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Morphology of cellulose and oxidised cellulose in powder form

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Abstract

A series of 2,3-dialdehyde cellulose (DAC), sodium 2,3-dicarboxylate cellulose (NaDCC), and 2,3-dicarboxycellulose (DCC) (30, 60, 80, and 98% based on glucose monomer units) were prepared from commercial cellulose powder. The morphology of these powdered samples were investigated by scanning electron microscopy. The cellulose powder was found to be in the form of fibres having an aspect ratio of 14, and this value decreased for all the 30% oxidised derivatives, in agreement with wide-angle X-ray diffraction results (WAXRD). For DAC and NaDCC, the SEM of higher derivatives (60% oxidation and above) did not show presence of discrete fibres, but for all the DCC derivatives, the SEM showed discrete fibres. The surface effects seen in SEM are not apparent in WAXRD spectra, offering a new insight into the physical form of the oxidised cellulose samples.

Keywords: Cellulose; SEM; WAXRD

1. Introduction

Oxidised cellulose products have been of great interest due to their diverse applications potential (Chavan, 1995; Domb, Kost, & Wiseman, 1997; Varma & Chavan, 1994, 2001). Partial oxidation of cellulose causes changes in the structure and crystallinity of the resulting molecule, which affects its chemical and physical properties. Previously we prepared a series of oxidised celluloses in order to obtain 2,3-dialdehyde cellulose (DAC), 2,3-dicarboxycellulose (DCC), and sodium 2,3-dicarboxylate cellulose (NaDCC), and have reported the changes observed in their crystallinity (Varma & Chavan, 1995a,b), solid state CP-MAS ^{13}C NMR spectral features (Varma, Chavan, Rajmohanan, & Ganapathy, 1997) and thermal properties (Varma & Chavan, 1995a,b). These studies had given us valuable insights into the structural changes that occur when cellulose is oxidised and in explaining the structure property correlations with respect to thermal properties, solvent absorption, etc. We now report on the scanning electron microscopy studies of these materials, in order to visually observe the changes occurring on cellulose powder on undergoing oxidation reactions.

2. Experimental

2.1. Materials

Cellulose powder CP-100 mesh fineness was the material used in this study. It was a product of Cellulose Products of India Ltd, Ahmedabad. It has an α-cellulose content of 85% and ether-extractable content of 0.2%.

2.2. Oxidised celluloses

The synthesis and characterisation of 30, 60, 80 and 98% oxidised DAC, DCC, and NaDCC are reported elsewhere in detail (Maekawa & Koshijima, 1984; Nevell & Whistler, 1964; Varma & Chavan, 1995a,b).

2.3. Scanning electron microscopy

Surface morphology of modified cellulose was studied by using Leica Cambridge (Stereoscan 440) Scanning Electron Microscope (Cambridge, UK). Sample specimens were coated with gold (30 μm thick) in an automatic sputter coater (Polaron Equipment, scanning microscope coating unit E 5000, UK). Accelerating potential was 20 kV. Photographs of representative areas of the sample were taken at 500 and 3000 magnifications.

3. Results and discussion

Fig. 1 shows the SEM of cellulose powder. It is seen that

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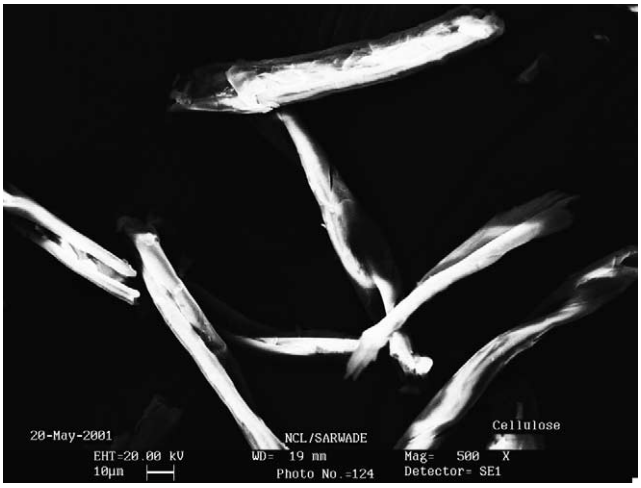

Fig. 1. SEM of cellulose powder of 100 mesh fineness.

