

Dyeing of Chemically Modified Celluloses. II. Effect of Chemical Modification of Cellulose on the Dyeing Properties of Some Direct Dyes

A. HEBEISH, A. Z. MOURSI, M. I. KHALIL, and F. A. ABDEL-MOHDY,
National Research Centre, Dokki, Cairo, Egypt

Synopsis

The behavior of partially acetylated cellulose, partially carboxymethylated cellulose, cyanoethylated cellulose, and cellulose grafted with polyacrylonitrile toward three direct dyes, namely, Chlorantine Fast Red 6 BLL, Solophenyl Orange T4RL, and Diphenyl Brilliant Flavine 7GFF, was studied. Partially acetylated cellulose having 2.06% combined acetic acid showed higher dye uptake than the unmodified cellulose. The amount of dye uptake increased as the acetyl content increased up to 4% combined acetic acid. Beyond this, enhancement in the dye uptake was not significant. Whereas partially carboxymethylated cellulose showed a lower dye uptake than the control. The dye uptake decreased considerably as the carboxymethyl groups increased. The same holds true for cyanoethylated cellulose where increasing the cyanoethyl content caused a substantial reduction in the dye uptake. On the other hand, cellulose grafted with polyacrylonitrile up to 18.3% graft yield showed much higher dye uptake than the ungrafted cellulose.

INTRODUCTION

Chemical modification of cellulose with the aim of imparting to it new properties has been extensively studied. Of the various processes that have been suggested or actually been used commercially to modify the cellulose are acetylation,¹⁻⁵ carboxymethylation,⁶⁻²² cyanoethylation,²³⁻³² and grafting.³³⁻³⁵

These reports are concerned with preparation and some properties of the resultant modified celluloses. Furthermore, their behavior toward reactive dyes has recently been studied.³⁶ However, to the authors' knowledge, not much work has been published yet on the dyeing behavior of these modified celluloses when direct dyes are used. It is the aim of this investigation to fill this gap.

EXPERIMENTAL

Materials

Regenerated cellulose sheet (cellophane S, Misr. Rayon Co., Kafr El-Dwar, Egypt) 0.028 cm thick was used.

Modification of Cellulose

Partial Acetylation. Samples of acetylated cellulose of different acetyl contents were prepared as follows. The regenerated cellulose films were treated with glacial acetic acid for 30 min. After being blotted between filter papers, the films were treated for 15 sec with a 2.5% solution of perchloric acid (catalyst) in glacial acetic acid. The films were blotted once more and then treated for 10 min with various concentrations of acetic anhydride in benzene using a liquor:film ratio of 100:1. Finally, the films were thoroughly washed and dried at room temperature. The acetyl content, expressed as combined acetic acid % yield, was determined according to a method reported by Hawiatt and Martin.³⁷ The control sample was given the same treatment except that the acetic anhydride was omitted.

Partial Carboxymethylation. Partially carboxymethylated cellulose was prepared as follows.⁸ Regenerated cellulose film was first padded with 3*N* sodium chloroacetate and then with sodium hydroxide of known concentration. It was then placed between two glass plates and stored for 24 hr. The film was then washed, neutralized with 1% hydrochloric acid for 2 hr, washed again and finally air dried. Partially carboxymethylated cellulose of various degrees of substitution (D.S.) was obtained by using different concentrations of sodium hydroxide ranging between 1*N* and 10*N*. The control samples were prepared under identical conditions except that sodium chloroacetate was omitted. The carboxymethyl groups, expressed as meq COOH/100 g cellulose, were determined by the method described by Ludtke.³⁸

Partial Cyanoethylation. Regenerated cellulose film was treated in 4% sodium hydroxide for 20 min and then washed with distilled water, neutralized with 0.5% hydrochloric acid for 5 min, washed again, and air dried at room temperature. It was then impregnated in a solution containing 10% sodium hydroxide, 10% sodium chloride, and specific concentration of acrylonitrile at room temperature for varying periods, and finally thoroughly washed with water and air dried. A control sample was prepared by subjecting the film to the same treatment in the absence of acrylonitrile. The nitrogen content of the cyanoethylated cellulose was estimated using the Kjeldahl method.

