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Recrystallization of Amorphous Cellulose

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Synopsis

Recrystallization of amorphous cellulose prepared by saponification of cellulose triacetate in an non-aqueous medium was found to occur only at very high relative humidities, i.e., near 100%. At lower relative humidities the amount of recrystallization occurring was slight though significant. Correspondingly, the accessibility decreased from 90% (for amorphous cellulose) to a minimum of 79%, the same as that for cellulose II. The mechanism of recrystallization is discussed in terms of the surface tension, plasticizing action, and the hydrogen bonding ability of the solvent used for bringing about the recrystallization.

It is well known that cellulose can be obtained in an amorphous form by grinding in a vibratory ball mill[1,2] or by saponification of cellulose acetate in a nonaqueous medium.[3] On immersion in water this amorphous cellulose crystallizes to cellulose II.[4] However, little attention has been paid to the details of the crystallization process.

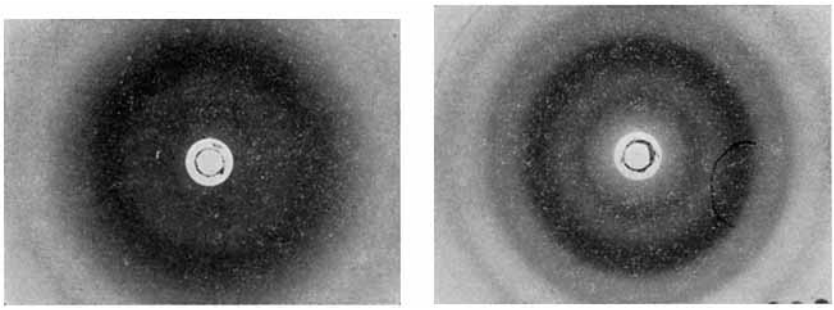
The present note describes an attempt to study more elaborately the recrystallization of cellulose by the use of the hydrogen exchange reaction between cellulose hydroxyl hydrogens and water and by x-ray diffraction.

The amorphous cellulose used was obtained by treating cellulose triacetate sheets with 1% sodium methylate dissolved in anhydrous methanol. The saponification was allowed to proceed for about 12 hr. The regenerated cellulose thus obtained was neutralized with glacial acetic acid and washed with various alcohols until free of acetic acid. As a control, one sample was also washed in H_2O. Subsequently the samples were dried in a vacuum desiccator. The following alcohols were used: anhydrous methanol, ethanol, propanol, *n*-butanol, and isobutanol.

In another series of experiments, amorphous cellulose was exposed to water vapor at different relative humidities obtained through the use of various saturated salt solutions.[5]

The accessibility of all samples was measured by the tritium exchange method.[6]

Kinetic studies of the recrystallization of amorphous cellulose were carried out by an x-ray diffraction method by using a Geiger counter diffractometer. The rate of development of the $10\bar{1}$ and 002 peaks was observed at various relative humidities.



a *b*

Fig. 1. X-ray diffraction diagrams of amorphous cellulose dried from: (*a*) methanol; (*b*) water.

The x-ray diffraction patterns were obtained in a flat-film camera using nickel-filtered CuKα radiation.

The accessibility of amorphous cellulose after treatment with water and various alcohols is presented in Table I. Representative examples of the corresponding x-ray diffraction patterns are shown in Figure 1. It is seen that all alcohol-treated samples show the same accessibility, i.e., 90%, whereas the water-treated sample has the significantly lower accessibility of 79%. This is consistent with the results of the x-ray diffraction experiments. For amorphous cellulose treated with alcohols the pattern is dominated by a single broad diffuse halo in all cases. This indicates that alcohols do not cause recrystallization of the cellulose. On the other hand, the x-ray pattern of the water-treated sample is well defined and corresponds to the structure of cellulose II.

In order for the amorphous cellulose to crystallize, intermolecular forces must come into play. The amount of recrystallization will depend upon the extent to which the treatment permits the development of these intermolecular forces. Since the intermolecular forces in cellulose arise almost exclusively from hydrogen bonding,[7] it is expected that the hydrogen-bonding capacity of the liquid will play an important role in the recrystallization process. The liquid plasticizes cellulose, permitting it to assume favorable orientations for hydrogen bonding.

