Structural study of cellophane

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Fine structural aspects of cellophane have been investigated using X-ray and electron diffraction techniques as well as a kinetic study of the dissolution of cellophane in 0.5 M cupriethylene diamine solution. The X-ray diffraction pattern for cellophane shows a typical cellulose II structure while the electron diffraction pattern highlights a typical cellulose I structure with very weak reflection for a cellulose II type lattice. The kinetics study of cellophane dissolution in cupriethylene diamine confirms the presence of these polymorphic forms of cellulose in cellophane. The paper also reports studies of the X-ray and electron diffraction patterns of cellophane in relation to crystallite size and degradation under electron beam. It is shown that the observed anomaly between the X-ray and electron diffraction patterns of cellophane is a consequence of (i) the larger minimum crystallite size requirement for producing diffraction patterns with X-rays than with the electron beam (ii) the much faster degradation of cellulose II crystallites than that of cellulose I crystallites under the electron beam and (iii) the reduction in the crystallite size of cellulose II in cellophane from that in wood pulp alkali cellulose during the process of regeneration.

Keywords Cellophane; cellulose polymorphs; X-ray diffraction; electron diffraction; dissolution kinetics; degradation

INTRODUCTION

The structure of regenerated cellulose fibres has recently received a great deal of attention particularly with respect to the fine details of their structures under different conditions[1–14]. However, in contrast to the regenerated cellulose fibres, cellophane which is regenerated cellulose film, seems to have evoked conspicuously limited interest in respect of its fine structure. Similarity between the fine structure of cellophane and the core structure of rayon fibres of relatively high degree of lateral order was indicated by the results of dye accessibility studies in regenerated cellulose by Wellisch *et al.*[15] The cellulose II structure of cellophane, as in other regenerated celluloses[2], was revealed for the first time by X-ray diffraction (XRD) and recorded by Vankateswaran and Akkar[16] and Venkateswaran[17]. But in the context of the controversy[1,13] over the fine structural elements of regenerated cellulose fibres, one has also to consider the relevant question of the presence of cellulose I or cellulose IV as an extraneous lattice in cellophane. It was hoped that the electron diffraction (ED) technique, not employed as yet in studying cellophane, would throw more light on this question. In the present work detailed XRD and ED studies of cellophane and NaOH-treated cellophane have been combined with a kinetics study of their dissolution in cupriethylene diamine to achieve a more accurate structural characterization of cellophane in terms of cellulosic polymorphs, which could be of great technological importance.

EXPERIMENTAL

Materials

Wood pulp, alkali cellulose made from wood pulp and cellophane (20 μ thick) were obtained by the courtesy of Kesoram Rayon, Calcutta, India.

The wood pulp, purified and bleached, was in the form of sheets. The alkali cellulose was washed several times with distilled water to make it alkali free. The film was soaked in running water for 24 h to remove the plasticizer, followed by washing in distilled water and then dried.

A 0.5 M aqueous solution of cupriethylene diamine (cuene) was prepared according to the ASTM standard method of preparation[18].

Methods

Sodium hydroxide treatment. The cellophane films, under a slack condition, were treated with 18% NaOH solution for 24, 48 and 72 h. In the case of 48 and 72 h NaOH-treatment the cellophane samples were repeatedly treated with fresh NaOH solution every 24 h. The NaOH-treated samples were then successively washed for 10 min in running cold water, 1% acetic acid and distilled water.

ED and XRD studies. All the cellophane samples, treated and untreated, were thoroughly beaten in distilled water for 3 h using a laboratory blender. The temperature of the specimen during fragmentation was kept low with an ice bath. A portion of the slurry was then diluted with distilled water and a drop of this was placed on uncoated 400 mesh copper grid.

The ED pattern of a selected area of the specimen was recorded using a Hitachi Hu 11-E electron microscope, as

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described in earlier publications[19,20] at an accelerating voltage of 75 kV, extremely low beam current, and exposure time of 5 s. Liquid nitrogen was used throughout the experiment to cool the specimen.

