Note

Thermal Properties of Newly Developed Acetylated Cellulose

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Abstract——A novel acetylated cellulose called cellulose oligo-oxymethylene ether acetate, COAc, was prepared by the homogeneous reaction in Paraformaldehyde/DMSO medium. Measurements of thermal deformation for COAc series with different degree of substitution (DS) revealed that the asending deformation for all samples went off at about 170°C. Heat treatment above this temperature caused remarkable change in thermal properties of COAc. A large weight loss of COAc was also observed in the region above this temperature From these results, the side chain of COAc was concluded to decompose above 170°C.

Key words: acetylated cellulose, thermal deformation, homogeneous acetylation, thermal decomposition

1. Introduction

Homogeneous acetylation of cellulose in Paraformaldehyde (PF)/DMSO solvent system is known to give a novel acetylated cellulose[1] called COAc, cellulose oligo-oxymethylene ether acetate. The COAc is somewhat different from the usual cellulose acetate in that it involves oxymethylene oligomer between glucopyranose ring and acetate group. The COAc gives off a clear and transparent films with flexibility, which indicates potential utility in various areas of application. For a series of cellulose oligo-oxymethylene ether acylates including COAc, we have been studying viscoelastic properties, and classified types of molecular motion present in them[2~4].

From the practical point of view, however, it is necessary to obtain information on the thermal properties, especially on the thermal stability of COAc, since such properties restrict temperature ranges of the materials to be used.

In our present article, we describe the results of thermal degradation of COAc using thermomechanical analyzer (TMA) and dynamic thermogravimeter (DTG).

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2. Experimental

2. 1 Preparation procedure of COAc

Dried cellulose power (Whatman cellulose CF-11) (2g) and paraformaldehyde (4 g) were well dispersed in DMSO (50 ml) at room temperature. The mixture was then heated with stirring to 120°C in a 100 ml Erlenmyer flask equipped with a condencer. After being held at this temperature for 3 hr, the cellulose solution so obtained was cooled to room temparature. To the cooled cellulose solution, triethylamine (6 mol/mol glucose) and specified amount of acetic anhydride (0∼6 mol) were added. After the addition, the reaction mixture was allowed to stand at room temperature for at least 5 hr. The reaction mixture was then poured into methanol. The DS value of the sample obtained were determined by saponification method.

2. 2 Measurements of thermal softening and weight loss of samples

The thermal softening of the sample was measured with thermomechanical analyzer (TMA), in which a column of the sample collapsed under a plunger which supported a constant load, when heated at a rate of 1°C/min. The weight loss of the sample was observed using dynamic thermogravimeter (DTG) in which the sample is heated at a rate of 2°C/min. The heating rate of 5°C/min was adopted for cellulose oligo-oxymethylene ether butyrate. Powder samples were used for both measurements.

3. Results and Discussion

Fig. 1 shows the diagram of thermal deformation versus temperature for COAc with DS of about 2.8. In the diagram, the deformation is normalized: the defor-
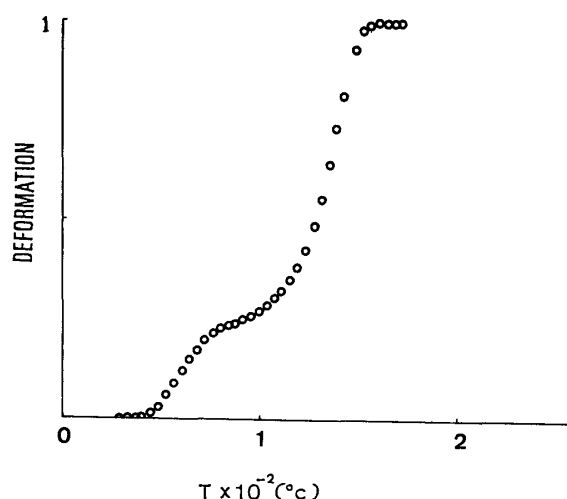

Fig. 1. Diagram of thermal deformation versus temperature for COAc with DS=2.8

mation is null at room temperature and unity at the temperature at which the plunger in TMA reaches the bottom of the glass capillary, indicating completion of liquid flow of the sample. In the diagram, we observed two well-defined transition regions. Regarding the transition appearing in the higher temperature range, the deformation curve rises gradually, and reaches unity. This region is regarded to be the flow region, and the gradual deformation of the curve indicates the sample to be almost amorphous in nature. This result is in accord with that of x-ray diffractgram.