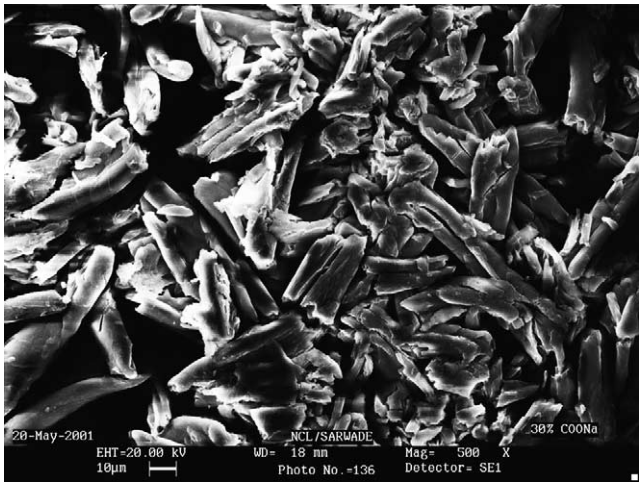

Fig. 3. SEM of 30% NaDCC.

the cellulose is still in the form of fairly long fibres (aspect ratio approximately 14). It should be noted that the α-cellulose content is only 85% which means that the content of adhering hemicelluloses and lignin account for about 15% of the materials and is the cause for the variation in the uniformity in thickness of the fibres. Fig. 2 is the SEM of 30% DAC. It is seen that the fibrous form of cellulose is retained, but the length of the fibres has reduced and there is a large distribution in the sizes of the particles (aspect ratio varying from 3 to 14). There seem to be a few unreacted fibres too in this sample, having close resemblance to the cellulose fibres (Fig. 1).

Conversion of 30% DAC to 30% NaDCC by further oxidative reaction with sodium chlorite (Varma & Chavan, 1995a,b) leads to a slight fall in particle size and greater clustering of the individual fibres (Fig. 3). When 30% NaDCC is converted to 30% DCC by exchanging the sodium ion with a hydrogen ion by immersing in strong hydrochloric acid, there was further size reduction (Fig. 4). However, a magnification of the latter particles (Fig. 5)

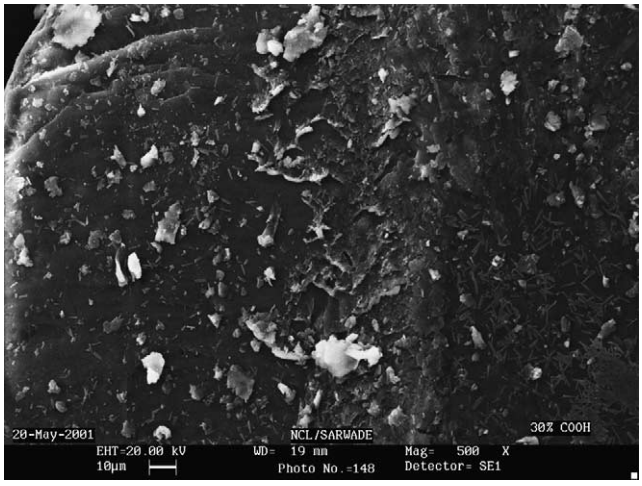

Fig. 4. SEM of 30% DCC.

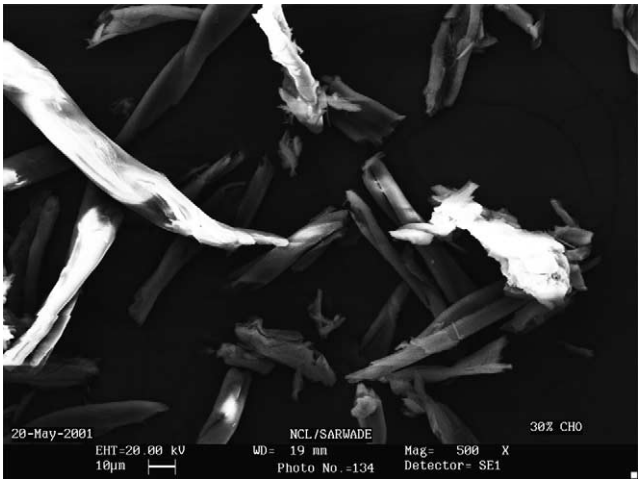

Fig. 2. SEM of 30% DAC.

