Carboxymethylation of γ-Irradiated Starch

Zongwen Wu, Xinyuan Song

College of Chemistry and Chemical Engineering, Donghua University, Shanghai 200051, China

Received 1 August 2005; accepted 13 October 2005
DOI 10.1002/app.23479

ABSTRACT: Low viscosity carboxymethyl corn starch was prepared by the reaction of γ-irradiated starch with monochloroacetic acid in the presence of alkali. It was found that irradiation dose influences the product viscosity remarkably. The viscosity decreases as the irradiation dose level increases; however, the viscosity increases with the increasing dose rate and the degree of substitution (DS). γ-Irradiation can activate the starch to react with monochloroacetic acid, and the more of the irradiation dose, the higher of the DS and the reaction efficiency. The product has the character of low viscosity at high concentration, and the more of the irradiation dose, the more similar of the rheological behavior to a Newtonian liquid. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2210–2215, 2006

Key words: low viscosity; carboxymethyl starch; gamma irradiation; degradation; carboxymethylation

INTRODUCTION

Carboxymethyl starch (CMS) is one of the most important starch ether derivatives. Usually, CMS is soluble in cold water and has the functions of thickening, adhesion, water-absorption, film-formation, etc. It is widely used in many industrial fields. High viscosity CMS has many applications in the area of thickening of food, printing, and coating materials. Low viscosity CMS is also used in many fields such as textile sizing, paper coating, and water-based adhesives. The solution of the low viscosity CMS has a good fluidity even with higher content.

A method for the preparation of low viscosity CMS by the combination of acid modification with etherification of starch was reported by Whistler.[1] We have used this method to prepare low viscosity carboxymethyl cannaedulisker starch used in textile sizing process.[2] In this article, a new method for the preparation of low viscosity CMS by the combination of γ-irradiation with etherification of starch was studied.

The effects of γ-radiation on starch have been studied by many researchers.[3–11] When starch is irradiated with γ-ray, its macromolecule is cleaved, the polymerization degree and viscosity decrease dramatically.[3–7] We have also reported that the γ-radiation is a significant method to produce low viscosity starch in our previous paper.[8] With its superior penetrating power, γ-ray reaches and destructs the inside region of the starch granule, including the amorphous and the crystal regions. According to Cieśla et al.,[9–11] this leads to the destruction of crystalline order and the decrease of relative crystallinity of γ-irradiated starch. Starch degradation by γ-radiation is quite unique comparing with chemical degradation process. Usually, as chemicals are difficult to get into the crystal regions of starch granule, chemical degradation such as acid hydrolysis or oxidization only occurs in the amorphous regions.[12–17] Furthermore, the irradiation process is operated easily without opening the package of starch and without physical contact with any chemicals.

The carboxymethyl irradiated starch (CMIS) is produced by carboxymethylation of γ-irradiated starch with monochloroacetic acid in the presence of alkali. The reaction formula is as follows

$$\mathrm{ST{-}OH + ClCH_2COOH \xrightarrow{2NaOH} ST{-}OCH_2COON_a + NaCl + H_2O}$$

At the same time, hydrolysis of monochloroacetic acid occurs as a side reaction:

$$\mathrm{ClCH_2OOH + 2NaOH \rightarrow HOCH_2COONa + NaCl + H_2O}$$

Usually, CMS can be prepared in aqueous medium,[18,19] organic solvent medium,[18,20–24] or dry medium.[20] Reactions in organic solvent produce the highest quality of product as the reaction proceeds efficiently and uniformly. The most used organic solvents are methanol, ethanol, isopropanol, and acetone. We choose ethanol as the reaction solvent because it is much more plentiful and cheaper than isopropyl alcohol in China, although

---

Correspondence to: Z. Wu (wu_zw@163.com).

Journal of Applied Polymer Science, Vol. 101, 2210–2215 (2006)

isopropanol may be the best solvent in terms of reaction efficiency (RE).

