Amorphized Cellulose

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Amorphized cellulose is partially or completely decrystallized cellulose. Natural celluloses isolated from terrestrial plants (e.g. cotton, wood, etc.), algae (e.g. Cladophora sp., Valonia ventricosa, etc.), shells of some marine tunicates (e.g. Ascidia sp., Halocynthia roretzi, etc.), and synthesized by some bacteria (e.g. Gluconacetobacter sp., Medusomyces gisevii, etc.) along with microcrystalline cellulose, are semicrystalline biopolymers with a crystallinity degree of 50 to 80%.

amorphized cellulose | amorphous nanocellulose | preparation methods | structural organization | characterization | accessibility | reactivity | enzymatic digestibility | applications

1. Introduction

Amorphized cellulose is partially or completely decrystallized cellulose. Natural celluloses isolated from terrestrial plants (e.g. cotton, wood, etc.), algae (e.g. *Cladophora sp., Valonia ventricosa,* etc.), shells of some marine tunicates (e.g. *Ascidia sp., Halocynthia roretzi,* etc.), and synthesized by some bacteria (e.g. *Gluconacetobacter sp., Medusomyces gisevii,* etc.) along with microcrystalline cellulose, are semicrystalline biopolymers having a crystallinity degree of 50 to 80% [1][2].

Due to increased crystallinity, natural celluloses exhibit low accessibility to reagents. In particular, they give a small yield of glucose after acidic [3] and enzymatic hydrolysis [4][5]. The high crystallinity of natural cellulose fibers hampers dyeing, diffusion, and sorption of water vapor, which negatively affects its use in textile materials. To increase the accessibility, reactivity, and sorption ability of natural celluloses, it is necessary to destroy the crystalline structure to obtain amorphized or completely amorphous cellulose materials. In addition, completely amorphous cellulose serves as an amorphous standard having zero crystallinity [1] and 100% enzymatic digestibility [6][7].

2. Methods of amorphization

Natural cellulosic materials can be partially amorphized by short-term dry grinding, treatment with 17-20% NaOH, ethylenediamine, primary amines, liquid ammonia, as well as by regeneration of cellulose from solutions in such solvents as CS_2/NaOH, Cuproxam, NMMO, SO_2-DEA-DMSO, etc. [8][9][10] (**Table 1**).

To obtain completely amorphous cellulose prolonged dry grinding is required. The other methods for making completely amorphous cellulose include saponification of cellulose acetate in non-aqueous media, regeneration of cellulose from solutions in H_3PO_4, LiCl/DMAA, NaOH/Urea, as well as swelling of natural cellulose in cold NaOH/Urea solvent [6][7][8][9] (**Table 1**). Moreover, NaOH/Urea is a very cheap solvent.

Table 1. Degree of crystallinity (X) and amorphicity (Y), and water vapor sorption (S) at R.H. = 70% for untreated and amorphized cotton cellulose [8].

Treatment	X, %	Y,%	S,%
Untreated	70	30	7.7
Ball-grinding for 5 h	32	68	17.0
Ball-grinding for 24 h	0	100	24.9
20% NaOH	54	46	11.7
Liquid ammonia	36	64	16.1
7%NaOH/12%Urea at *R=3	26	74	19.0
7%NaOH/12%Urea at *R=10	0	100	25.0

*R is solvent to cellulose ratio

3. Characterization of amorphized cellulose

Amorphous and amorphous celluloses can be characterized by a variety of methods, including WAXS, SAXS, NMR, FTIR, Raman spectroscopy (RS), sorption, calorimetry, thermal analysis, etc. Methods of WAXS, CP/MAS ^{13}C NMR, sorption of water vapor, and study of wetting enthalpy are used to determine degrees of crystallinity and amorphicity of initial cellulose materials and structural changes due to amorphization [1][2][8][9][10][11]. In addition, the size of crystallites and interplanar spacings can be calculated from X-ray patterns. SAXS and the sorption of inert gases and vapors are used to study the porous structure. FTIR and RS show chemical changes of cellulose after

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amorphization. The thermal stability of initial and amorphized cellulose materials can be studied using methods of thermal analysis.

Study of completely amorphous cellulose by WAXS method allows determine average interplanar spacings (d_m = 0.44-0.45 nm) between planes in a distorted mesomorphous lattice and calculate the average size (D_m=1.8-1.9 nm) of mesomorphous clusters. Moreover, the function of the radial distribution of electron density and packing density of amorphous cellulose can be studied. The estimated density of mesomorphous clusters was 1.48-1.49 g/cm^3, which is slightly higher than the average density, 1.44-1.45 g/cm^3, of entire amorphous cellulose.

4. Potential applications of amorphized cellulose

For commercial production of amorphized cellulose, it is most advisable to choose cheap raw materials such as mixed waste paper and use a cost-effective amorphization method, e.g. treatment of the raw material with NaOH/Urea solvent. Using enzymatic hydrolysis of commercial amorphized cellulose, the relatively cheap glucose can be obtained for its further use as a substrate in biotechnology.

The swollen form of amorphous cellulose is capable of holding large amounts of water, and therefore it can be used in cosmetics as a moisturizing mask. In addition, being a water reservoir, the swollen form of amorphous cellulose would find application in agriculture and soil technology. Moreover, after usage, amorphous cellulose is completely decomposed by the microorganisms present in the soil.

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