On the other hand, the lower temperature transition can be ascribed to the micro-Brownian motion of the segment along the main chain, and thus the rapidly changing deformation is associated with the glass transition of COAc.

The information on the transition for COAc with DS=2.8 (i.e. triacetate) described above aids considerably in the assignment of transitions for COAc series with different DS values. Fig. 2 represents thermodiagram for a series of COAc with DS=2.8 to 0, where the COAc with DS=0 corresponds to regenerated cellulose obtained from PF/DMSO solution. From the figure, we observe that the glass transition region regularly shifts to higher temperature as the DS values decrease from 2.8 to 1.35. From this evidence, it is learned that the decrease in the amount of the COAc side groups which are randomly distributed along the cellulose chain causes increased interaction between cellulose main chain, thus supressing the main chain motion. The regularity of the change in the glass transition region observed above is thought to be typical of cellulose derivatives prepared by homogeneous reaction. It should be noted, however, that such glass transition disappears for COAc with DS less than 0.74. Similar trends are recognized in the flow region, i.e., the flow region shifts to higher temperature with decreasing DS, and it disappears for the sample less than DS=1.81. In connection with this, it can be seen from the diagrams at DS=2.10 and 2.04 that the ascending deformation curve in the flow region goes down at about 170°C prior to the completion of liquid flow. Furthermore, the deformation in the glass transition region for the sample with DS=1.35 also appears to be suppressed at about 170°C.

From these facts, it is expected that some structural change in COAc might occur at around 170°C. For further information, we measured thermal deformation for COAc with DS=2.8 after heat treatment at specified temperatures for 1 hr. The resulting diagrams at 155, 182, 200 and 220°C are shown in Fig. 3. It is known from the figure that the deformation curve of the sample after the treatment at 155°C is the same as that of untreated one. However, all the curves treated at more than 182°C are quite different in shape from those for untreated samples, though their glass transition regions appear at a temperature comparable to that for untreated
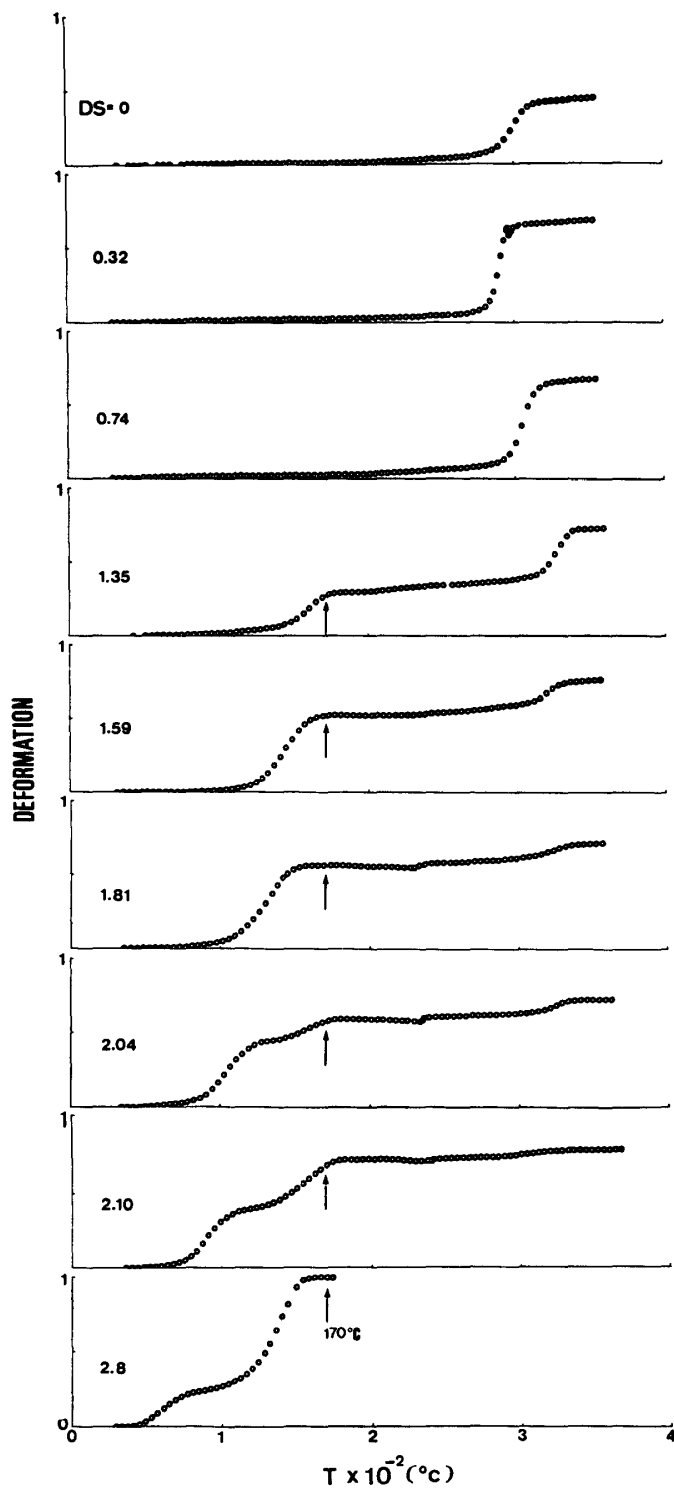
Fig. 2. Diagram of thermal deformation versus temperature
for a series of COAs with DS = 2.8 to 0