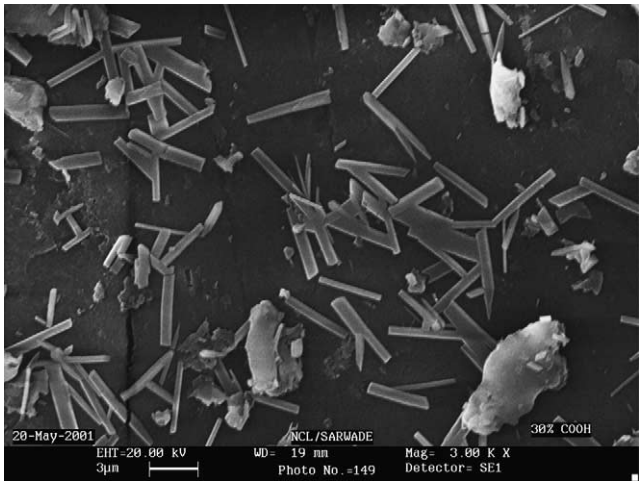

Fig. 5. SEM of 30% DAC at higher magnification.

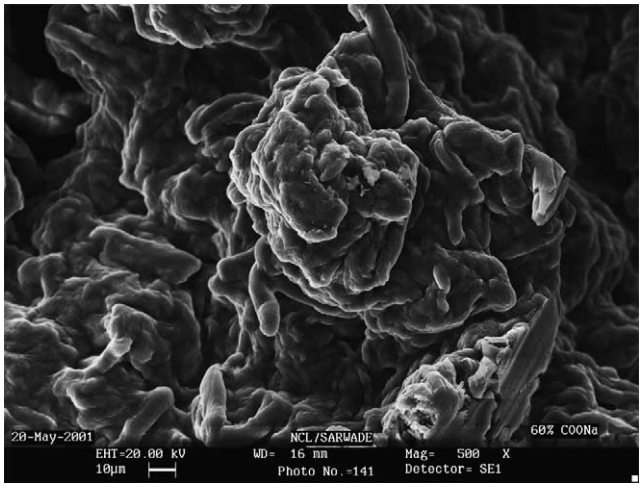

Fig. 6. SEM of 60% NaDCC.

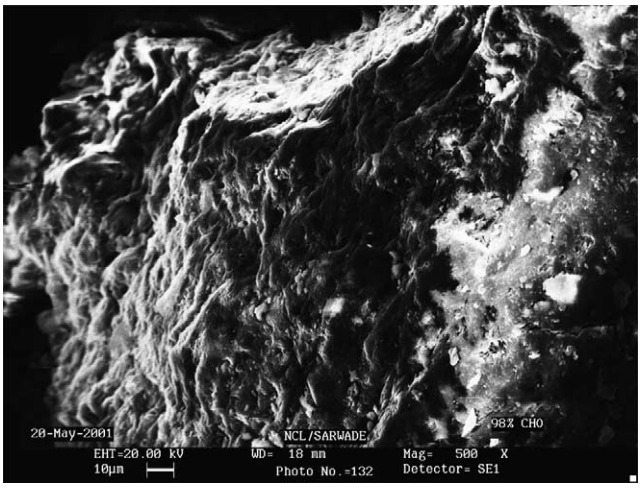

Fig. 9. SEM of 98% DAC.

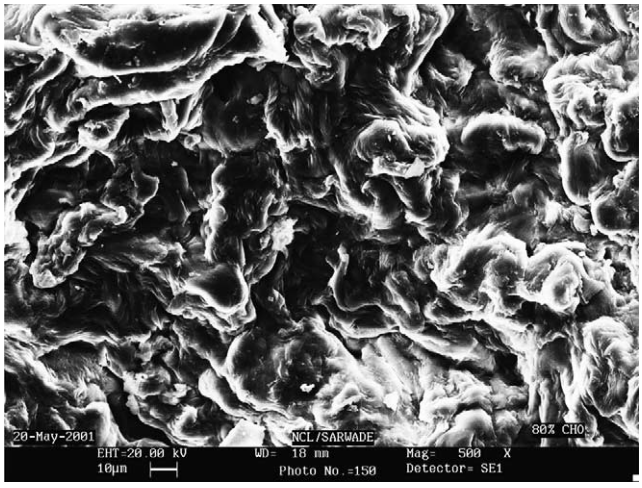

Fig. 7. SEM of 80% DAC.