EXPERIMENTAL

Materials

Corn starch containing approximately 12.5% moisture was provided by Yongchang Co. Ltd (Henan, China). Food grade ethyl alcohol was obtained from Xinxiang Alcohol Factory (Henan, China). Monochloroacetic acid, >97% purity, was obtained from Dongda Chemical Co. Ltd (Henan, China). Sodium hydroxide, >99% purity, was made by Tianjin Chemical Plant (Tianjin, China).

Methods

Irradiation

The starch samples (200 g) were packed in kraft paper bags with dimensions of 12 × 24 × 2 cm. Irradiations of starch samples were carried out in air at ambient temperature with a ^{60}Co source of 20,000 Ci, which was installed in the Isotope Institute, Academy of Science of Henan Province, China. Unless otherwise stated, the dose rate for all irradiations was 10 Gy/min. The full set of experiment parameters are listed in the Appendix.

Preparation

The carboxymethylation procedure is based on our preliminary study.[2] γ-Irradiated starch (40 g) was slurried in 100 mL ethyl alcohol in 250 mL, 3-necked, round-bottomed reaction flask equipped with a PTFE-sealed stirrer and reflux condenser. A certain weight of sodium hydroxide had been dissolved in 10 mL water previously and the cooled solution was added into the flask (The volume ratio of alcohol and total water was 82.6:17.4, and the water inside the starch and inside the ethyl alcohol was included in the total water. The weight ratio of sodium hydroxide and monochloroacetic acid was kept at 0.9:1.0). The slurry mixture was stirred for 30 min following the addition of monochloroacetic acid. After stirring for 30 min, the reaction mixture was heated to 70°C and stirred at this temperature for 60 min. After cooling to 40°C, the reaction mixture was neutralized with hydrochloric acid, filtrated, and washed with 80% ethyl alcohol to remove chloride, and dried to get the product CMIS.[20–24]

Analysis

Dose rate: The dose rate was measured with the Fricke dosimeter.

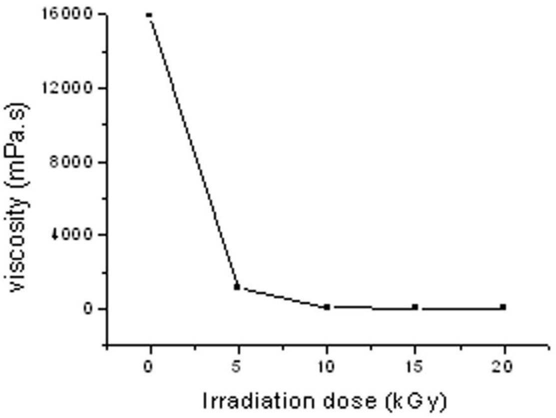

Figure 1 Effects of irradiation dose on the viscosity of CMIS.

Viscosity: Unless otherwise stated, viscosity of 6% (dry base) CMIS solution was measured by NDJ-1 viscometer (made in Shanghai Balance Instruments Factory, Shanghai, China) at a speed of 12 rpm at 20°C.

Degree of substitution: Degree of substitution (DS) of the CMIS was determined according to the method of ISO 11216: 1998(E).[25]

Carboxyl group content: Carboxyl group content in the irradiated starch was determined according to the method of ISO 11214: 1996(E).[26]

IR spectra: The IR spectra of corn starch, γ-irradiated starch, and CMIS were recorded with KBr discs by a Nicolet Nexus 470 IR spectrophotometer (Thermo Nicolet, USA).

RESULTS AND DISCUSSIONS

Effect of irradiation dose on the viscosity of CMS

Starch irradiated with different doses was carboxymethylated under same reaction condition (dose rate: 10 Gy/min; monochloroacetic acid: 8.0 g). Relationship between viscosity of the CMIS and the irradiation dose is shown in Figure 1.

As shown in Figure 1, irradiation dose influences the viscosity dramatically. The viscosity decreases as the irradiation dose level increases, as the γ-irradiation cleaves the polysaccharide chains and the degree of polymerization drops. The trend of the decrease in viscosity of the CMIS with the increase of irradiation dose is consistent with that of irradiated starch.[4–8] The difference is that irradiated starch dissolves only in hot or alkali water, but after it is carboxymethylated, the CMIS can dissolve in cold water.