sample. It should be emphasized that these samples do not exhibit flow region,
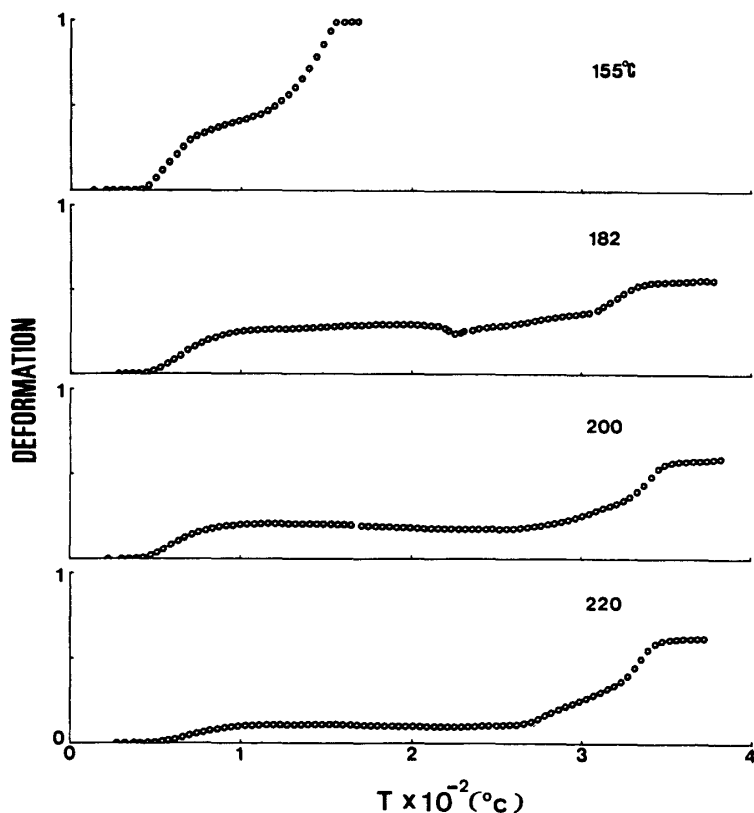but show apparent deformation due to the decomposition around 280°C at which

Fig. 3. Effect of heat treatment on thermal deformation
curves for COAc with DS=2.8

cellulose itself decomposes. This point will be mentioned later using DTG data. In addition, the deformation magnitude in the glass transition region become smaller with increasing temperature. From these facts, it is evident that the COAc changed markedly in structure after heat treatment above ca. 170°C.