The XRD studies were carried out using CuKα radiation with a Philips stabilized X-ray generator with diffractometer attachment. Radial X-ray diffractograms from these samples, randomized by fragmentation, were recorded on a strip chart recorder. The intensity data were then normalized after subtracting the background so that the areas under the intensity curves between the limiting ordinate of $2\theta = 5°$ and $2\theta = 32°$ were the same for all the samples.

Crystallite size. The sizes of the crystallites perpendicular to the 101 plane were obtained from the analysis of the equatorial X-ray reflection following an established procedure[21,22]. The half intensity width was determined in each case and corrected for instrumental broadening. Crystallite size (L) was obtained by using the Scherrer equation[22],

$$L = \frac{k\lambda}{\beta \cos\theta}$$

where k is taken as 0.9, $\lambda = 1.542$ Å for CuKα line, θ = Bragg's angle and β = angular width in radians corresponding to the half intensity width in the diffractogram.

Kinetics study of cuene dissolution. Pre-dried and pre-weighed cellophane films cut into 3 cm × 3 cm sizes were immersed in the 0.5 M cuene solution at 30°C, the material liquor ratio being 1:200, and after 4 s the whole beaker with solution was quickly plunged into 5 litres of water to halt the dissolution. The solution was filtered immediately through a pre-weighed Gl sintered glass crucible. The residue was washed several times with water and finally treated with ethylene diamine for 10 min until all the blue colour disappeared. An excess of 1 N H_2SO_4 was then added and the solution was filtered through the same sintered glass crucible. The residue was then washed several times with hot water and finally with distilled water. It was then dried at 105°C for 4 h and weighed. The above experiment was repeated with identical samples of cellophane for 8 s, 10 s, 15 s, etc. A graph was plotted with time against percentage dissolution. Similarly, experiments were also carried out with the 24 h, 48 h and 72 h NaOH-treated samples.

Degradation in the electron beam. The ED patterns of cotton cellulose I and II were observed on the fluorescent screen and the time taken for disappearance of the patterns due to degradation in the electron beam was noted using a stop watch. The average time taken for degradation was obtained on the basis of observations made on 25 ED patterns, for both cellulose I and II.

RESULTS AND DISCUSSION

ED and XRD patterns of cellophane

Figure 1a is the microdensitometer equatorial scan of the ED pattern of fragmented cellophane. The scan consists of mainly three peaks, viz., the 101, $10\bar{1}$ and 002 peaks of cellulose I crystal lattice with $d = 5.91$ Å, 5.38 Å, and 4.00 Å respectively. In addition, two peaks with $d = 7.24$ Å and 4.33 Å are also present but with a very much reduced intensity. These correspond to the 101 and $10\bar{1}$ reflections of the cellulose II crystal lattice. It is important to mention that the ED scan in *Figure 1a* provides perhaps the first direct evidence that cellulose I persists in cellophane. In this context, it is relevant to recall the conclusion of Manjunath and Peacock[13], arrived at indirectly from XRD studies, that the extraneous lattice in viscous rayon may be cellulose I and not cellulose IV.

The ED observations are contradictory to the results of our and earlier[16,17] XRD studies of cellophane. *Figure 1b* is the normalized radial XRD profile of fragmented cellophane. The diffraction peaks due to the 101, $10\bar{1}$ and 002 reflections are those typical of a cellulose II structure. It may be pointed out that earlier workers were not able to resolve the $10\bar{1}$ and 002 peaks because of persisting orientation effects in the specimen, which are removed in the present work by fragmentation.

The observed anomaly between ED and XRD studies was investigated with respect to the fine structure of cellophane in two ways. Firstly, confirmation of the presence of cellulose I in cellophane was made by an independent method, viz., a kinetics study of the dissolution of cellophane in cuene. Secondly, an investigation was made into the cause of the appearance of cellulose I and the virtual disappearance of cellulose II in the ED pattern of cellophane by detailed ED and XRD studies of wood pulp, alkali cellulose and NaOH-treated cellophane. The results are presented in the subsequent sub-sections.

