DSC Study on Recrystallization of Amorphous Cellulose with Water

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Synopsis

The recrystallization of amorphous cellulose at various relative humidities was studied to clarify the relation between the amount of adsorbed water in cellulose and the molecular motion by the DSC method. The initial recrystallization kinetics of amorphous cellulose at various relative humidities were observed on the basis of the exothermic peak between 380° and 470°K in a DSC curve. The recrystallization occurred easily by conditioning at higher than 80% R.H., but hardly by conditioning at lower than 65% R.H. These facts suggest that the conformation of cellulose seems to be easily changeable if cellulose has a moisture regain which is approximately comparable to capillary water. When the Avrami equation was applied to the slope of calorific value versus conditioning time at higher than 80% R.H., it also appeared that the mode of recrystallization growth of amorphous cellulose exposed to water vapor is one-dimensional.

INTRODUCTION

There are a number of studies on adsorbed water in cellulose.[1] Although it has long been known that one of the physical changes of cellulose is the swelling caused by adsorbed water, the complexity of noncrystalline structure in cellulose has prevented detailed investigations. By the use of broad-line NMR, the authors[2] have partly clarified the influence of absorbed water responsible for the molecular motion of cellulose.

The fact[3–5] that amorphous cellulose recrystallizes with water or moisture suggest that the molecular motion of cellulose by adsorbed water becomes active enough to change the main-chain conformation. As a result of swelling, the degree of freedom for molecular motion increases and the intra- and intermolecular forces decrease markedly with the cleavage of hydrogen bonding. Sobue and Fukuhara[3] have also estimated that the recrystallization of amorphous cellulose with water is due to the micro-Brownian motion. The relation between molecular motion and adsorbed water might be partially clarified if the recrystallization process of amorphous cellulose with water or moisture could be observed.

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Based on the modern concept of the interaction between cellulose and adsorbed water, the various states of moisture adsorption may be classified as follows: monolayer water, multilayers water, and capillary water. These water adsorption states correspond to the adsorption isotherms of cellulose plotted against moisture. The changes of molecular motion and physical properties of cellulose which are influenced by adsorbed water are not continuous with moisture regain, but must be determined stepwise for each adsorbed state. From the results[2,6] that water adsorbed to a certain extent by cellulose lowers the glass transition temperature to room temperature, the recrystallization of cellulose may be assumed to also occur on exposure to water vapor at an appropriate relative humidity instead of immersion in water. Hatakeyama and Kanetsuna[7] discovered a large exothermic peak of amorphous cellulose at 380°–470°K in a DSC (differential scanning calorimeter) curve. The authors assume that this exothermic peak is an indication of crystallinity. In order to detect the initial stage of the crystallization, this DSC method seems to be superior to the other methods such as x-ray diffraction patterns, infrared absorption spectra, specific volume, etc. which have been generally used to measure the crystallinity of high polymer.

The purpose of this paper is to clarify by the DSC method how adsorbed water influences the molecular motion of cellulose which is conditioned at various relative humidities.

EXPERIMENTAL

Preparation of Amorphous Cellulose

Amorphous cellulose was prepared by treating cellulose triacetate sheets with 1% sodium ethylate dissolved in anhydrous ethanol. The saponification was allowed to proceed for two days at room temperature. The regenerated cellulose thus obtained was washed repeatedly with anhydrous ethanol and dried in vacuo at 10^{-2} mm Hg over phosphorous pentoxide.

Conditioning of Amorphous Cellulose

The samples were placed for a given period of time at 20°C in desiccators adjusted to a constant relative humidity of 20, 44, 52, 65, 80, 90, and 100% by the use of saturated salt solution or aqueous solution of sulfuric acid. The sample after conditioning was washed repeatedly with anhydrous ethanol to eliminate the effect of surface tension force in the drying process[4] and dried in vacuo at 10^{-2} mm Hg over phosphorous pentoxide.

Equipment

The DSC apparatus was a Perkin-Elmer DSC 1B type. The sample, 7–10 mg, was analyzed by increasing the temperature at a rate of 16°C/min in a stream of nitrogen.

RESULTS AND DISCUSSION

Amorphous cellulose prepared by the saponification of cellulose triacetate was proved to be completely amorphous by measurement of wide-angle x-ray diffraction diagrams.

A DSC curve of amorphous cellulose had a large exothermic peak between 380° and 470°K, as shown in Figure 1, and pronounced pyrolysis was observed at about 480°K. A large exothermic peak, however, was not observed in a DSC curve measured after cooling from 470°K to room temperature. This indicates that the exothermic reaction of amorphous cellulose is irreversible. Hatakeyama et al.[7,8] assumed that this exothermic peak could be assigned to the formation of hydrogen bonding between free hydroxyl groups which were regenerated by the saponification of cellulose triacetate. In a case of linter cellulose, the baseline changes slowly toward the endothermic side above 370°K and continues to the pyrolysis. As shown in Figure 1, the DSC curve of amorphous cellulose after cooling from 470°K to room temperature is similar to that of linter cellulose.