In an effort to elucidate the significance of this structural change DTG measurements were made for COAc. Figs. 4a, 4b, 4c and 4d illustrate normalized weight loss (W) versus temperature curves for Whatman cellulose CF-11, regenerated cellulose, triacetylated COAc, and cellulose oligo-oxymethylene ether butylate, COB, respectively. In each figure, dW/dT curve is also shown for reference. Regarding cellulose (Fig. 4a), observable weight loss begins at around 280°C, accelerated until an inflection point near 310°C, and levels off somewhat above 330°C. This loss is due to the decomposition of cellulose chain. The similar curve is obtained for regenerated cellulose (Fig. 4b), although slight decrease which can be attributed to the evaporation of some contaminants such as formaldehyde involved begins around 220°C. On the other hand, a remarkable weight loss for COAc (Fig. 4c) is observed between 170 and 280°C in advance of cellulose chain degradation. This difference in thermal properties between cellulose and COAc is thought to arise from different

chemical structure in the side chain. Thus, it is most probable that the drop in loss curve before main chain degradation stems from the decomposition of oligo oxymethylene ether acetate side chain in COAc examined. If this is the case, the weight loss should become much greater when the alkyl portion in the COAc side chain is replaced by butylate groups whose molecular weight is higher than that of acetate. From Fig. 4d, we see that the drop in weight loss for COB occurs markedly in the temperature range corresponding to the above, although higher heating rate (5°C/min) is adopted in this case. Consequently, we may conclude that the COAc side chain decomposes at around 170°C, and is reduced to the regenerated cellulose prior to the disintegration of cellulose itself.
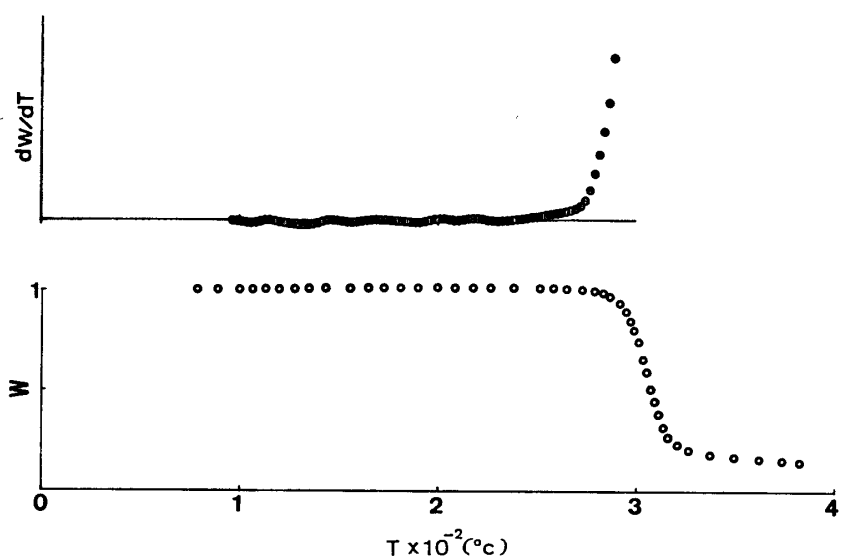

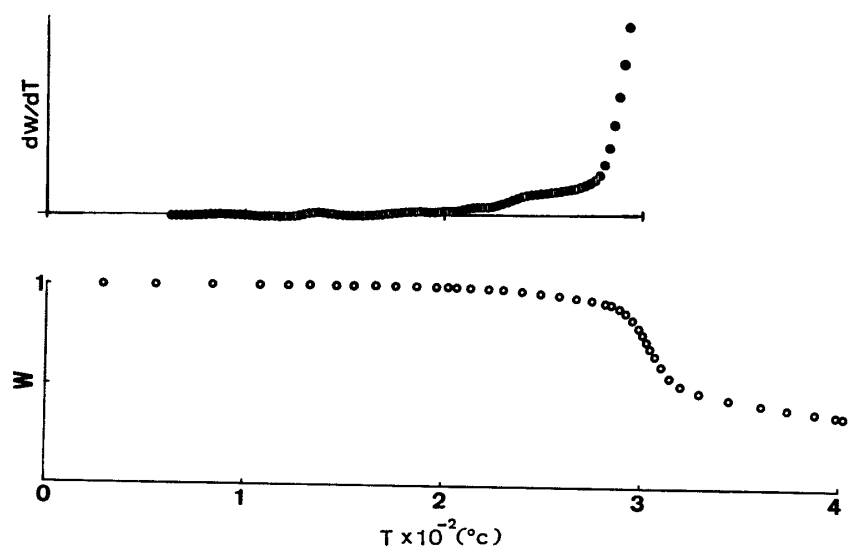Fig. 4a. Dynamic thermogravimetric trace of unmodified cellulose