TABLE I
Accessibility of Amorphous Cellulose Dried from Various Liquids

Saponified cellulose triacetate dried from:	Accessibility (at 50% R.H.), %
Methanol	91
Ethanol	90
Propanol	89
n-Butanol	89
Isobutanol	89
Water	79

TABLE II
Accessibility of Amorphous Cellulose at Various Relative Humidities

Relative humidity, %	Accessibility (at 50% R.H.), %
100	79
75	81
50	84
20	85
10	88
0	89

Surface tension forces operating between cellulose surfaces during the final stages of drying would also be expected to play a role in the recrystallization.

Thus the effectiveness of water as compared to the alcohols in promoting the recrystallization of amorphous cellulose would be related to its high surface tension and hydrogen-bonding capacity. For the alcohols, both of these properties are lower.

The recrystallization of amorphous cellulose also occurs on exposure to water vapor at high relative humidity. This can be seen in Table II, which shows the accessibility of amorphous cellulose as a function of relative humidity. The accessibility decreases from 89 to 79% as the relative humidity is increased from 0 to 100%. At the lower relative humidities the process of recrystallization was extremely slow. For example, after an exposure time as long as 30 days at 75% R.H. and 25°C., only a very slight amount of recrystallization could be detected in the x-ray diffraction pattern.

However, at 100% R.H., recrystallization occurred in a comparatively short time. This effect is illustrated by the data in Figure 2, which shows a plot of the intensity of the $10\bar{1}$ peak against time of exposure for amorphous cellulose at 100% R.H. and a temperature of 25°C. It is seen that under these conditions the amorphous cellulose crystallizes quite rapidly initially and in about 4 hr. reaches an asymptotic value after which further exposure produces only a very slight change. Similar experiments were also carried out at temperatures of 50 and 100°C. In both cases, the results were

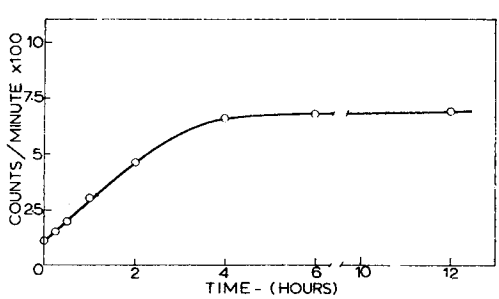


Fig. 2. Plot of intensity of the $10\bar{1}$ peak against time of exposure for amorphous cellulose at 100% R.H. and 25°C.

similar to those obtained at 25°C. Thus within this range temperature has no effect on the recrystallization. Unfortunately, such measurements could not be made above 100°C., as another modification of cellulose (i.e., cellulose IV) was then formed.

Finally, it is interesting to note that the accessibility of amorphous cellulose is not 100%. The possibility that this might have been caused by a small amount of recrystallization during the accessibility measurement will be considered elsewhere.

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Résumé

La recristallisation de la cellulose amorphe préparée par saponification du triacétate de cellulose en milieu non-aqueux a lieu uniquement à des taux d'humidité relative très élevés, situés aux environs de 100%. À des taux d'humidité relative plus faibles, la quantité de recristallisation ayant lieu est faible quoique significative. Parallèlement, la possibilité d'obtention diminue depuis 90% (pour la cellulose amorphe) jusqu'à un minimum de 79%, le même que celui pour la cellulose II. Le mécanisme de recristallisation est discuté sur la base de la tension superficielle, de l'action plastifiante et de l'aptitude du solvant à former une liaison hydrogène, utilisée pour entraîner la recristallisation.

Zusammenfassung

Rekristallisation von amorpher, durch Verseifung von Zellulosetriacetat in einem nichtwässrigen Medium dargestellter Zellulose findet nur bei sehr hoher relativer Feuchtigkeit, d.h. nahe 100% statt. Bei niedrigerer relativer Feuchtigkeit war der Betrag an Rekristallisation war gering, aber signifikant. Entsprechend nahm die Angreifbarkeit von 90% (für amorphe Zellulose) auf ein Minimum von 79%, dem gleichen wie für Zellulose II, ab. Der Rekristallisationsmechanismus wird in bezug auf Oberflächenspannung, Weichmacherwirkung und Wasserstoffbindungsfähigkeit des zur Erreichung der Rekristallisation verwendeten Lösungsmittels diskutiert.

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