

# Chemical Modification of Starch. II.

## Cyanoethylation

A. HEBEISH, I. ABD EL-THALOUTH, and M. A. EL-KASHOUTI,  
*National Research Centre, Textile Research Division, Dokki, Cairo, Egypt*

### Synopsis

Rice starch was cyanoethylated by reacting it with acrylonitrile in presence of sodium hydroxide at different concentrations of acrylonitrile and various reaction temperatures. The effect of cyanoethylation on the rheological and solubility properties of starch was examined. It was found that the extent of the cyanoethylation reaction [expressed as %N and degree of substitution (DS)] increased by increasing acrylonitrile concentration provided that the latter was not less than 8 ml acrylonitrile per 10 g starch. A temperature of 50° C constituted the optimal temperature for the cyanoethylation of starch under the conditions studied. Examination of the rheological properties of the modified starch revealed that regardless of the DS, cyanoethylated starches are characterized by pseudoplastic behavior of particular interest were the results of the viscosity. Cyanoethylated starch having smaller amounts of cyanoethyl groups had higher viscosity than those of relatively larger amounts. On the other hand, the cyanoethylated starches were soluble in water regardless of the extent of cyanoethylation.

### INTRODUCTION

Starch is one of the most important thickeners used in the textile industries principally in warp sizing, finishing, thread glazing, and printing.<sup>1-3</sup> To improve solubility, viscosity performance, and resistance to ageing of native starch and of solutions or thickening prepared therefrom, it is necessary to change the physical and/or chemical structure of starches. The physical and/or chemical structure of starch could be achieved by subjecting starch to acid treatment,<sup>4</sup> oxidation,<sup>5</sup> etherification and esterification,<sup>6,7</sup> as well as grafting.<sup>8-14</sup>

In this laboratory, there is a long-term research project dealing with modification of rice starch with a view of improving its properties and thereby increasing its utilization. In part I<sup>14</sup> of these studies, we have reported on the chemical modification of rice starch via grafting with acrylonitrile. The present work deals with the cyanoethylation of starch and the effect of this type of modification on the rheological and solubility properties of starch.

### EXPERIMENTAL

#### Materials

Egyptian rice starch was kindly supplied from Misr Co. for Starch and Yeast, Alexandria. Chemical analysis showed that while this starch acquired a moisture content of 14.75 and ash content of 0.53%, it was free from protein.

Acrylonitrile (bp 78.5°C) was freshly distilled before use.

### Procedure

Cyanoethylation of starch was performed as per a reported method.<sup>15</sup> The experimental technique adopted was as follows: 200 ml of 10% sodium hydroxide (dissolved in 80% ethyl alcohol and 20% water) was introduced into a 500-ml stoppered flask equipped with mechanical stirrer. To this, 10 g of starch and a certain amount of acrylonitrile were successively added. The reaction was allowed to proceed for 4 hr at 25°C. The mixture was then cooled in ice and neutralized with dilute HCl. The product was precipitated in ethyl alcohol (95%), extracted with alcohol, and finally dried in a dessicator containing calcium chloride.

### Analysis

Nitrogen was determined by the Dumas method. The degree of substitution (DS) was calculated from the nitrogen content using the following formula<sup>15</sup>:

$$DS = \frac{162 \times \%N}{1400 - 53 \times \%N}$$

The caboxyl content was determined according to a reported method.<sup>16</sup>

Characterization of flow properties was determined using cyanoethylated starch samples dispersed in distilled water at a concentration of 15% for all samples. The viscometer was a "Rheotest," type R.V., veb. prufgraterwerk Medingen, G.D.R., used under the following experimental conditions: (1) ranges of rate of shear were between 81 and 1312 sec<sup>-1</sup> for the upward curve, and the same, in a descending order, for the downward curves; (2) readings were taken after shearing times of 30 sec at each rate; (3) and temperature was 25°C.