Graft Copolymerization. Graft copolymerization of acrylonitrile onto regenerated cellulose was carried out according to the method described by Hebeish and Mehta.³⁹ The control sample was prepared under grafting conditions in the absence of monomer.

Dyes

Commercial samples of Chlorantine Fast Red 6 BLL, Solophenyl Orange T4RL, and Diphenyl Brilliant Flavine 7GFF were used without further purification. These dyes were kindly supplied by Ciba-Geigy, Switzerland.

General Dyeing Procedure

The regenerated cellulose film (24.5 cm × 3.8 cm) was held on a stainless steel frame. The frame was then immersed in 50 ml of 0.1% dye liquor in 850 ml distilled water. To this 100 ml sodium sulfate solution (10%) was gradually

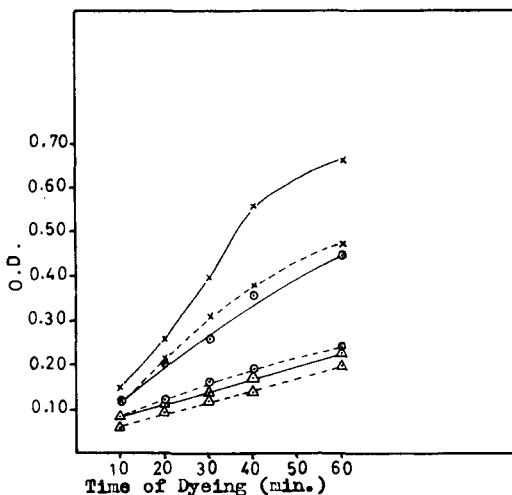


Fig. 1. Dye uptake by partially acetylated cellulose (combined acetic acid = 2.06%) and control: (—) partially acetylated cellulose; (---) control; (O) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (X) Diphenyl Brilliant Flavine 7GFF.

added with continuous shaking. The dyeing operation was performed for different periods of time ranging from 10 to 60 min. In the following step, the sample was washed thoroughly with water, given a light soaping (1 ml/l. Nekalin LN) at the boil for 1 hr. Finally, the sample was thoroughly washed with water and air dried.

Measurement of Dye Uptake

The dye uptake, expressed as optical density (O.D.), was measured on UNICAM S.P. 800 spectrophotometer at the peak of maximum absorption.

RESULTS AND DISCUSSION

Partially Acetylated Cellulose

Partially acetylated cellulose having 2.06% combined acetic acid and a control sample were dyed under similar conditions with the said three direct dyes. Results of the dye uptake (expressed as O.D.) are shown in Figure 1. It is clear that with the three dyes examined, partially acetylated cellulose acquires a higher rate of dyeing than untreated cellulose.

The amount of dye uptake would depend on diffusion of the dye from the aqueous phase to the cellulose phase as well as on the adsorption of dye by the cellulose film. Both diffusion and adsorption, in turn, depend on the swellability and adsorptive sites on the substrate. Introduction of very small amounts of acetyl groups seems to open up the cellulose structure and facilitate diffusion of the dye into cellulose while keeping its adsorption power intact. This would account for the faster rate of dyeing obtained with partially acetylated cellulose as compared with untreated cellulose.

Figure 2 shows that increasing the acetyl content up to ca. 4% combined acetic

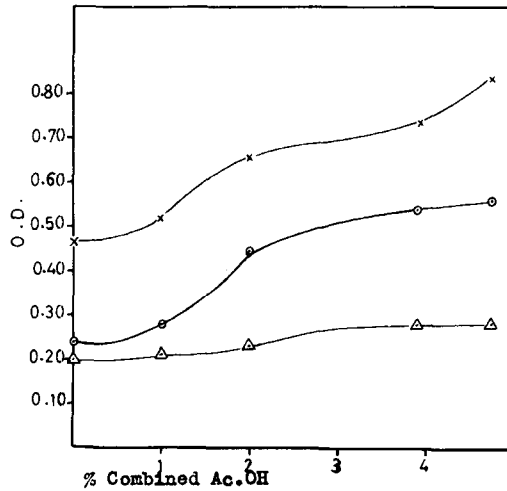


Fig. 2. Relationship between the dye uptake expressed as optical density (O.D.) and the acetyl content expressed as combined acetic acid percent of partially acetylated cellulose: (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (×) Diphenyl Brilliant Flavine 7GFF.

