DEGRADATION OF STARCH BY HIGH PRESSURE JET.

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Introduction.

It has been reported that it is possible to shatter the liquid[1],[2] and to decrease the molecular weight of polyethylene[3] by the way of high pressure jet. For the purpose of confirming the phenomenon of the degradation of the molecule of polymer, the authors experimented with an aqueous solution of the amylose extracted from starch and confirmed the decrease of the molecular weight by measuring viscosity and reducing power. And moreover, they experimented with inuline–chain structure as amylose–, maltose, lactose and sucrose, and studied the effect of high pressure jet on the degradation of molecule.

Apparatus and Experimental.

The apparatus used are all the same as in the case of the previous paper,[3] the pressures being 2000 and 4000 atm, the nozzle diameter 0.50 mm, the distance between the nozzle and the crashing plate 10 mm, and the maximum number of jetting 35 times.

Samples.

Potato starch of the Japanese pharmacopoeia is purified by the following method, namely, the proteins in starch are extracted by stirring in a 0.2% NaOH solution for about 50 hours, and the fats are extracted with methanol for 10 hours by means of a Soxlet extractor. For the purpose of obtaining the uniform size of amylose molecule, after pre-treating the starch for half an hour with hot water of 50° C, the starch was separated by centrifuging, and then stirring it for 1 hour with hot water of 61° C, the extracted aqueous solution of amylose was separated by centrifuging. The molecular weight of amylose was about 50,000. When the temperatures of pre-treating and extracting were 60° C and 65° C respectively, the molecular weight of amylose was found to be about 100,000. Commercial inuline, maltose, lactose and sucrose were used.

Experimental Results.

As the method of measuring the molecular weight, they used the way of viscosity and used the equation of Staudinger $\lim_{c \to 0} \eta_{sp}/c = K_m \times M$. Lampitt, Fuller

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(1) R. Kiyama, H. Kinoshita and K. Suzuki, *This journal*, 21, 82 (1951)

(2) R. Kiyama, H. Kinoshita and K. Suzuki, *ibid.*, 22, 46 (1952)

(3) R. Kiyama and H. Kinoshita, *ibid.*, 22, 1 (1952)

and Goldenberg[4] used 4×10^{-4}, and Samec and his coworkers[5][6] 1.0×10^{-4} for the K_m value of a aqueous solution of amylose. The authors determined the K_m value of aqueous solution by using the relation of the intrinsic viscosity of a lN-KOH solution of amylose and the osmotic pressure measured by I. A. Wolff, L. J. Gundrum and C. E. Rist[7] (For the molecular weights of 130,000 and 64,000, the intrinsic viscosities of a 1N-KOH solution of amylose are 1.41 and 0.57 respectively). It is clear that the value of K_m depends on the shape of molecule, and moreover it may depend on the distribution of molecule. In the present experiment the greater the degree of the inclination of the straight lines of viscosity and concentration, the smaller the value of K_m. Accordingly, for the calculation of the molecular weight they used the value of $0.73 \sim 0.93 \times 10^{-4}$, corresponding to the inclination of that straight line. The method of Hanes[8] is used for measuring the reducing power, namely, the solution of K-ferricyanide and the reducing agent are warmed in a water bath. Ferric

Table 1.

Exp. No.	Press. (atm)	Conc. (%)	Number of jetting	Molecular weight	Degree of polymerization
1	2000	0.80	0 9 16	88800 63300 58000	548 391 358
2	2000	0.55	0 9 16	106900 61000 56800	660 377 351
3	2000	0.73	0 35	99200 49300	612 306
4	4000	0.55	0 9 16	60000 38700 35600	370 238 220
5	4000	0.73	0 35	39900 24100	246 149

Table 2.

Exp. No.	Press. (atm)	Conc. (%)	No. of jetting	Molecular weight	Degree of polymerization	s*	Reducing power mg glucose/gm	Reducing power increased
6	4000	0.71	0	98200	606		4.13	
			1	60000	370	1.30	5.68	1.55
			2	51100	316	1.83	6.44	2.31
			3	46600	288	2.21	7.54	3.41
			10	39000	241	3.03	10.00	5.87
			20	35800	221	3.48	12.39	8.26

s*: number of bond split, calculated from equation $s = 2\left(\frac{n}{p} - 1\right)$[9], where n is the initial degree of polymerization.