Figure 2 shows the DSC curves of amorphous cellulose which was heat treated at 416°K for 0.5–25 min and then cooled to room temperature. The exothermic peak was diminished by heat treatment and vanished finally. The peak area decreased with increasing heating time and the temperature of the peak shifted to somewhat higher temperature. As mentioned previously by Hatakeyama and Kanetsuna,[7] the area of exothermic peak corresponds to the amounts of free hydroxyl groups in amorphous cellulose. These results suggest that the formation of hydrogen bonding accompanied by the exothermic reaction may restrict the molecular motion. Thus, cellulose may be changed from an original state into a more stable one by increasing the time of heating. A plot of calorific value calculated from Figure 2 against heating time is shown in Figure 3. Heat treatment for about 18 min at 416°K extinguished completely the exothermic peak.
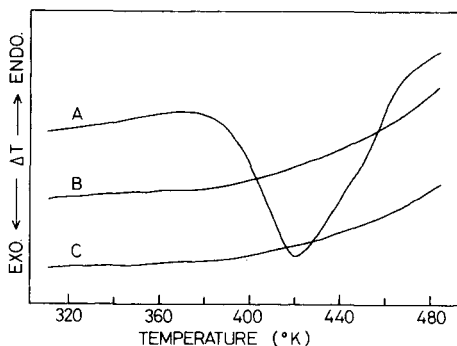

Fig. 1. DSC curves of cellulose: (A) amorphous cellulose; (B) amorphous cellulose (scanning after cooling curve A from 470°K to room temperature); (C) linter cellulose.
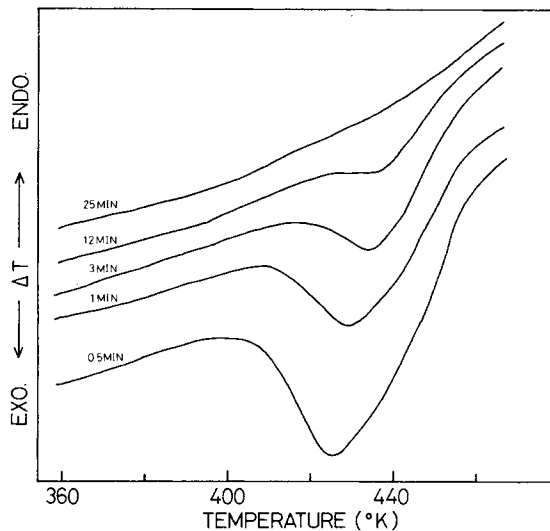
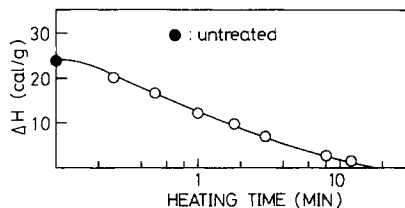Fig. 2. Exothermic peaks of amorphous cellulose treated at 416°K.

Fig. 3. Calorific value vs. heating time of amorphous cellulose treated at 416°K.

It is well known that amorphous cellulose recrystallizes to cellulose II by immersion in water. Wadehra and Manley[4] have shown that the accessibility of cellulose decreases from 89% to 79% with increasing relative humidity from 0% to 100%. In our investigation, the exothermic peak area of amorphous cellulose was also diminished by treatment at an appropriate relative humidity. When amorphous cellulose was conditioned at each relative humidity, the exothermic peak separated into two peaks with increased conditioning time, though only one peak in the case of heat treatment was observed.