## RESULTS AND DISCUSSION

Rice starch was cyanoethylated by reacting it with acrylonitrile in presence of sodium hydroxide. The cyanoethylation reaction was carried out under a variety of conditions. Variables studied embrace acrylonitrile concentration and reaction temperature. The changes in the physical and/or chemical structure of starch brought about by cyanoethylation were assessed by monitoring the rheological properties of starch before and after modification.

### Acrylonitrile Concentration

The effect of acrylonitrile concentration on the extent of the cyanoethylation reaction (expressed as % N and DS) is shown in Table I. It is clear that the extent of reaction increases by increasing acrylonitrile (AN) concentration provided that the latter was not less than 8 ml AN/10 g starch. Practically little or no reaction occurs upon using up to 6 ml AN/10 g starch.

This suggests that a specific arrangement among the starch hydroxyl groups, the acrylonitrile, the alkali, and the water molecules might be necessary to provide the cyanoethylation reaction, and this arrangement is justified at certain concentration of acrylonitrile. That is, below a certain concentration of acrylonitrile this specific arrangement is not attainable and therefore no reaction occurs under the conditions studied, and some reaction barrier or sink is operating until a crucial concentration of acrylonitrile is reached.

TABLE I  
Effect of Acrylonitrile Concentration on the Extent of Cyanoethylation of Starch<sup>a</sup>

Weight of starch (g)	ml of AN	% N	DS	mequiv CCOH/ 100 g dry cyanoethy- lated starch	Solubility in:	
					cold water	ethyl alcohol
10	4	Traces	—	1.40	Soluble	Insoluble
10	6	0.05	0.006	4.70	Soluble	Insoluble
10	8	0.30	0.035	5.61	Soluble	Insoluble
10	10	1.85	0.230	6.04	Soluble	Insoluble

<sup>a</sup> Temperature 25° C, reaction time 4 hr.

It may be further noted that the low extent of cyanoethylation reaction is not to be unexpected and is a consequence of low concentration and a fixed reaction time. Very recent work on aqueous cyanoethylation<sup>17</sup> revealed that the extent of the reaction in question is quite low compared to reaction in 100% aqueous systems, reflecting differences in the swelling properties of starch in the aqueous and nonaqueous media.

### Reaction Temperature

Table II shows the effect of the reaction temperature on the extent of cyanoethylation of starch. As is evident, increasing the reaction temperature from 25 to 50°C causes an outstanding enhancement in the extent of the reaction. Further increase in temperature (up to 65°C) brings about a decrease in the extent of cyanoethylation.

The higher extent of cyanoethylation reaction at 50°C than at 25°C could be associated with increased swellability of starch and higher mobility of the acrylonitrile molecules. Both starch swellability and acrylonitrile molecules mobility facilitate adsorption of the acrylonitrile on the surface of starch, its diffusion inside the starch structure and its adsorption on the internal surfaces thereby promoting the reaction. It is understandable that starch hydroxyl groups are immobile. Reaction of hydroxyl groups with acrylonitrile would depend on the availability of AN molecules in their vicinity. Whereas the lower cyanoethylation at 65°C than at 50°C is unequivocally due to partial conversion

TABLE II  
Effect of Temperature on the Extent of Cyanoethylation of Starch

Temperature (°C)	ml of AN	Weight of starch	% N	DS	mequiv COOH 100 g dry cyanoethy- lated starch	Solubility in:	
						water	ethyl alcohol
25	8	10	0.30	0.035	5.61		
50	8	10	3.68	0.494	12.50	Soluble	Insoluble
65	8	10	1.62	0.200	14.95		

of the cyanoethyl groups to carboxyethyl groups under the influence of alkali at higher temperature, i.e., 65°C. Indeed, the higher amount of carboxyethyl groups, expressed as milliequivalent —COOH group/100 g dry cyanoethylated starch, obtained at 60°C than at 50°C as shown in the sixth column of Table II, confirms this.

