

## 論文の内容の要旨

生物材料科学 専攻  
平成 22 年度博士後期課程進学

スー シャオボー

氏 名 蘇 暁博  
指導教員名 和田 昌久

### 論文題目 Research on complexation and adsorption behavior of cellulose with hydrazine

(セルロースとヒドラジンの錯体形成および吸着挙動に関する研究)

## 1. Introduction

Cellulose is the most produced and utilized bio-synthesized material on earth. This  $\beta$ -1,4 glucoside-bonded biopolymer maintains chain structure despite of various synthesizing mechanisms. Cellulose arises in many polymorphs in terms of chain direction and hydrogen bonding arrangement, basically including native and regenerated forms. The intercalation and allomorphic conversion of cellulose with ammonia and amines have been reported by many groups, helping us better understand the mechanism of dissolution and enzymatic biolysis.

As the simplest diamine, hydrazine ( $N_2H_4$ ) is recently highlighted because of the development of direct hydrazine fuel cell system, not only exhibiting a fascinating power output, but achieving zero- $CO_2$ -emission as well. Unfortunately, to overcome the chemical toxicity and biological hazardousness, which considered as the major drawback of hydrazine as power source, promising storage material was sought after.

In this research, the interaction between cellulose and hydrazine, including complexation and physical adsorption behavior, was thoroughly investigated and discussed.

## 2. Stoichiometry of cellulose-hydrazine complexes

### 2.1 Experiments

Green alga (*Cladophora sp.*) sample was collected as the source of cellulose I, treated in 4% NaOH and 0.3 %  $NaClO_2$ , followed by water washing. The resulting

cellulose material was homogenized and made into uniaxially oriented film by the rotational shear flow technique. Ramie fiber were neatly aligned, immersed in NaOH and washed in water to prepared oriented mercerized fibers. After repeated 3 times, the fibers were vacuum-dried over night.

## 2.2 Results and discussion

Analysis of Fig. 1 allowed determination of a two-chain monoclinic unit cell of cellulose I-hydrazine complex as:  $a = 8.57 \text{ \AA}$ ,  $b = 9.22 \text{ \AA}$ ,  $c = 10.38 \text{ \AA}$  and  $\gamma = 94.4^\circ$ , with unit cell volume of  $819 \text{ \AA}^3$ . The meridional reflections  $00l$  with odd  $l$  were absent, indicating that the space group was  $P2_1$ . Moreover, the hydrazine complex of mercerized ramie (not shown) also shows a high degree of crystalline order. With all the peaks refined, the unit cell parameters were determined as:  $a = 10.42 \text{ \AA}$ ,  $b = 10.46 \text{ \AA}$ ,  $c = 10.38 \text{ \AA}$ ,  $\gamma = 129.7^\circ$ , with a two-chain monoclinic unit cell, with space group  $P2_1$  and unit cell volume of  $870 \text{ \AA}^3$ . The expansion of the unit cells leads to the stoichiometry of approximately 1 hydrazine molecule incorporated versus 1 glucose residue.