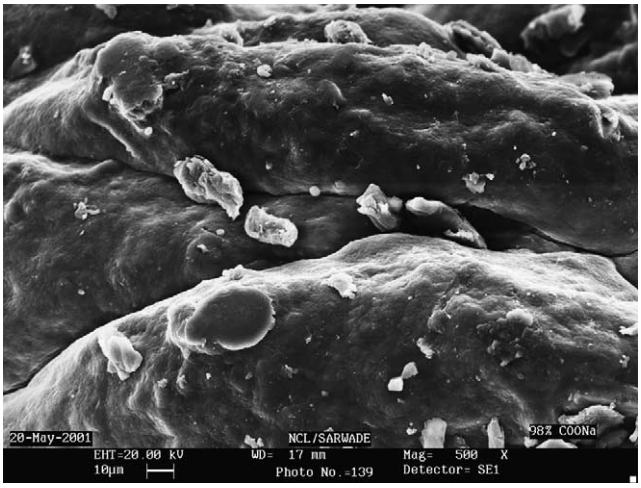

Fig. 10. SEM of 98% NaDCC.

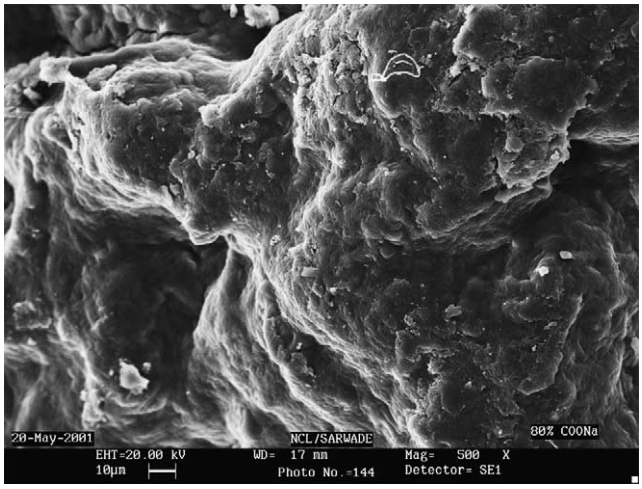

Fig. 8. SEM of 80% NaDCC.

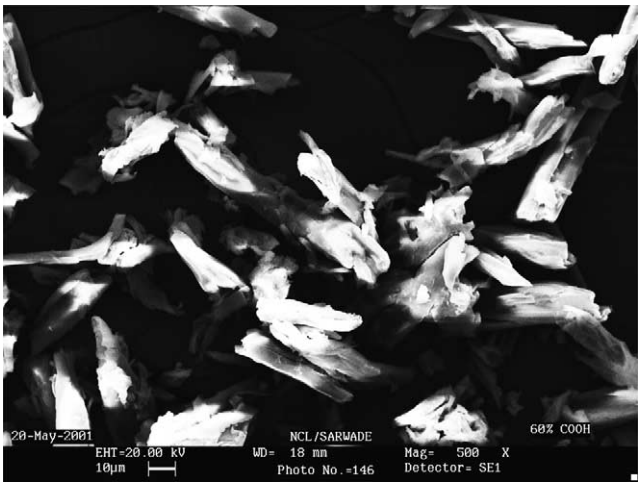

Fig. 11. SEM of 60% DCC.

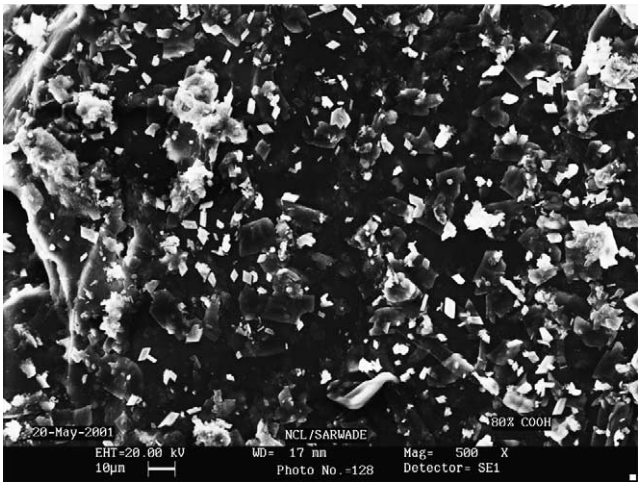

Fig. 12. SEM of 80% DCC.