As the curve shows, the viscosity decreases very rapidly as the irradiation dose increases from 0 to 5 kGy. However, the viscosity decreases slower in the irradiation dose 5–10 kGy, and much slower as the irradiation dose increases above 10 kGy.

TABLE I
Effect of Dose Rate on Viscosity

Dose rate (Gy/min)	Viscosity (mPa S)
3	65
7.6	80
10	100
15	250

Effect of dose rate on viscosity

Starch irradiated with different dose rate for the same dose of 10 kGy was carboxymethylated under same reaction condition. The effect of the irradiation dose rate on the viscosity of the CMIS is shown in Table I.

Given the same irradiation dose, the more of the dose rate, the higher of the viscosity. That means longer irradiation time at a lower irradiation dose rate is more efficient for starch degradation than the higher dose rate for a shorter irradiation time. One reason for this phenomenon may be that the oxygen in air plays an important role for starch degradation during the γ-irradiation process, and the effect of "partly absence of oxygen" may occur at higher dose rate in a high dose level to lead to a lower G (degradation) value. Another reason may be that higher irradiation dose rate may generate a higher concentration of radical and cause the radical chain reaction terminated faster (by self-coupling) than that in the lower dose rate case. It may be this inefficient radical process that results in a lower G (degradation) value.

Effect of DS on viscosity

Starch irradiated for 10 kGy was carboxymethylated with different amounts of monochloroacetic acid and sodium hydroxide under the otherwise same reaction conditions. The DS and viscosity of the CMIS are shown in Table II.

The data in Table II indicates that to some degree, the viscosity of the CMIS increases as the DS increases. The carboxymethyl group content in the CMIS molecules increases with the increasing DS, and the hydrophilic property of carboxymethyl group helps the CMIS molecules to dissolve and extend in the solution. This leads the viscosity to raise as the DS increases.

TABLE II
Effect of DS on Viscosity

Monochloroacetic acid (g)	DS	Viscosity (mPa · S)
5	0.183	57
7.5	0.216	65
10	0.262	76

TABLE III
Effect of Irradiation Dose on DS and RE

Irradiation dose (kGy)	DS	RE (%)
0	0.198	53.1
5	0.207	55.6
10	0.227	61.0
15	0.233	62.6
20	0.238	63.9

Effects of irradiation dose on DS and RE

Many factors influence the DS and the RE in etherification reaction. The parent starch, choice of solvent system, the molar ratio of starch/alkali/monochloroacetic acid, water concentration in reaction medium, and the reaction conditions are all important factors in determining the DS and RE, and all these factors have been studied in Refs. 21–24. Here, we just focus on the effects of irradiation dose on the DS and the RE.

Starch irradiated with different doses was carboxymethylated under the same reaction conditions. The results of DS and RE obtained are listed in Table III.

The data in Table III indicates that the DS of CMIS is higher than that of the CMS (D = 0 kGy), and the more of the irradiation dose, the higher of the DS. It also shows that γ-radiation seems to activate the starch to react with monochloroacetic acid, and the irradiated starch has a higher RE than that of unirradiated starch.

As carboxyl groups are created by γ-irradiation in starch, the carboxyl group content increases with the increasing irradiation dose.[6,8] The carboxyl groups contribute to the analytic result of DS. Carboxyl group contents of irradiated starch are determined and calculated into DS according to formula 1. The results are shown in Table IV.

$$\mathrm{DS} \approx \frac{\mathrm{COOH\%}}{45} \div \frac{100}{162} = \frac{162}{100 \times 45} \times \mathrm{COOH\%} \quad (1)$$

In the formula 1, the COOH% is carboxyl group content percent; 45 and 162 are the molecular weights of carboxyl group and starch respectively.