Kinetics study of dissolution of cellophane in cuene

It can be seen from *Figure 2* that the dissolution curve for the control falls into three distinct parts, part A

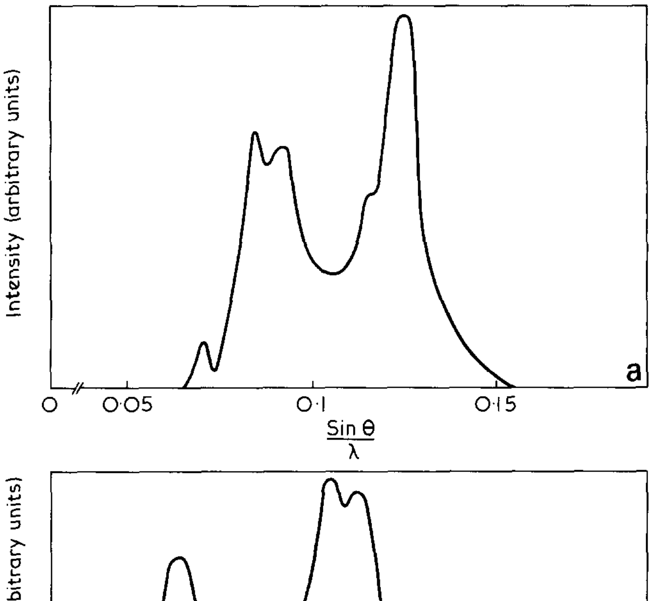

Figure 1 (a) Intensity tracing along the equator of the ED pattern of cellophane; and (b) normalized radial XRD profile of cellophane fragments

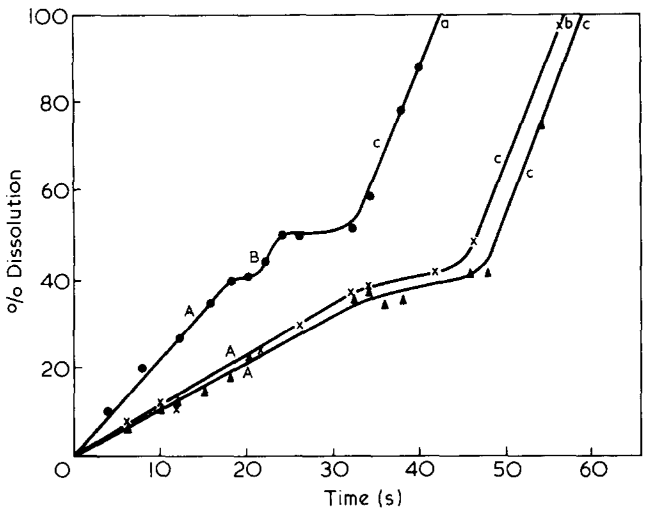

Figure 2 Dissolution curves of cellophane in cuene: (a) control, (b) 48 h NaOH-treated, and (c) 72 h NaOH-treated