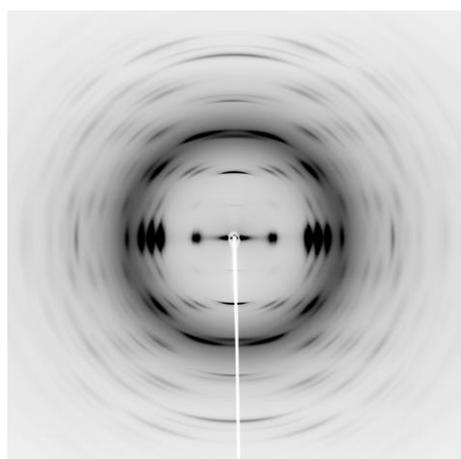


Fig. 1 X-ray diffraction pattern of cellulose I-hydrazine complex

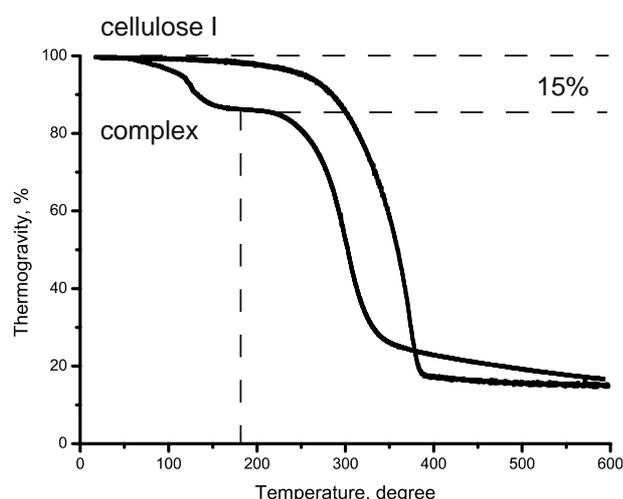


Fig. 2 Thermogravimetric curves of cellulose I and its hydrazine complex

Another evaluation of stoichiometry was performed by thermogravimetry of the cellulose-hydrazine complexes as in Fig. 2. The weight decrease of cellulose I hydrazine complex was 15.0%, translated into molecular ratio of 0.89 hydrazine molecule per glucose.

## 3. Stability and allomorphic conversion

### 3.1 Experiments

The hydrazine complexes were treated in the excess water, methanol and ethanol. Synchrotron X-ray diffraction analysis was carried out to monitor the allomorphic conversion of the subjects.

### 3.2 Results and discussion

Fig. 3 exhibits the X-ray diffraction equatorial profiles of the starting cellulose, hydrazine complex, and cellulose recovered by water or alcohol treatments (cellulose II profiles not shown). The complexation disrupts hydrogen bonds between cellulose and hydrazine with alcohol treatments, leading to the formation of cellulose III-type structure, i.e. the non-staggered mutual arrangement of cellulose chains. When hydrazine is extracted by water, cellulose recovers its original structure, cellulose I; but the resultant crystal has somewhat reduced crystallinity, and crystal type was changed from cellulose I $\alpha$  to cellulose I $\beta$ . This change is indicated by the slightly narrower interval between (1-10) and (110) peaks.

On the other hand, extraction of hydrazine by alcohols resulted in the formation of mixtures of cellulose III<sub>I</sub> and cellulose I $\beta$ . The ratio of the two forms was about 7:3 for both alcohols (Figs. 3d and 3e). The overall behavior is similar to those of alkylamine complexation of cellulose, giving cellulose III<sub>I</sub> of higher purity, meaning that the action of hydrazine is intermediate between alkylamines and water.

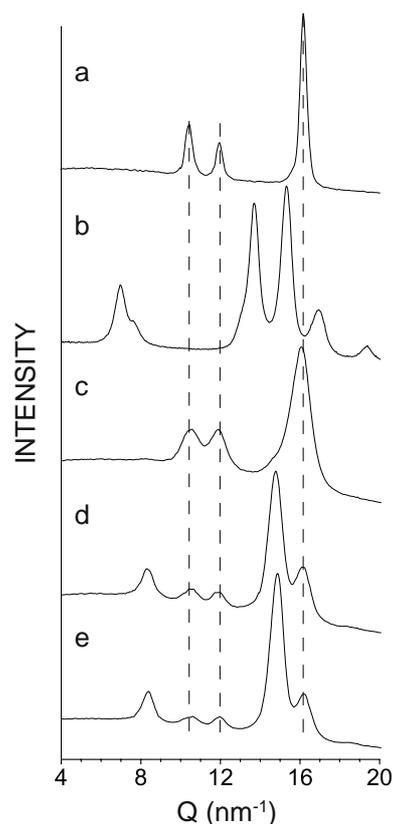


Fig.3 Equatorial X-ray profiles of cellulose I (a), complex (b), complex treated by water (c), methanol (d) and ethanol (e).