TABLE IV
Carboxyl Group Content of Irradiated Starch and Its Contribution to DS

Irradiation dose (kGy)	Carboxyl group content (%)	Contribution to DS from carboxyl
0	0.017	0.0006
5	0.050	0.0018
10	0.067	0.0024
15	0.071	0.0026
20	0.085	0.0031

TABLE V
Comparativeness of the DS of the CMS of Precarboxymethylation and Postirradiation

CMS samples	Irradiation dose (kGy)	DS
CMS_1	0	0.220
	200	0.228
CMS_2	0	0.328
	200	0.334

It is found in Table IV that the contribution from carboxyl group in irradiated starch to the DS of CMIS is very little. This result demonstrates that the increase of the DS mainly comes from activation effect on starch by γ-irradiation and the higher RE rather than from the carboxyl group. Meanwhile, a comparison experiment is carried out by precarboxymethylation and postirradiation; the change of DS of the CMS after irradiation is small. The result is shown in Table V. It also verifies the activation effect on carboxymethylation of starch by γ-irradiation.

According to Bhattacharyya et al.,[23] the efficiency of etherification depends upon the diffusion or penetration of the swelling agent and etherification agent into the starch granular structure. The processes of carboxymethylation of starch have something to do with the structural parameters of starch.[23] Usually, as chemicals are difficult to get into the crystal regions of starch granule, chemical modification reaction always occurs only in the amorphous regions.[12–17] But, γ-rays can reach and destruct any region inside the granule of starch, including the amorphous and the crystal regions. According to Cieśla et al.,[9–11] the relative crystallinity of starch decreases after it is γ-irradiated. The decreasing relative crystallinity means the increase of amorphous regions, and this may lead more reagents to diffuse or penetrate into the starch granular structure. And therefore the DS and RE increase.

Effect of concentration on viscosity

One of the remarkable properties of the CMIS is the low viscosity. Its solution has a high fluidity at a high concentration. Figure 2 is the curves of viscosity–concentration of CMS (D = 0 kGy) and CMIS with the irradiation dose of 10 and 20 kGy.

Figure 2 shows that the viscosity of the CMS raises up at a tremendous rate with the increasing concentration. It has high viscosity about 1000 mPa·S at the concentration of 2%. However, the viscosity of the CMIS irradiated with the dose of 10 and 20 kGy only have 19 and 6.5 mPa·S, respectively, at the same concentration. The difference between them is about 100-folds. Moreover, their viscosity only gets about to 400 and 100 mPa S even at the concentration of 12%. They have the property of low viscosity at high concentration, and getting more remarkable as the irradiation dose increases. These effects are due to the difference of macromolecule chains between CMS and CMIS. The higher viscosity of the CMS even at lower concentration mainly comes from the enlacing of its longer macromolecule chains. The lower viscosity of the CMIS at higher concentration shows that its macromolecule chains are mostly cleaved. These curves further confirm the significant degradation effect of γ-radiation on starch.

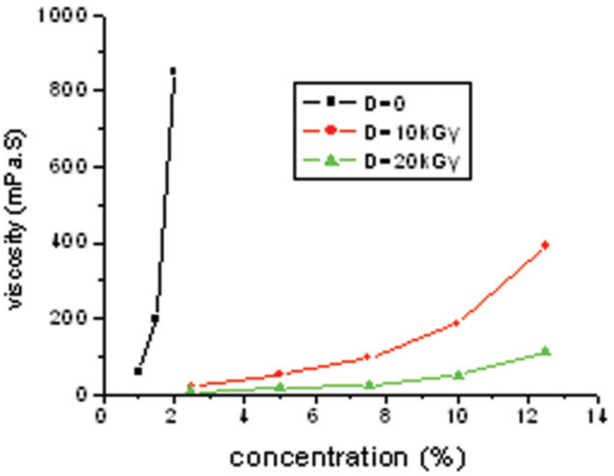

Figure 2 The curves of viscosity–concentration of CMIS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Rheological properties

Rheological behavior is essential for a polymer fluid. We can estimate the rheological properties from the relationship between the viscosity and shear stress or from the printing viscosity index (PVI) level. PVI is defined as the ratio of viscosity to different shear rates (usually 10/1).[27] Most PVI values of polymer aqueous solution tend to be in the range 0–1. A fluid with PVI = 1 is a Newtonian liquid, whose viscosity is independent of shear stress. The smaller PVI level is, the greater is the influence of the shear stress on viscosity, and it is a non-Newtonian liquid. Table VI displays the effect of shear rate on the viscosity of CMS and CMIS.