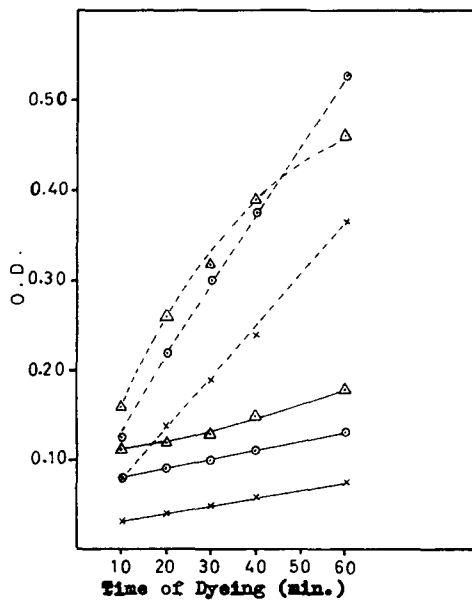


Fig. 3. Dye uptake by partially carboxymethylated cellulose (Meq COOH/100 g cellulose = 25.0) and control cellulose: (—) partially CMC; (---) control; (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (×) Diphenyl Brilliant Flavine 7GFF.

acid enhances, to a considerable extent, the dye uptake. Thereafter, enhancement in the dye uptake is only small. At relatively high acetyl content, the advantage gained by opening up the cellulose structure seems to be outweighed by the adverse effect of the acetyl groups on the adsorptive power of the cellulose.

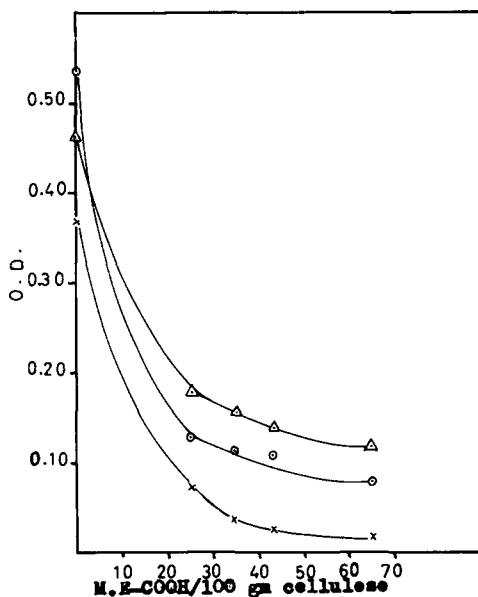


Fig. 4. Relation between dye uptake expressed as optical density (O.D.) and carboxymethyl group expressed as meq COOH/100 g cellulose of partially carboxymethylated cellulose: (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (×) Diphenyl Brilliant Flavine 7GFF.

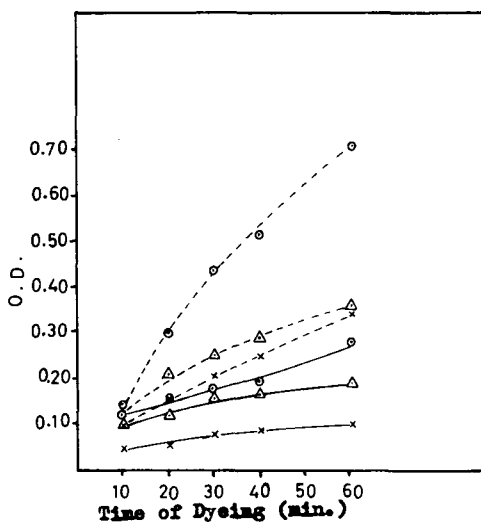


Fig. 5. Dye uptake on partially cyanoethylated cellulose (nitrogen content 1,2%) and control: (—) partially cyanoethylated; (- - -) control; (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4LL; (×) Diphenyl Brilliant Flavine 7GFF.