## 4. Complexation and crystal size

### 4.1 Experiments

Cellulose samples, including Funacel (microcrystal powder), CF11 (microcrystal fiber) and tunicate cellulose (purified, homogenized and dried) were treated in aqueous hydrazine with various concentrations and the formation of complex was monitored by X-ray diffraction.

### 4.2 Results and discussion

Table. 1 Crystal size (Å) of cellulose samples, calculated by Scherrer's equation.

Samples	Crystal planes		
	(1-10)	(110)	(200)
Tunicate	96.6	129.8	118.3
CF11	58.8	50.0	68.7
Funacel	44.0	34.1	43.6

According to Table. 1, tunicate cellulose exhibits the largest crystal size, approximately 100 Å, followed by CF11, 50-70 Å. Funacel is the least crystalline samples of all, the crystal size is only 30-45 Å. Fig. 4 indicates that the complex formation is achieved within a narrow concentration range of 30-45%. Furthermore, it is an obvious result that cellulose with smaller crystal size tends to form complex easily.

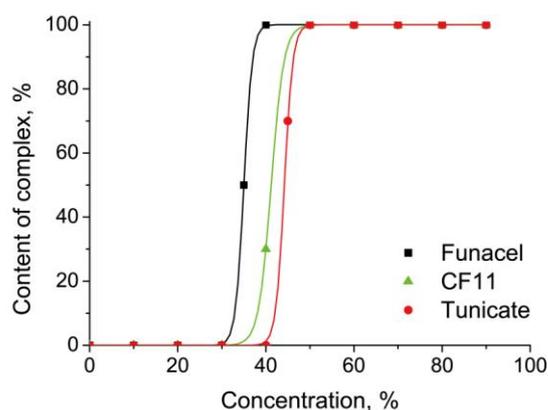


Fig. 4 Content of complexes with increasing concentration of aqueous hydrazine.

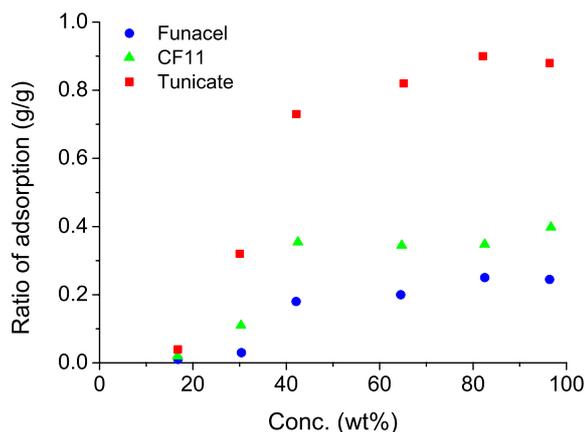


Fig. 5 Adsorption isotherm of hydrazine onto cellulose in aqueous hydrazine.

## 5. Adsorption behavior of hydrazine on cellulose

### 5.1 Experiments

Adsorption isotherm of hydrazine onto cellulose in liquid phase is plotted in Fig. 5. Concentration difference before and after cellulose treatment was measured through absorbance of hydrazine aqueous.

### 5.2 Results and discussion

Considering one hydrazine molecule is uptake per glucose unit (discussed above), the incorporated hydrazine molecules within cellulose unit cell also contributed to the concentration decreasing. Thus, some 0.2 (molecular weight of hydrazine/glucoopyranose unit: 32/162) of ratio of adsorption was not actually attributed to physical adsorption occurring on the surface of cellulose fibrils. With this portion being subtracted, the ratio of adsorption ascribed to pure physical adsorption is determined as about 0 for Funacel, 0.15 for CF11 and 0.75 for tunicate cellulose, respectively.

Assisted with electronic scanning microscopy and nitrogen adsorption analysis (data not shown), it is an evident result that cellulosic materials with fiber network structure and high pore volume could make a good storage material of hydrazine.