TABLE VI
Viscosity of the CMIS with Different Irradiation Dose at Different Shear Rate, and the PVI Value

Irradiation dose (kGy)	Rotation Rate (r/m)				PVI
	6	12	30	60	
0 (2%)	2400	1750	1160	874	0.36
10 (10%)	200	187.5	165	147	0.735
20 (10%)	50	50	48	47	0.94

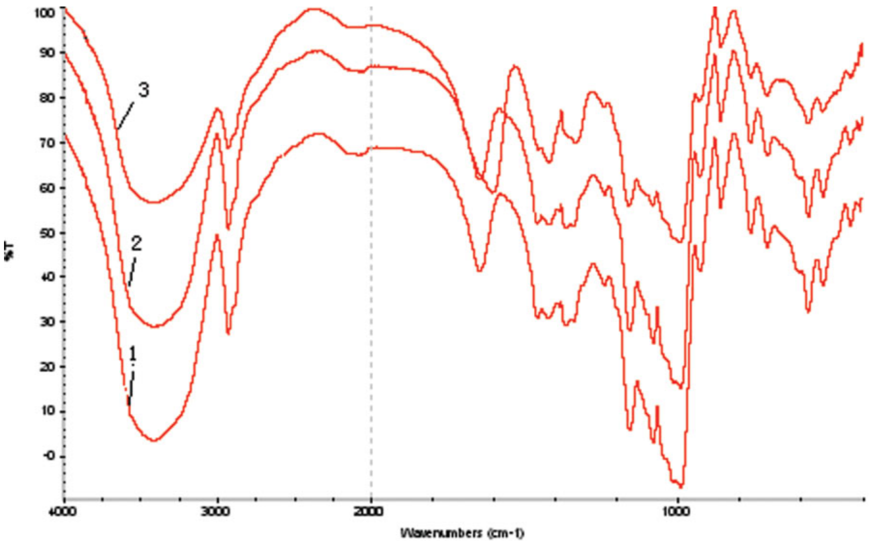

Figure 3 The IR spectra of corn starch (1), γ-irradiated starch (2), and CMIS (3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

As shown in Table VI, the CMS (2%), the CMIS with 10 kGy(10%), and with 20 kGy (10%) have the PVI values of 0.36, 0.735, and 0.94 respectively. The rheological behavior of the CMS displays the typical shear-thinning behavior, with a significant reduction in viscosity as the shear increases. Obviously, it is a non-Newtonian liquid. However, the viscosity of the CMIS does not change much when the shear stress increases or decreases, and the more of the irradiation dose, the higher of the PVI, and its rheological behavior is more similar to a Newtonian liquid.

Structure analysis

The IR spectra of corn starch, γ-irradiated starch (20 kGy), and CMIS (20 kGy) are shown in Figure 3.

As shown in Figure 3, there is little change between the curve 1 and the curve 2. This indicates that few change occurs in molecular structure of starch after irradiation, although the polymerization degree decrease. However, curve 3 has new and strong characteristic absorption peaks of carboxyl at 1608, 1424, and 1337 cm^{-1}. This indicates that the carboxyl group was introduced into the CMIS molecule.

CONCLUSIONS

The low viscosity CMS was prepared by the combination of γ-irradiation with the carboxymethylation of starch. It shows the property of low viscosity at high concentration.

Irradiation dose influences the viscosity of the CMIS remarkably. The viscosity decreases as the irradiation dose level increases. It increases with the increasing dose rate and the DS.

γ-Radiation can activate starch to react with monochloroacetic acid, the more of the irradiation dose, the higher of the DS and the RE.