### Rheology

Figure 1 is a rheogram showing the rate of shear as a function of shearing stress for cyanoethylated starch having different degrees of cyanoethylation, using a concentration of 15% of the modified starch. Trials to draw a rheogram for a control sample, i.e., starch treated with sodium hydroxide under identical conditions of cyanoethylation but in absence of acrylonitrile, have failed owing to the high fluidity of the alkali-treated starch when monitored at the same concentration of cyanoethylated starch.

It is clear (Fig. 1) that regardless of the cyanoethyl content, those modified starches are characterized by a pseudoplastic behavior, that is, the up and down curves are coincident.<sup>18-20</sup>

Furthermore, the rheograms of all these modified starches acquire similar shape which tend to concave toward the rate of shear axis. In other words, when the viscosity of the cyanoethylated starch solution is measured using a large applied force, the apparent viscosity is less than that of the same solution determined with a smaller force and slower rate of shear.

However, the curves representing the rheogram for cyanoethylated starch having relatively higher amounts of cyanoethyl content lie above those of lower amounts. Since, as already pointed out, the rheogram of a control sample was

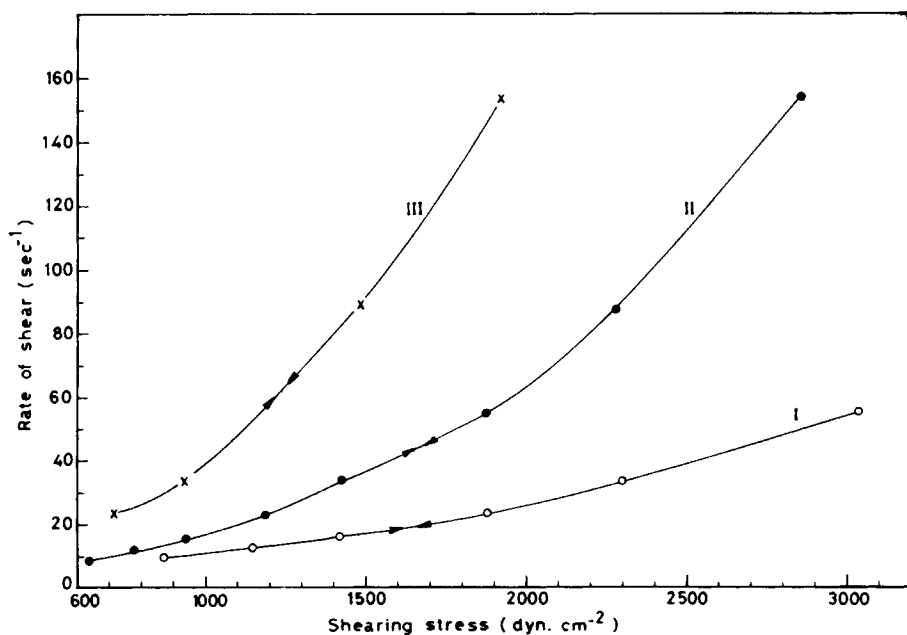


Fig. 1. Rate of shear vs. shearing stress of cyanoethylated starch. % N (I) 0.03; (II) 1.85; (III) 3.68. pH of dispersions 7; modified starch concentration 1.5%.

not possible to obtain because of the high fluidity of its solution, the present data indicate that the viscosity of starch increases significantly by introducing cyanoethyl groups in the starch molecules up to a certain limit, in accordance with previous reports.<sup>21</sup> Further increase in the cyanoethyl groups decreases the viscosity of starch.

A more clear picture of the dependance of the viscosity of cyanoethylated starch on the extent of cyanoethylation is given in Table III. The viscosity was calculated by applying the following equation:

$$\eta = \tau/D$$

where  $\eta$  is the apparent viscosity,  $\tau$  is the shearing stress, and  $D$  is the rate of shear.