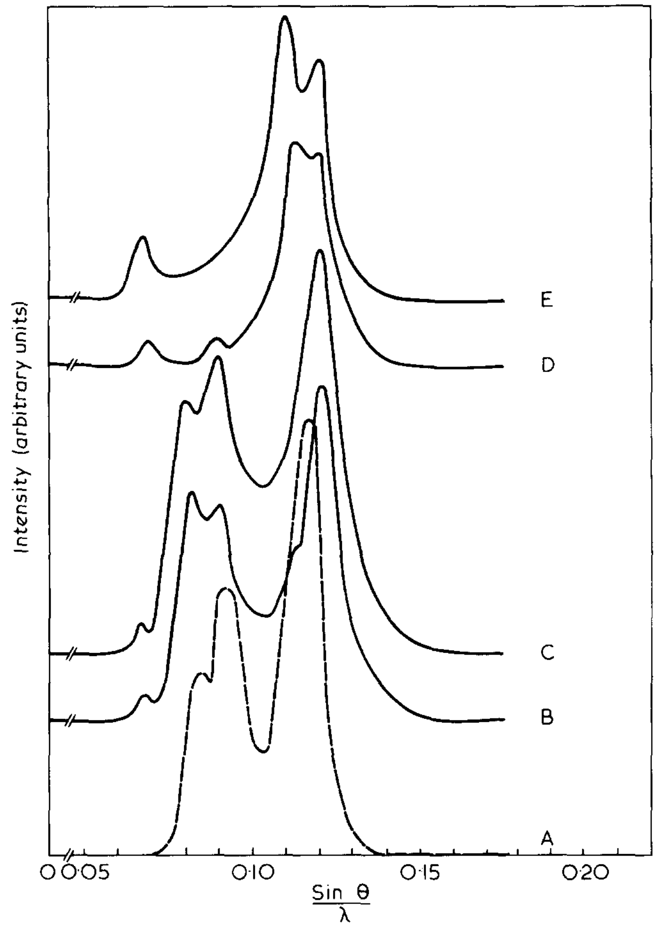

Figure 3 Intensity tracings along the equator of the ED patterns of: (A) wood pulp, (B) cellophane, (C) 48 h NaOH-treated cellophane, (D) 72 h NaOH-treated cellophane, and (E) alkali cellulose

representing the initial straight portion of the plot, part B having an initial nearly horizontal portion followed by a change of slope to the onset of the next nearly horizontal portion and part C consisting of this nearly horizontal portion followed by a change of slope. We find that the masses dissolved in part A, B and C represent approximately 40%, 10% and 50% of the total mass of the film respectively. Considering that the amorphous mass would dissolve first[23-26] and also that cellulose II is known to be more resistant to cuene than cellulose I, we attribute part A to the penetration-cum-dissolution of the amorphous mass and part B, to that of cellulose I and the remaining part C, to that of cellulose II. Thus, the dissolution curve for the control confirms the presence of cellulose I in cellophane, first detected by ED study, and the presence of cellulose II as the predominant crystalline component, in accordance with the XRD results.

The percentage dissolution vs. time plots for both the 48 h and 72 h NaOH-treated film are seen to differ from that for the control in three respects: (i) in the much lower initial rate of dissolution, (ii) in the almost complete disappearance of part B and (iii) in the longer time required for starting the dissolution of the material corresponding to part C and for completing it. One may attribute observation (i) to the filling-up of voids and pores, brought about by shrinkage, and to the larger crystallite size obtained in treated samples. When cellophane was treated with NaOH, most of the cellulose I present might have been converted to cellulose II and this explains observation (ii). Observation (iii) may be the result of an increase in crystallite size produced by NaOH-treatment.

ED and XRD studies of wood pulp and wood pulp alkali cellulose

Typical microdensitometer equatorial scans of ED patterns of wood pulp—the starting material in the manufacture of cellophane, and alkali cellulose—an intermediate product, are shown in *Figures 3A* and *3E*. The former shows a typical cellulose I structure and the latter shows a typical cellulose II structure. It can be seen from *Figure 4* that the same structures are also shown by the