Figures 4 and 5 show DSC curves of the samples conditioned at 65% and 80% R.H., respectively. As the relative humidity becomes higher, the area of exothermic peak decreases promptly and the standing time required to separate into two peaks becomes shorter. Such a tendency is very significant at higher than 80% R.H. DSC curves of the samples conditioned at 90% and 100% R.H. were also similar to that at 80% R.H. Here, the initial temperature of the exothermic curve is designated as T_i, the first (lower) peak temperature is as T_{p1}, the second (higher) peak temperature is T_{p2}, and the terminal temperature of the exothermic curve is as T_t. As shown in Figure 5, T_{p2} and T_t shift to the higher temperature side by
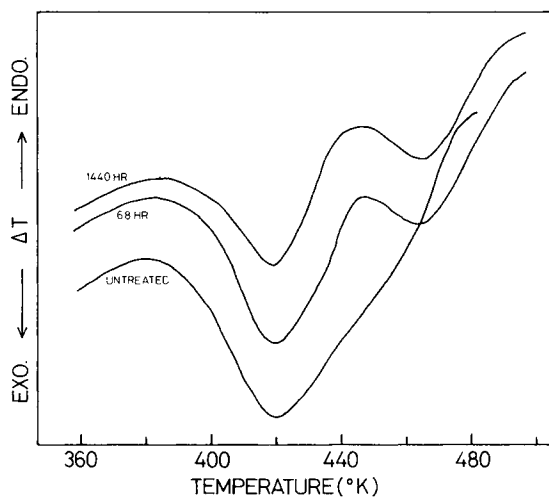
Fig. 4. DSC curves of amorphous cellulose treated at 65% R.H.
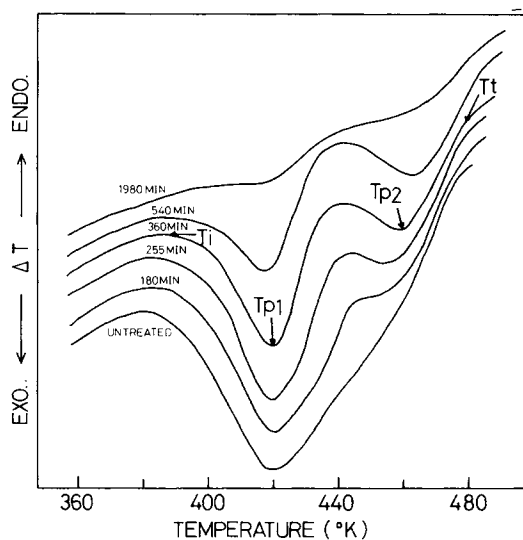

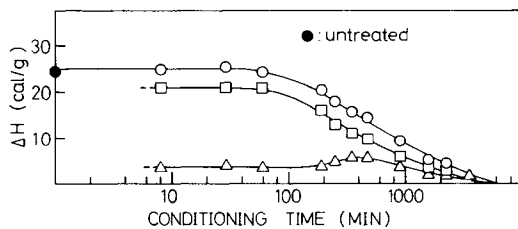Fig. 5. DSC curves of amorphous cellulose treated at 80% R.H.

Fig. 6. Plot of calorific value vs. conditioning time of amorphous cellulose at 80% R.H. and 20°C: (O—O) total calorific value; (□—□) calorific value calculated from first exothermic peak; (△—△) calorific value calculated from second exothermic peak.

Fig. 7. Plot of calorific value vs. conditioning time of amorphous cellulose at 90% R.H. and 20°C: (O—O) total calorific value; (□—□) calorific value calculated from first exothermic peak; (△—△) calorific value calculated from second exothermic peak.
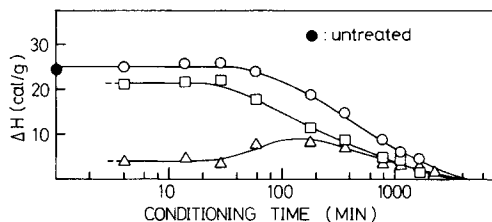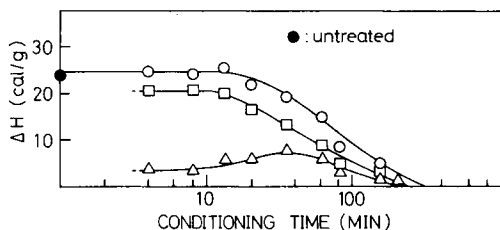

Fig. 8. Plot of calorific value vs. conditioning time of amorphous cellulose at 100% R.H. and 20°C: (O—O) total calorific value; (□—□) calorific value calculated from first exothermic peak; (△—△) calorific value calculated from second exothermic peak.

increasing the conditioning time. On the other hand, T_i and T_{p1} are not affected by the conditioning time. The pyrolysis temperature also shifted to the higher temperature side with increased conditioning time. The phenomenon that the exothermic peak separates into two peaks is discussed later.

The calculated calorific value from the exothermic peak area was plotted as a function of conditioning time, as shown in Figures 6, 7, and 8. From these figures, it is seen that the peaks vanished completely after about 6000, 4000, and 300 min of conditioning time at 80%, 90%, and 100% R.H., respectively. It should be emphasized that such a DSC study seems to correspond to the kinetic one in the initial state of the recrystallization process of amorphous cellulose at various relative humidities, since the curves as shown in Figures 6, 7, and 8 were obtained. Therefore, the decreasing ratio of the exothermic peak area may correlate to the crystallinity of cellulose. In the recrystallization of amorphous cellulose at 100% R.H., the intensity of the 10ī peak came to maximum in about 4 hr.[4] This agrees well with the results of our DSC measurements at 100% R.H., as shown in Figure 8. Although such an agreement is of interest, it should be recognized that the "content" of crystallinity measured by x-ray diffraction differs from that measured by DSC.