Partially Carboxymethylated Cellulose

In Figure 3 is shown the dye uptake obtained with partially carboxymethylated cellulose and control when both substrates were dyed independently with the three dyes in question. It is clear that regardless of the dye used, the dye uptake is much lower on partially carboxymethylated cellulose than on the control. This

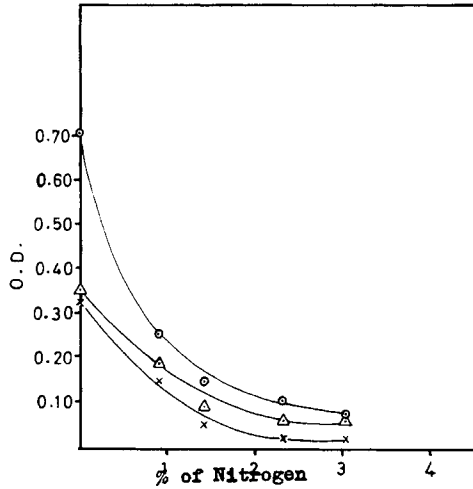


Fig. 6. Relationship between dye uptake expressed as optical density (O.D.) and nitrogen content of partially cyanoethylated cellulose: (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (×) Diphenyl Brilliant Flavine 7GFF.

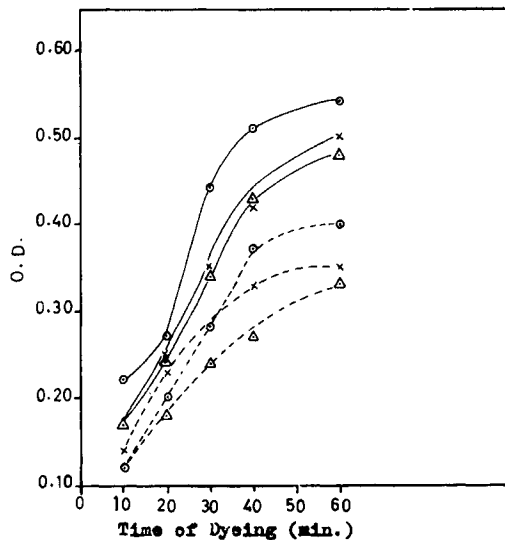


Fig. 7. Dye uptake by cellulose graft copolymer (% graft yield 15.8) and control: (—) graft copolymer; (---) control; (○) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (×) Diphenyl Brilliant Flavine 7GFF.

implies that introduction of carboxymethyl groups into the cellulose molecule substantially reduces its acceptability of direct dyes.

Introduction of carboxymethyl groups into the cellulose molecules causes (a) blocking some of the cellulose hydroxyls (sites for dye adsorption) and (b) increasing the negative surface potential of cellulose; the carboxyl groups ionize and repel the similarly charged dye anions.⁴⁰ This would account for the lower dye uptake obtained with partially carboxymethylated cellulose.

Figure 4 shows the dye uptake with partially carboxymethylated celluloses having different carboxymethyl contents. Obviously, the dye uptake decreases

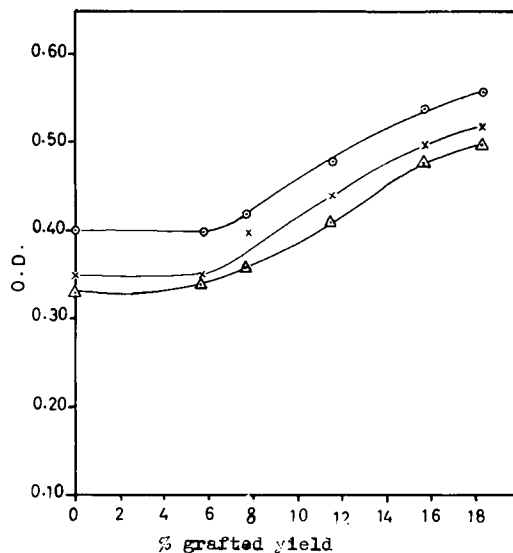


Fig. 8. Relationship between dye uptake expressed as optical density (O.D.) and graft yield of cellulose graft copolymer: (O) Chlorantine Fast Red 6BLL; (Δ) Solophenyl Orange T4RL; (\times) Diphenyl Brilliant Flavine 7GFF.

with increasing carboxymethyl groups in the modified cellulose, in full agreement with the above observation.