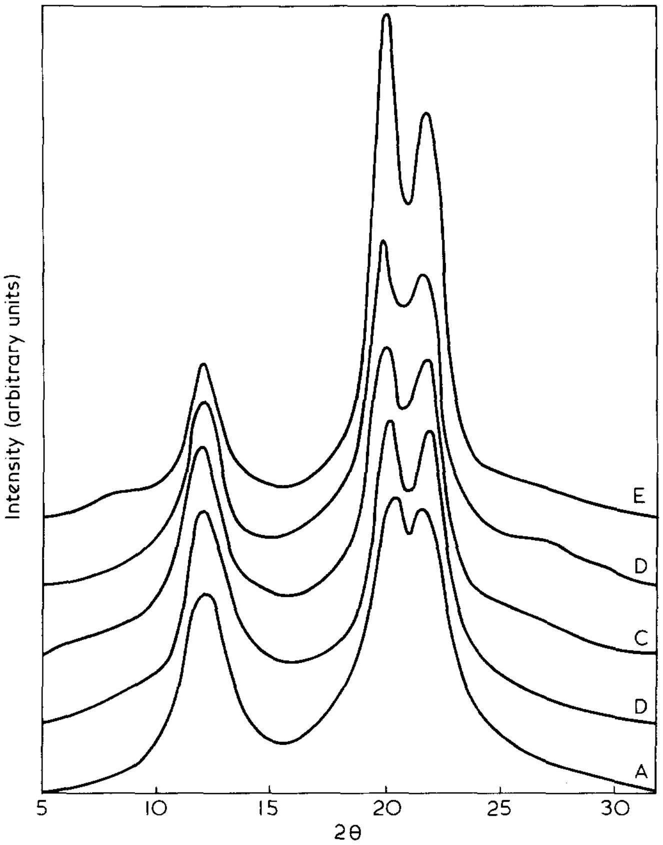

Figure 4 Normalized radial XRD profiles of: (A) cellophane, (B) 24 h NaOH-treated cellophane, (C) 48 h NaOH-treated cellophane, (D) 72 h NaOH-treated cellophane and (E) alkali cellulose

XRD patterns of wood pulp and alkali cellulose. Thus the alkali cellulose does not show any cellulose I in its ED and XRD patterns. But as we have seen before from the ED scans of cellophane (*Figure 1a*), the final product shows an apparently predominant cellulose I structure, while a typical cellulose II structure is indicated by its XRD patterns (*Figure 1b*). This apparent anomaly might have arisen from the finer structural changes that occurred during the regeneration of cellulose, viz., those after the formation of sodium cellulose xanthate and its subsequent dissolution in 4% NaOH solution. The alkali cellulose obtained after NaOH-treatment of wood pulp seems to still contain some cellulose I seeds as a sort of 'nuclei' in the core of the microfibrils, which possibly grow during further processing and thereby are detected in the ED patterns. The reason why the cellulose I structure detected by ED patterns of cellophane is not revealed by the XRD study seems to be two fold: (i) the minimum size requirement for producing XRD peaks could not be met frequently in the cellulose I crystallite size distribution in cellophane and (ii) the crystallites satisfying the minimum size requirement, because of the very small quantity of matter involved, produced very weak diffraction peaks which got submerged in the amorphous background. The weak appearance of cellulose II in the ED pattern of cellophane in contrast to its predominant presence in the ED pattern of wood pulp alkali cellulose calls for an investigation of cellulose II crystallite size in both cases, and this will be discussed later.

ED study of NaOH-treated cellophane

In further investigations the ED patterns of 24, 48 and 72 h NaOH-treated cellophane were taken. The scan of the ED pattern of the 24 h NaOH-treated sample is not shown as it is identical to that of the 48 h NaOH-treated sample (*Figure 3C*), showing cellulose I predominantly in a mixture of cellulose I and cellulose II. Scans of most of the ED patterns of the 72 h NaOH-treated cellophane samples showed a predominantly cellulose I structure as in the case of the 48 h NaOH-treated sample. In this context, it should be noted that, unlike the ED patterns, the corresponding dissolution curves (*Figure 2*) do not show, within the limit of experimental accuracy, the presence of cellulose I. This might possibly indicate that in cellophane some cellulose II crystallites might have grown during the regeneration process with cellulose I crystallite cores. These cellulose I cores remained unconverted during the NaOH treatment. Before the cuene dissolution of the cellulose II envelope had been completed, the cellulose I core could be reached and attacked by cuene and remained undetected in the dissolution curve.