(4) L. H. Lampitt, C. H. F. Fuller and N. Goldenberg, *J. Soc. Chem. Ind.*, **67**, 41 (1948)
(5) Samec and Dalar, *Z. Physik. Chem.*, **259**, 204 (1939)
(6) Samec and Rakusa, *ibid.*, **263**, 17 (1940)
(7) I. A. wolff, L. J. Gundrum and C. E. Rist, *J. Amer. Chem. Soc.*, **72**, 5188 (1950)
(8) C. S. Hanes, *Biochem. J.*, **23**, 99 (1929)
(9) J. Osugi, *Proc. Japan Academy*, **27**, 241 (1951) No. 5.
W. H. Durfee and Z. I. Kertesz, *J. Amer. Chem. Soc.*, **62**, 1196 (1940)

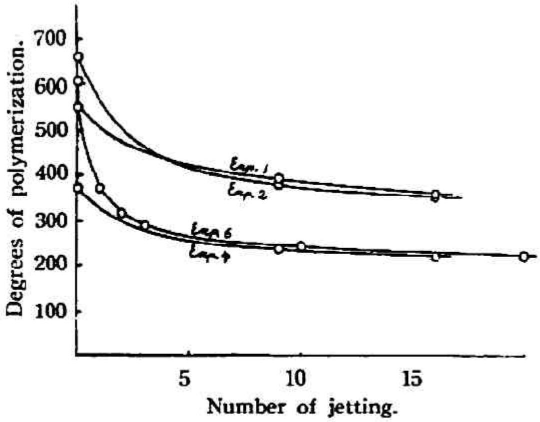

Fig. 1 Relation between degrees of polymerization and number of jetting.

ion is reduced to ferrous ion and a solution of KI is added. The deposited iodine which is oxidized by residual ferric ion is titrated with Na-thiosulphate. The experimental results and conditions are given in Tables 1 and 2 and Fig. 1.

Considerations.

(1) In the case of decreasing the molecular weight of polyethylene, the mechanism of destruction was considered as a kind of mechanical destruction and it was effective to make the pressure higher and to make the distance between the nozzle and the crashing plate shorter. In the case of jetting the solution of amylose, the same effects are expected, and from the experimental results of Table 1 the molecular weight is smaller, as the pressure is higher, namely the speed is higher.

(2) As the temperatures of water in extracting amylose from starch are 61°C and 65°C, the molecular weights are 50,000 and 100,000 respectively. And the rate of decreasing the molecular weight is smaller, as the initial molecular weight is smaller. This result is coincident with the fact that the effect of the jetting diminishes when the jetting is repeated over 10 times. Accordingly, it is anticipated that there is a limit to the size of the molecule destroyed in the present experiment. For the purpose of recognizing this fact, they experimented with inuline. The structure of inuline is a chain like that of amylose and its molecular weight is about 5000. The viscosity and the reducing power are unchangeable after the jetting of 1% and 4% solutions. As to the dimer, they experimented with various concentrations of maltose, lactose and sucrose, and confirmed from the measurement of the reducing power that the dimer is not destroyed by jetting. Consequently, in the experimental conditions used, the molecular weight of 10,000~20,000 may be the limit of the size of molecule, but such samples are not in hand.

(3) The inclination of the straight line indicated by the relation of viscosity to concentration, approaches to the horizontal line in consequence of the increase of the number of jetting.

(4) The relation of the number of bond split of amylose to the increase of reducing power is shown in Fig. 2. The fact that there holds no straight relation shows that the way of destruction is not at random, but is partially due to the distribution of the degraded sample. As described formerly, in this experiment, it is anticipated that it will be difficult to degrade the smaller molecule from the

reason that the limit of molecular size corresponding to the experimental conditions exists. Therefore, it is impossible to consider that the way of destruction is at random. When the molecular weight is smaller, it is capable to prepare the samples of uniform molecules, but it is difficult to obtain the quantity enough to use for this experiment.

(5) As to the mechanism of the degradation of amylose molecule, they thought it mechanical, but anticipated the effects of temperature and oxygen. When the room temperature is 20°C, the temperature of the crashing plate is 32.5°C after the jetting of 20 times under a pressure of 4000 atm. Therefore, the effect of temperature is negligible. In comparison of the sample experimented in the air with that in the stream of argon, there exists no difference between them, and so the effect of oxygen is also negligible.

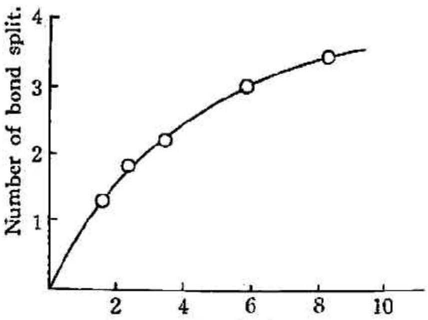

Fig. 2 Relation between increased reducing power and number of bond split.

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