Partially Cyanoethylated Cellulose

Figure 5 shows the dye uptake obtained with cyanoethylated cellulose of nitrogen content 1.2%. The dye uptake found with the control cellulose is also shown in the same figure for comparison.

It is apparent that the dye uptake obtained with cyanoethylated cellulose is much smaller than the corresponding dye uptake found with the control. It follows that introducing cyanoethyl groups into the cellulose molecules reduces the affinity of direct dyes for cellulose.

Figure 6 shows variation of dye uptake with cyanoethyl content of partially cyanoethylated cellulose. As is evident increasing the cyanoethyl content is accompanied by a substantial reduction in the dye uptake, a point which supports the above finding.

Cellulose Grafted with Polyacrylonitrile

Figure 7 shows the dye uptake by unmodified cellulose (control) and by cellulose grafted with polyacrylonitrile. It is clear that the dye uptake found with cellulose grafted with polyacrylonitrile is much higher than that of the unmodified cellulose, in accordance with very recent work.⁴¹

Grafting occurs exclusively in the accessible amorphous regions of cellulose.⁴²⁻⁴⁴ Dye absorption is also confined to these regions since dyeing was carried out in aqueous medium. The physical and/or chemical changes in the structure of cellulose brought about by grafting are reflected by the affinity of the dye for cellulose. For a given dye, this affinity would essentially rely on

prevalent sites for dye adsorption, i.e., the cellulose hydroxyls. A decrease in the latter hinders dye adsorption. It appears that at lower grafting, such as the substrate in question, the grafted polymer chains open up the cellulose structure while keeping most of the cellulose hydroxyls intact. As a result, higher dye uptake occurs.

The effect of the amount of polymer grafted, i.e., graft yield, on the dye uptake may be realized from Figure 8. The data make it evident that within the range studied, the dye uptake increases as the graft yield increases, in accordance with the above results.

It should be pointed out that regardless of the substrate used, the value of the dye uptake differs from one substrate to the other, though the three dyes examined belong to one class, i.e., direct dyes. This reflects the nature of the dye which is essentially governed by substituents present, steric configuration, and diffusibility.⁴⁵