However, some ED scans of the 72 h NaOH-treated samples showed typical cellulose II structure with the presence of very little cellulose I (*Figure 3D*). This might be the result of a situation in which after the NaOH treatment, some of the cellulose II crystallite could stand the degrading effect of the electron beam. It is relevant to investigate whether this phenomenon has any correlation with the effect of NaOH-treatment on cellulose II crystallite size. In view of these and previous results, we undertook an XRD study of the change in cellulose II crystallite size brought about by the industrial processing of wood pulp alkali cellulose and NaOH-treatment of cellophane. The results of this study are discussed below.

Cellulose II crystallite size in alkali cellulose, untreated and NaOH-treated cellophane

The cellulose II crystallite dimensions perpendicular to the 101 plane were determined and found to be 48.4 Å in alkali cellulose and 38.1 Å in cellophane. The observed reduction in cellulose II crystallite size in cellophane occurred during the processing of alkali cellulose in the manufacture of the cellophane. This reduced size might have been too small to produce an ED pattern under the degradational effect of the electron beam.

The normalized radial XRD profiles of fibrillar fragments of the 24, 48 and 72 h NaOH-treated cellophane are shown in *Figure 4*. The cellulose II crystallite dimensions perpendicular to the 101 plane in each case, were found to be 38.9 Å, 42.1 Å and 47 Å respectively. The increase in cellulose II crystallite size with the increase in the duration of NaOH-treatment is shown in *Figure 5*. Similar observations were made by earlier workers in the case of cotton cellulose[27]. We, therefore, correlate the appearance, though still not frequent, of cellulose II ED patterns in the 72 h NaOH-treated cellophane with the increase of cellulose II crystallite size brought about by NaOH-treatment. Compared to wood pulp alkali cellulose the appearance of these ED patterns was still infrequent and this may be attributed to the fact that the average cellulose II crystallite size attained by 72 h NaOH-treatment was still below the average cellulose II crystallite size in wood pulp alkali cellulose.

Degradation under electron beam

Finally, we are confronted with the question: why cannot cellulose II crystallites in cellophane and NaOH-treated cellophane, big enough to enable the recording of XRD patterns, produce an easily observable ED pattern, while cellulose I crystallites in cellophane, though too small for XRD patterns, can do so? This question focusses our attention on the degradation of cellulosic materials under the electron beam.

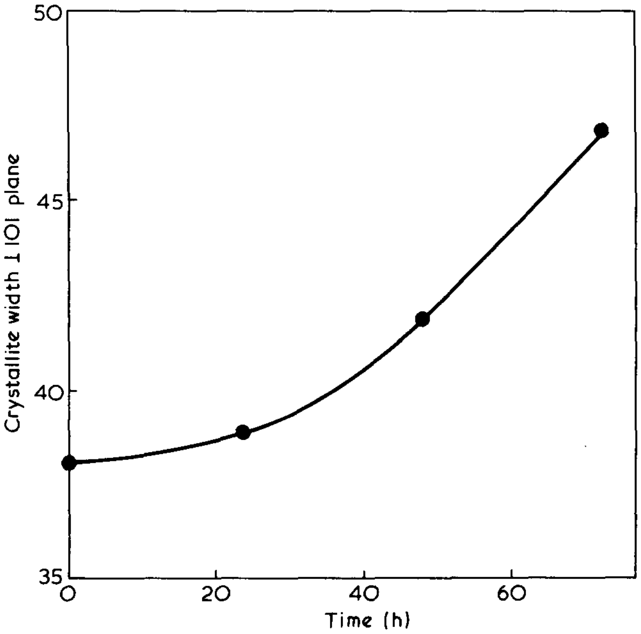

Figure 5 Effect of NaOH-treatment on the crystallite width ⊥ to 101 plane of cellophane cellulose II

In cellulosic materials the actual minimum crystallite size of a certain polymorphic form required to produce an observable ED pattern is governed by the rate of its degradation under an electron beam. We investigated the possibility that a preferentially drastic degradation of cellulose II compared with cellulose I might occur in cellophane under the electron beam. If so, the actual minimum crystallite size required for observing an ED pattern of cellulose II in cellophane before fading due to degradation might be larger than for cellulose I and seldom met in cellophane. Since cellulose II ED patterns do not usually appear, this investigation was carried out mostly with cotton cellulose I and II.