APPENDIX

Full Set of Experiment Parameters

Trial no.	Dose (kGy)	Dose rate (Gy/min)	Monochloroacetic acid (g)	Sodium hydroxide (g)
Figure 1	0	10	8.0	7.2
	5			
	10			
	15			
	20			
Table I	10	3	8.0	7.2
		7.6		
		10		
		15		
Table II	10	10	5.0	4.5
			7.5	6.75
			10	9
Table IV	0	10		
	5			
	10			
	15			
	20			
Table V	20	10	–	–

Figures 2 and 3: the experiment parameters are same as those of Figure 1.

Tables III and VI: the experiment parameters are same as those of Figure 1.

References

1. Whistler, R. L. Starch: Chemistry and Technology, 2nd ed.; Academic Press: New York, 1984; p 537.

2. Zongwen, W.; Xinyuan, S.; Wei, L. In Proceedings of the Textile Institute 83rd World Conference, Shangai, China, May 23–27, 2004; Vol. 2, p 794.
3. Samec, M. J Appl Polym Sci 1960, 3(8), 224.
4. Hofreiter, B. T. J Polym Sci Polym Chem Ed 1974, 12, 2755.
5. Sokhey, A. S.; Hanna, M. A. Food Struct 1993, 12, 397.
6. Hebeish, A.; El-Naggar, A. M.; El-Sisi, F.; Abdel-Hafiz, S.; El-Salmwi, K. Polym Degrad Stab 1992, 36, 249.
7. Kang, I. J.; Byun, M. W.; Yook, H. S. Radiat Phys Chem 1999, 54, 425.
8. Zongwen, W.; Aimei, L.; Hongying, Z.; Guoshi, C. Nucl Tech 1998, 21, 634.
9. Cieśla, K.; Gwardys, E.; Żółtowski, T. Starch 1991, 43(7), 251.
10. Cieśla, K.; Żółtowski, T.; Mogilevski, L. Y. Starch 1992, 44(11), 419.
11. Cieśla, K.; Eliasson, A. C. Radiat Phys Chem 2002, 64, 137.
12. Schmorak, J.; Lewin, M. J Polym Sci Part A: Gen Pap 1963, 1, 2601.
13. Kuakpetoon, D.; Wang, Y. J. Starch 2001, 53, 211.
14. Cowie, J. M. G.; Greenwood, C. T. J Chem Soc 1957, 2658.
15. Atichokudomchaia, N.; Shobsngobb, S.; Varavinita, S. Starch 2000, 52, 283.
16. Atichokudomchaia, N.; Shobsngobb, S.; Chinachotic, P.; Varavinita, S. Starch 2001, 53, 577.
17. Wang, L. F.; Wang, Y. J. Starch 2001, 53, 570.
18. Khalil, M. L.; Hashem, A.; Hebeish, A. Starch 1990, 42(2), 60.
19. Mofit, A.; Hassan, E. A.; Salama, J. Y.; El-Sabban, M. M. B. Starch 1982, 34(11), 375.
20. Shufen, Z.; Weiqun, Z.; Jinzong, Y. Fine Chem 1999, 16, 53.
21. Sloan, J. W.; Mehltretter, C. L.; Senti, F. R. J Chem Eng Data 1962, 7, 156.
22. Tijsen, C. J.; Kolk, H. J.; Stambuis, E. J Carbohydr Polym 2001, 45, 219.
23. Bhattacharyya, D.; Singhal, R. S.; Kulkarni, P. R. Carbohydr Polym 1995, 27, 247.
24. Stojanovic, Z.; Jeremic, K.; Jovanovic, S. Starch 2000, 52, 413.
25. International Standard. Modified starch—Determination of content of carboxymethyl groups in carboxymethyl starch, ISO 11216:1998(E).
26. International Standard. Modified starch—Determination of carboxyl group content of oxidized starch, ISO 11214:1996(E).
27. Xiaodong, Z.; Xin, L.; Wenying, L. J Appl Polym Sci 2003, 89, 3016.