References

1. E. V. Anderson and A. S. Cooper, Jr., *J. Ind. Eng. Chem.*, **51**, 608 (1959).
2. O. J. McMillan, Jr., K. M. Decosas, A. S. Cooper, Jr., C. Hamalainen, A. L. Murphery, and E. E. Pollard, *Amer. Dyest. Rep.*, **49**, 839 (1960).
3. E. J. Honold, E. J. Kesting, and E. L. Skau, *Text. Res. J.*, **27**, 400 (1957).
4. V. W. Trip, T. R. Giuffria, and I. V. deGruy, *Text. Res. J.*, **27**, 14 (1957).
5. A. Hebeish, A. Kantouch, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **15**, 11 (1971).
6. M. Kamel, A. Kantouch, and A. Hebeish, U.A.R. Pat. 6625 (Nov. 1962).
7. M. Kamel, A. Kantouch, and A. Hebeish, *Text. Prax.*, **19**, 1114 (1964).
8. M. Kamel, A. Kantouch, and A. Hebeish, *Text. Prax.*, **20**, 577 (1965).
9. R. M. Reinhardt and T. W. Fenner, *Ind. Eng. Chem., Prod. Res. Dev.*, **4**, 82 (1965).
10. C. M. Conrad, *J. Text. Inst.*, **50**, 133 (1955).
11. G. C. Daul and J. D. Reid, U.S. Pat. 2,584,114 (1952); C. A., **46**, 3767 (1952).
12. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Text. Res. J.*, **22**, 787 (1952).
13. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Text. Res. J.*, **23**, 719 (1953).
14. J. N. Grant, *Text. Res. J.*, **26**, 74 (1956).
15. J. N. Grant, A. W. McDonald, and G. C. Humphery, *Text. Res. J.*, **28**, 60 (1958).
16. R. M. Reinhardt, T. W. Fenner, and J. D. Reid, *Text. Res. J.*, **27**, 873 (1957).
17. E. Frieser, *Z. Ges. Text. Ind.*, **60**, 977 (1959).
18. R. M. Reinhardt, T. W. Fenner, and J. D. Reid, *Amer. Dyest. Rep.*, **50** (9), 67 (1961).
19. M. Kamel, A. Kantouch, and A. Hebeish, *Indian J. Technol.*, **5**, 58, (1967).
20. R. M. Reinhardt, J. D. Reid, T. W. Fenner, and R. Y. Mayne, *Text. Res. J.*, **29**, 802 (1959).
21. R. M. Reinhardt, T. W. Fenner, and J. D. Reid, *Text. Res. J.*, **32**, 735 (1962).
22. A. Kantouch, A. Hebeish, and M. H. El-Rafie, *Eur. Polym. J.*, **6**, 1975 (1970).
23. G. C. Daul, R. M. Reinhardt and J. D. Reid, *Text. Res. J.*, **25**, 246 (1955).
24. R. M. Reinhardt, A. R. Markezich, H. B. Moore, and J. D. Reid, *Text. Res. J.*, **26**, 423 (1956).
25. L. W. Mazzeno, Jr., R. M. Reinhardt, J. D. Reid, and J. D. Dickson, *Text. Res. J.*, **26**, 594 (1956).
26. N. M. Bikales and L. Rapoport, *Text. Res. J.*, **28**, 737 (1958).
27. C. M. Conrad, *Text. Res. J.*, **29**, 287 (1959).
28. W. H. Martin and J. Compton, *Text. Res. J.*, **40**, 813 (1970).
29. R. J. Demint, J. C. Arthur, Jr., and W. F. Mcsherry, *Text. Res. J.*, **31**, 821 (1961).
30. J. C. Arthur, Jr., and R. J. Demint, *Text. Res. J.*, **31**, 988 (1961).
31. R. Marunov, R. G. Zhdarkov, Yu. G. Krayazhev, and Z. A. Rogovin, *Vysokomol. Soedin.*, **5**, 150 (1963).
32. A. Kantouch, A. Hebeish, and M. H. El-Rafie, *J. Appl. Polym. Sci.*, **15**, 1007 (1971).
33. E. H. Immergut, *Encyclopedia of Polymer Science and Technology*, Vol. 3, H. F. Mark, N. G. Gaylered, and N. M. Bakler, Ed., Interscience, New York, 1965, p. 242.

34. A. Hebeish, *Kolorisztikai Ertesito*, **13**, 12 (1971).
35. F. K. Guthrie, *Polymer*, **16**, 134 (1975).
36. M. Kamel, A. Hebeish, and A. Z. Moursi, *J. Soc. Dyers Colour.*, **90**, 352 (1974).
37. F. Hawiatt and E. Martin, *J. Text. Inst.*, **35**, T1 (1944).
38. M. Lüdtke, *Z. Angew. Chem.*, **48**, 650 (1935).
39. A. Hebeish and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1625 (1968).
40. A. Hebeish, I. Abdel-Thlouth, and M. Kamel, *Amer. Dyest. Rep.*, **62** (2), 28 (1973).
41. M. M. Kamel and A. Hebeish, *J. Appl. Polym. Sci.*, to appear.
42. T. Toda, *J. Polym. Sci.*, **58**, 411 (1962).
43. Y. Iwakura, T. Kurasaki, K. Uno, and Y. Imai, *J. Polym. Sci. C*, **4**, 673 (1964).
44. I. Sakurada, T. Okada, M. Uchida, and E. Kugo, *Doitai To Hoshasen*, **2**, 316 (1959).
45. M. Kamel, A. Hebeish, and A. Al-Aref, *Text. Res. J.*, **45**, 131 (1975).

Received June 21, 1976