The exothermic peak separates into two peaks in the initial state of recrystallization, as described above. The first peak seems to be identical with the exothermic peak of untreated amorphous cellulose. On the other hand, the second peak may come from the restriction of molecular motion
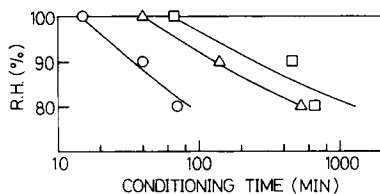
Fig. 9. Plot of R.H. vs. conditioning time: (O—O) induction period before the decrease of calorific value; (△—△) conditioning time to attain the maximum value of the second peak; (□—□) half-value period of exothermic reaction.

of cellulose in the amorphous region by cellulose crystallite produced in the initial state of recrystallization. The validity of such a consideration is due to the independence of T_i and T_{p1}' and dependence of T_{p2} and T_t on the duration of conditioning time. As shown in Figures 6, 7, and 8, a curve of the calorific value of the second peak has characteristically a maximum value for the conditioning time. In the case of conditioning at higher than 80% R.H., a second peak has been observed to increase with the progress of recrystallization; and with further progress of recrystallization, the first and second peaks start to decrease together. It is obvious from Figure 9 that the induction period before the decrease of calorific value, the conditioning time to attain the maximum value of the second peak, and the half-value period of exothermic reaction are definitely correlated with changes in relative humidity. From the results shown in Figure 9, the higher relative humidity causes the more prompt recrystallization of cellulose.

Summarizing the results mentioned above, the recrystallization of amorphous cellulose has been classified into two processes from the DSC curves: a fast process at higher than 80% R.H. and a very slow one at lower than 65% R.H. This suggests that molecular motion of cellulose becomes active suddenly if cellulose rises to some level of moisture regain. On the basis of the data by Brecht[9] and Wada,[10] the approximate classification of water sorption may be summarized as follows: (a) at 0%–20% R.H., monolayer water is merely packed among cellulose molecules and contributes little to molecular motion of cellulose; (b) at 20%–70~80% R.H., multilayers of water adsorbed by the cleavage of intermolecular hydrogen bond weaken the intermolecular forces of cellulose; and (c) at higher than 70–80% R.H., capillary water is retained in the capillary of 10^{-6} cm diameter. If cellulose has moisture regain which is approximately comparable to capillary water, the conformation of cellulose seems to be easily changeable. On the other hand, although the cellulose chain in the amorphous region becomes flexible in the range of 20% to 65% R.H., its conformation is hardly changeable because of its bulk or insufficient swelling. The appearance of two peaks in a DSC curve, however, suggests that the cellulose chain may be locally reoriented during the conditioning.

By the quantitative analysis of rate curve of recrystallization of synthetic polymers, some information has often been obtained about the nature of the nucleation and growth process. The recrystallization kinetics for bulk

polymers may be expressed by the general Avrami equation.[11] When the Avrami equation was applied to the slope of calorific value versus conditioning time in Figures 6, 7, and 8, the following was obtained:

$$\frac{C_t - C_0}{C_\infty - C_0} = \exp(-kt^n)$$

where C_∞ = calorific value after infinite conditioning ($=0$); C_0 = calorific value of unconditioned cellulose, 24.7 cal/g; C_t = calorific value after conditioning time t; k = rate constant of recrystallization; t = conditioning time; and n = number reflecting the type of crystal growth, i.e., polyhedral, plate-like, or lineal growth. Every n was almost 1 at 80%, 90%, and 100% R.H., respectively. Such a small integral value of n suggests that the mode of recrystallization growth is one-dimensional.

CONCLUSIONS

The initial recrystallization kinetics of amorphous cellulose at various relative humidities were studied on the basis of the exothermic peak between 380° and 470°K in a DSC curve instead of x-ray diffraction diagram, infrared spectrum, specific volume, etc. The main conclusions to be drawn from the present work are as follows:

1. The exothermic peak separates into two peaks in the initial state of the recrystallization. A higher exothermic peak suggests that the stable parts for heating in which the molecular motion of cellulose is hindered by the neighboring regenerated crystallite may be present in the amorphous region.

2. The recrystallization occurred easily by conditioning at higher than 80% R.H., but was insignificant at lower than 65% R.H.

3. When the Avrami equation was applied to the slope of calorific value versus conditioning time at higher than 80% R.H., it became apparent that the mode of recrystallization growth is one-dimensional.

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