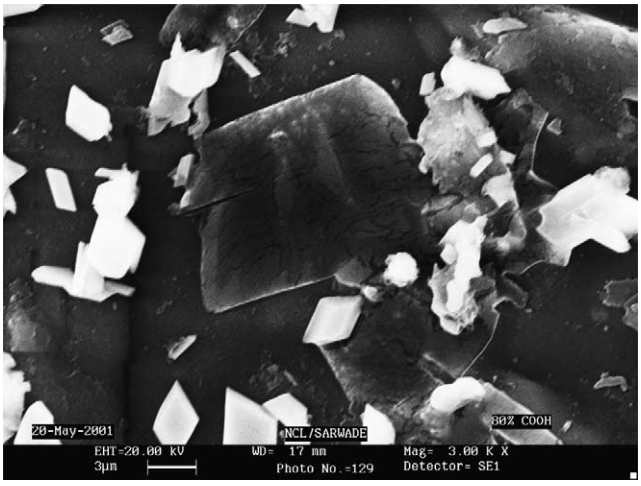

Fig. 13. SEM of 80% DCC at higher magnification.

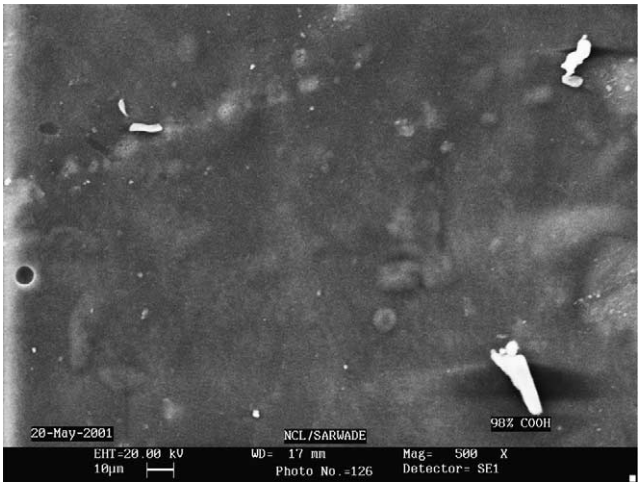

Fig. 14. SEM of 98% DCC.

Table 1
Wide angle X-ray diffraction (WAXRD) data for cellulose and oxidised celluloses (DAC, NaDCC, and DCC) (Varma & Chavan, 1995a,b)

Sample	Percent crystallinity $100\times$ crystalline peak height at $2\theta = 22.7°$/ peak height of cellulose at $2\theta = 22.7°$
Cellulose	100
30% DAC	80
60% DAC	37
80% DAC	23
98% DAC	17
30% NaDCC	53
60% NaDCC	39
80% NaDCC	16
98% NaDCC	6
30% DCC	59
60% DCC	43
98% DCC	14

shows that the crystalline form is retained. All these results are in agreement with the wide-angle X-ray diffraction (WAXRD) study reported earlier (Table 1) (Varma & Chavan, 1995a,b), wherein, starting with the assumption that the starting cellulose has 100% crystallinity, 30% DAC had a residual crystallinity of 80% and 30% NaDCC had a crytallinity of only 53% (ascribed to chain degradation) (Varma & Chavan 1995a,b). Thirty percent DCC had a crystallinity of 59%, nearly the same as 30% NaDCC, as expected.

Whether discrete crystalline fibres are visible in SEM for lower degrees of crystallinity than those seen in Figs. 1–5 seems to depend upon intermolecular H-bonding. Thus, for 60% NaDCC (Fig. 6), separate fibres are not seen, and the SEM appears that of 'wetted' fibres. The same is true for 80% DAC (Fig. 7), 80% NaDCC (Fig. 8), 98% DAC (Fig. 9), and 98% NaDCC (Fig. 10).

Surprisingly for the DCC, discrete fibres are seen in the SEM for all samples, i.e. 60% DCC (Fig. 11), 80% DCC (Figs. 12 and 13), and 98% DCC (Fig. 14), in spite of the fact that the WAXRD data in Table 1 shows these samples to have nearly the same crystallinity as the corresponding DAC and NaDCC samples. The surface effects seen in the SEM's are not apparent in the WAXRD studies and offer a new insight into the physical form of the oxidised cellulose samples under investigation. Thus SEM studies are important in obtaining a composite picture of the cellulose fibres under investigation.

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