep other factors such as alkali dosage 0.9g/g, alkalization time 90min, etherifying agent dosage 1.2g/g, etherifying temperature $75\,^{\circ}\text{C}$ and etherifying time 150min stable, research the effect of alkalization temperature on the viscosity, the result can be seen in Table 2.

Table 2. Effect of alkalization temperature on viscosity of

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alkalization temperature (℃)	25	30	35	40	45
viscosity (cP)	450	680	2200	1380	1120

From Table 2, it is found that as the alkalization temperature increase, the viscosity of CMC increase at first and then decrease, when the alkalization temperature is $35\,^{\circ}\mathrm{C}$, the viscosity is the highest. When the reaction temperature is too low, so the alkalization is not enough, the viscosity of the product is low; when the temperature is too high, CMC will hydrolyze, this is also the reason why the viscosity of the product decrease. The best alkalization temperature is $35\,^{\circ}\mathrm{C}$.

2.3 Effect of alkalization time on viscosity of CMC

Keep other factors such as alkali dosage 0.9g/g ,alkalization temperature $35\,^{\circ}\text{C}$, etherifying agent dosage 1.2g/g, etherifying temperature $75\,^{\circ}\text{C}$ and etherifying time 150min stable, research the effect of alkalization time on the viscosity, the result can be seen in Table 3.

Table 3. Effect of alkalization time on viscosity of CMC

alkalization time (min)	30	45	60	90	120
viscosity (cP)	340	380	540	2750	79.3

From Table 3, it is found that as the alkalization time increase, the viscosity of CMC increase at first and then tend to stable. The alkalization of the cellulose is complete gradually, with the diffusion of the alkali solution, the alkali go deep into the crystallization field, this can increase the reactivity of the cellulose; but the increase of the viscosity is not obvious if the alkalization time was



prolonged. So the best alkalization time is 90min.

2.4 Effect of etherifying agent dosage on viscosity of CMC $\,$

Keep other factors such as alkali dosage 0.9g/g, alkalization temperature $35\,^{\circ}\mathrm{C}$, alkalization time 90min, etherifying temperature $75\,^{\circ}\mathrm{C}$ and etherifying time 150min stable, research the effect of etherifying agent dosage on the viscosity, the result can be seen in Table 4.

Table 4. Effect of etherifying agent dosage on viscosity of CMC

etherifying agent dosage (g/g)	0.9	1.0	1.1	1.2	1.3
viscosity (cP)	74.2	152	455	2350	502

Note: etherifying agent dosage (g/g) means etherifying agent dosage/paper pulp consumption

From Table 4, it is found that as the etherifying agent dosage increase, the viscosity of CMC increase at first and then decrease. If etherifying agent dosage is too large, the dosage of etherifying agent will increase and the side effects will increase too; if the etherifying agent dosage is too small, the cellulose can not be etherified fully. So the best etherifying agent dosage is 1.2g/g.

2.5 Effect of etherifying time on viscosity of CMC

Keep other factors such as alkali dosage 0.9g/g ,alkalization temperature $35\,^{\circ}\mathrm{C}$, alkalization time 90min, etherifying agent dosage 1.2g/g and etherifying temperature $75\,^{\circ}\mathrm{C}$ stable, research the effect of etherifying time on the viscosity, the result can be seen in Table 5.

Table 5. Effect of etherifying time on viscosity of CMC

etherifying time (min)	60	90	120	150	180
viscosity (cP)	340	380	540	2280	79.3

From Table 5, it is found that as the etherifying time increase, the viscosity of CMC increase at first and then decrease. If the etherifying time is too short, the reaction is not full, so the viscosity of the product is very low; if the etherifying time is too long, the main reaction and the side effect are both fully, and the side reaction is faster than the main reaction, the viscosity of the product will decrease. So the best etherifying time is 150min.

2.6 Effect of rotation speed on viscosity of CMC

According to the result above, the best process conditions to get better product are alkali dosage 0.9g/g, alkalization temperature $35\,^{\circ}\mathrm{C}$, alkalization time 90min, etherifying agent dosage 1.2g/g and etherifying time $150\mathrm{min}_{\,\circ}$ research the effect of the rotation speed on the viscosity of CMC which prepared according to this process condition, the result can be seen in Table 6.

Table 6. Effect of rotation speed on viscosity of CMC

Rotation speed(r/min)	20	30	40	50	60
viscosity(cP)	2250	1900	1750	1720	1583.3

From Table 6, it is found that as the rotation speed increase, the viscosity of CMC decrease, this is because that CMC is pseudoplastic, when the rotation speed increase, the viscosity decrease, when the sheer stress disappear, the viscosity will recover.

2.7 Effect of CMC on properties of coated paper

Coat the paper by the CMC prepared according to the best process condition, research the properties of the coated paper, the result can be seen in Table 7.

Table 7. Effect of CMC on properties of coated paper

properties	smoothness (s)	glossiness (%)	whiteness (%)	Tensile strength (KN/m)	Fracture length (km)	Folding endurance (times)
paper	15.34	3.26	93.3	52.19	53.25	128
Coated paper	12.61	3.14	95.2	65.15	66.47	313

From Table 7, it is found that the smoothness, glossiness and whiteness of the paper which coated by CMC have no apparent change, this means that these properties is not affected by the CMC. Both of the tensile strength and fracture length increase apparently, this is because that the CMC with high viscosity can fill the void of the paper cellulose and bond the fibers obviously. The folding endurance of the coated paper improve obviously, this is because that the coated layer has a excellent effect on bond the paper void and make the binding force of the fibers more strong, so the folding endurance increase.

3 Conclusion

- (1) CMC was prepared in lab by hydrophily method, the effect of process conditions on the viscosity of CMC was researched by single factor experiment, the best process conditions to prepare CMC with high viscosity are: alkali dosage 0.9g/g, alkalization temperature 35℃, alkalization time 90min, etherifying agent dosage 1.2g/g and etherifying time 150min.
- (2) The effect of rotation speed on the viscosity of CMC was researched, CMC is pseudoplastic, when the ro-



- tation speed increase, the viscosity decrease, when the sheer stress disappear, the viscosity will recover.
- (3) The smoothness, glossiness and whiteness of the paper which coated by CMC have no apparent change. But, the tensile strength and fracture length increase apparently. This is because that the coated layer has a excellent effect on bond the paper void and make the binding force of the fibers more strong. At the same time, the folding endurance of the coated paper improve obviously.

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