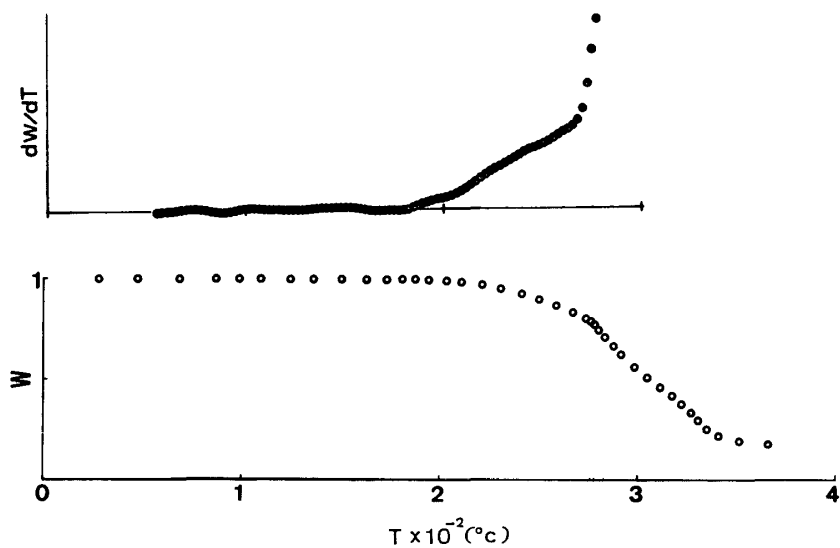Fig. 4b. Dynamic thermogravimetric trace of regenerated cellulose

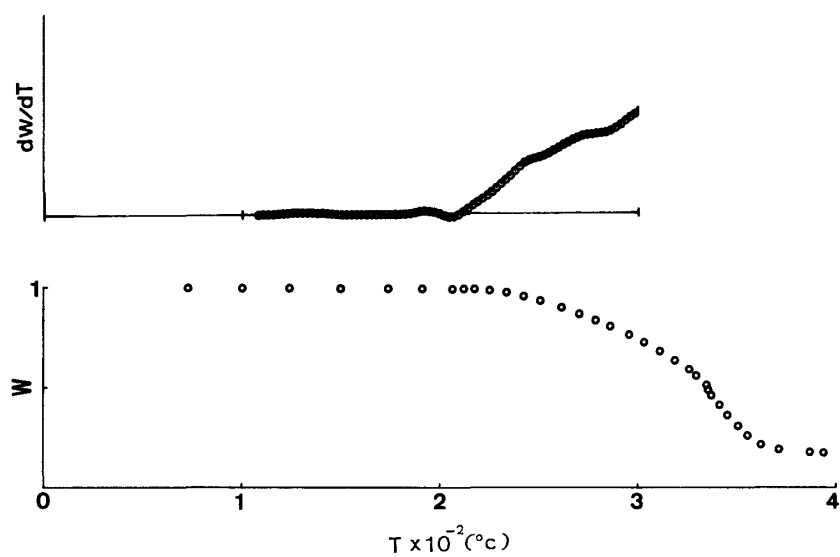Fig. 4c. Dynamic thermogravimetric trace of COAc with DS=2.8

Fig. 4d. Dynamic thermogravimetric trace of Cellulose oligo
oxymethylene ether butyrate, COB

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