Thrice mercerized cotton cellulose after confirmation by XRD to be pure cellulose II, was used in the present study. The initial cellulose II crystallite size in the samples, viz., 50 Å perpendicular to the 101 plane, was reduced to 42 Å by treatment with 0.5 M cuene for a period of 50 s. It was observed that the ED patterns of these cuene-treated cellulose II samples disappeared faster than those of the untreated cellulose II samples. This indicates that the smaller the size of cellulose II crystallites, the less their stability in the electron beam, and the more difficult the recording of their ED patterns.

But it is important to note that crystallite size is not the only factor governing crystallite degradation under the electron beam. The cuene-treated cotton cellulose II samples mentioned above and the 48 h NaOH-treated cellophane have both cellulose II crystallites of almost the same size, viz., 42 Å and 42.1 Å respectively, perpendicular to the 101 plane, but the cellulose II crystallites in cellophane are found to be prone to faster degradation under the electron beam than in cotton cellulose II and it was more difficult to record the ED pattern. We also made a comparative study of the critical degradation time for cotton cellulose I and cellulose II crystallites under the electron beam. It was found that in the case of cotton cellulose I crystallites the critical degradation time was 50 s whereas in the case of cotton cellulose II crystallites it was 15 s. It is known that cotton cellulose II crystallites are slightly smaller than cotton cellulose I crystallites[21], which, from the point of view of size, fails to explain the ratio 1:3.3 between the critical degradation times in both cases. This leads to the conclusion that cotton cellulose II crystallites are more unstable in the electron beam than the cotton cellulose I crystallites. This conclusion is in agreement with the finding of Dobb and Murray[28] and it is important to recall, as we have seen before, that the degradation of cellulose II crystallites under the electron beam is much faster in cellophane than in cotton cellulose.

All these results together bring out the very significant role played by degradation under the electron beam in showing off cellulose I as the predominant polymorphic form compared with cellulose II in cellophane ED patterns. Due to the much faster degradation of cellulose II crystallites *vis-a-vis* cellulose I crystallites in cellophane under the electron beam the cellulose II crystallite size is preferentially reduced during exposure time so much so that the true minimum crystallite size requirement for ED pattern, if there were no degradation, is not satisfied and as a result no ED pattern is usually obtained except for very large initial crystallite sizes. Comparatively the degradation being much slower in cellulose I, its effect on ED pattern is far from drastic.

CONCLUSION

In conclusion, it may be said that the present work has been able to provide a somewhat fuller structural picture of the crystalline domains of cellophane. It seems to be now firmly established that cellophane is not entirely cellulose II as it is known so far as crystalline domains are concerned but a sizeable part of it belongs to cellulose I. This results is of great significance in view of the controversy over the extraneous lattice in regenerated cellulose fibres. The glaring anomaly observed in the present work in respect of the contradictory XRD and ED patterns of cellophane points to the risks of making conclusions regarding fine structures of cellulosic materials based on information from XRD or ED patterns alone and to the need for an independent corroborative method. The importance of the method of kinetics study of cuene dissolution in this connection is highlighted by the present work. The investigations of the anomalous XRD and ED patterns of cellophane have brought out the roles of both the minimum crystallite size requirement for producing XRD and ED patterns and relative degradation rates of the polymorphic components in cellulosic materials under the electron beam in showing off certain polymorphic components more than others.

Regarding the origin of cellulose I in cellophane, one has to envisage, on the basis of observed facts reported in this work, the presence of cellulose I seeds as a sort of 'nuclei' in the alkali cellulose obtained by conversion from wood pulp. These are too small in size for even an ED pattern. The growth of these cellulose I seeds during the regeneration process to cellulose I crystallites, big enough for an ED pattern, seems to be an inescapable conclusion in view of the observed facts. The same was virtually implied in suggestions[13] made earlier on indirect evidence. The understanding of the exact mechanism of this growth process requires further investigation.

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