The finding that the viscosity of starch samples having smaller amounts of cyanoethyl groups is higher than those having larger amounts is rather interesting and could be explained in terms of the molecular theory.<sup>22</sup> The latter is based upon a lattice structure for the liquid, containing some unoccupied sites or holes. These sites move at random throughout the liquid as they are filled and created anew by nearby molecules jumping from one site to another. Under an applied stress the probability of such jumps is higher in the direction that relieves the stress. It is likely that there is a critical point for modification of starch via cyanoethylation. At this point, the starch molecules are modified in such a way to justify creation of modified molecules capable of swelling, dispersing, and jumping in aqueous medium without complete elimination of intermolecular forces between the solvent (water) and solute (cyanoethylated starch). The fact that the viscosity decreases by increasing the cyanoethyl group in starch substantiates the contribution of these intermolecular forces. It is to be expected that because of their nature, presence of larger amounts of cyanoethyl groups in the starch molecules would reduce the intermolecular forces.

### Solubility

The solubility properties of cyanoethylated starch having different amounts of cyanoethyl groups are shown in Tables I and II. As can be seen, cyanoethylated starch samples are soluble in water and insoluble in ethyl alcohol. This is observed irrespective of the amount of cyanoethyl groups.

TABLE III  
Variation of the Viscosity of Cyanoethylated Starch at Different Rates of Shear

% N of cyanoethylated starch	Viscosity (poise) at rate of shear (sec <sup>-1</sup> ) of:						
	5.4	9	16.2	27	48.6	81	145.8
None	—	—	—	—	—	—	—
0.3	212	158	116	85	62	46	32
1.85	144	103	74	53	39	28	20
3.68	—	60	44	34	24	18	13

### References

1. M. W. Rutenberg "Modified Starches," in *Water Soluble Resins*, R. Davidson and M. Sittig, Eds., Reinhold, New York, 1968.
2. J. Compton and W. H. Martin, in *Starch Chemistry and Technology, Vol. II, Industrial Aspects*, R. L. Whistler and E. F. Paschall, Eds., Academic, New York, 1967, p. 147.
3. C. Moore, "An Economic Evaluation of Starch Use in Textile Industry," Agricultural Economic Report No. 109, March, 1967.
4. P. Schildneek and E. C. Smith, in ref. 2, p. 217.
5. R. L. Scallet and E. A. Sowell, in ref. 2, p. 237.
6. R. L. Whistler and R. Schweiger, *J. Am. Chem. Soc.*, **29**, 449 (1964).
7. L. H. Kruger and M. W. Rutenberg, in ref. 2, p. 147.
8. G. F. Fanta, in *Block and Graft Copolymerization*, Vol. 1, R. J. Ceresa, Ed., Wiley-Interscience, New York, 1973, p. 1.
9. G. F. Fanta, M. O. Weaver, and W. M. Doane, *Chem. Technol.*, **4**(11), 675 (1974).
10. G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **21**, 425 (1977).
11. B. T. Hefreiter, *J. Appl. Polym. Sci.*, **21**, 761 (1977).
12. D. Trimmell, E. I. Stout, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **21**, 655 (1977).
13. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.*, **21**, 1647 (1977).
14. A. Hebeish, I. Abd El-Thalouth, M. A. El-Kashouti, and S. H. Abdel-Fattah, *Angew. Makromol. Chem.*, **78**, 101 (1979).
15. M. Kamel and I. Abd El-Thalouth, *Cellul. Chem. Technol.*, **10**, 17 (1976).
16. A. Pacault and M. Bouttemy, *Bull. Soc. Chim. Fr.* **17**, 663 (1950).
17. I. Abd El-Thalouth, M. A. El-Kashouti, and A. Hebeish, *Angew. Makromol. Chem.*, accepted for publication.
18. R. L. Whistler, *Industrial Gums*, Academic, New York and London, 1959, pp. 643-674.
19. E. H. DeButts, J. A. Hudy, and J. H. Elliot, *Ind. Eng. Chem.* **49**, 94 (1957).
20. E. Ott and J. H. Elliott, *Makromol. Chem.*, **18**, 352 (1956).
21. T. E. Yeates, M. E. Carr, C. L. Mehlretter, and B. T. Hofreiter, *Tappi*, **48**, 509 (1965).
22. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

Received February 6, 1979

Accepted April 17, 1980