



Modification of starch by glow discharge plasma

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Abstract

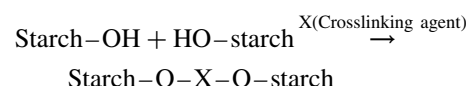
A novel method for starch modification is investigated. Starch is highly cross linked by glow discharge plasma, without the assistance of conventional chemical agents, thus avoiding any environmental concerns. An energy-charge-transfer mechanism is suggested for the function of plasma. This process could be useful for the production of large quantities of modified starch.

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Keywords: Starch; Modification; Crosslinking; Glow discharge; Plasma

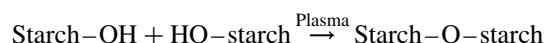
1. Introduction

Starch is a low-cost renewable biosynthesized polymer. Apart from being an important constituent of the human diet, a significant amount of this material has been used in the paper, textile and chemical industries. Depleting fossil hydrocarbon resources will require an increasing range of novel applications for starch-based materials including crosslinked starches. These will replace synthetic polymers and promote new degradable materials (Delville, Joly, Dole, & Bliard, 2002; Fang, Fowler, Tomkinson, & Hill, 2002; Gross & Kalra, 2002). Crosslinking is generally performed by treating granular starch with the following crosslinking agents in heterogeneous media: sodium trimetaphosphate (Woo & Seib, 1997), epichlorohydrin (Kuniak & Marchessault, 1973; Šimkovic, 1997), and phosphoryl chloride (Yook, Pek, & Park, 1993). The chemistry can be summarized as:



The use of chemicals inevitably causes environmental concern. Growing interests in environmental protection requires more environmentally friendly processes (Poliakoff, Fitzpatrick, Farren, & Anastas, 2002; Stephen, Roger,

Akash, Roger, & Gerhard, 2002). Some scientists have attempted to find environmentally safe crosslinking agents (Delville et al., 2002; Šimkovic, 1997). In this article we report a new approach to the modification of starch without added chemicals. A glow discharge plasma is used which can produce high energy electrons and other highly active species at room temperature. This approach has been extensively used in material modification (Coburn, 1991; Liu, Vissokov, & Jang, 2002). When applied to starch, the highly active species can excite chemical groups in starch, inducing modification process without the assistance of other chemicals. Thermal degradation is minimised. In the present work, the modification of starch by glow discharge plasma is investigated. Starch is extensively crosslinked probably through the following mechanism



2. Experimental

2.1. Preparation of modified starch

The process was conducted in a glow discharge plasma apparatus (Fig. 1). The commercial soluble starch (Kemio Chemical Reagents R&D Center, Tianjin) was mixed with de-ionized water. The slurry was treated in the positive column zone of the glow discharge for 45 min. A dc voltage

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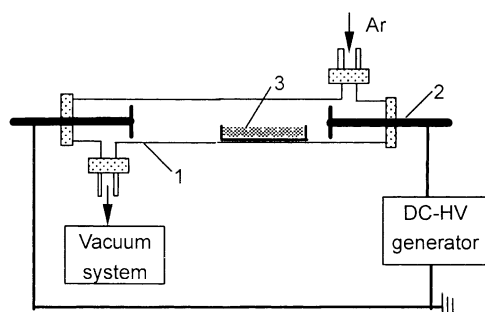


Fig. 1. Schematics of glow discharge plasma apparatus. The apparatus involves a quartz tube (1) and two brass electrodes (2). Starch slurry (3) is placed in a quartz boat for discharge treatment.

generator (manufactured by Tianjin University) was applied to supply high voltage of 700 V igniting the gas discharge. Argon was used as discharge gas with a pressure of 200 Pa. The plasma modified starch slurry was dried at 60 °C for 5 h after plasma treatment.

2.2. Characterization

The IR spectra were recorded on a Bruker VECTOR22 spectrometer using KBr pellets dried at 85 °C for an hour. SEM characteristics were carried out with a Philips XL 30 SEM scanning electron microscope. X-ray diffraction patterns were obtained with a C/MAX-2500X powder diffractometry under the following conditions: X-ray tube Cu K α (Ni filter); voltage 36 kV; current 20 mA; scanning from $\theta = 10^\circ$ to 35° .

^1H - and ^{13}C -NMR measurements were performed with a Bruker AC-P spectrometer at 200 MHz, with a 5 mm diameter C–H dual probe, with solutions in DMSO- d_6 at 40 °C. Chemical-shift values were referenced from the solvent of DMSO- d_6 (2.49 ppm for ^1H and 39.41 ppm for ^{13}C). C and H were determined from the chemical-shift of peaks in NMR spectra (Dicke, Rahn, Haack, & Heinze, 2001). Considering the relative stability of H-4, H-5 ($\delta = 4.5$ ppm) assigned to α -D-glucose, it is reasonable to regard these as unaffected by the discharge modification. The relative areas of four peaks in the ^1H -NMR spectra was summarized using the area of H-4, H-5 as standard.

3. Results and discussion

The two components of starch, amylose and amylopectin, are both high molecular weight, polydisperse(1 \rightarrow 4)- α -glucans (Michael & Stephen, 1985). ^{13}C -NMR results show little difference between the native and plasma-modified starch. It means that plasma modification does not disrupt the basic glucose units. ^1H -NMR analysis (Table 1), however, indicates that the area of peak belonging to hydroxyl group protons decreases significantly, showing the loss of OH groups in the modified starch.

Table 1

Relative area of H protons determined from the ^1H -NMR spectra

Sample	Relative area			
	H-1, H-3	H-2, H-6 α , 6-H β	H-4, H-5	O-H (2,3,6)
Native	1.65	1.49	1.0	5.02
Modified	1.34	1.19	1.0	3.67

Two possible reactions, oxidation and crosslinking, can cause the decrease of protons in the hydroxyl groups. A peak at about 1720 cm^{-1} in the IR spectra identifying carbonyl should appear if starch is oxidized. But both the IR and ^{13}C -NMR spectra show no evidence for the existence of C=O bands in the plasma modified starch. It is reasonable to suppose that the decreased OH is due to the cross linking of α -D-glucose units. In fact, as Ar is the discharge gas, only a few O-containing species can be produced from the decomposition of H_2O in the slurry.

In the plasma zone, a large amount of high energy electrons are produced by discharge. These electrons can attach on to argon atoms and converts them to an excited state ($\text{Ar}^{\text{e-}}$, Ar^*). The helical structure of native starch leads to hydrophobic channels in which polarizable organic molecules or species with charges can be adsorbed (Bekkum, 1994; Jeffrey, James, Christopher, & Karen, 2001). $\text{Ar}^{\text{e-}}$ species entering the helical channels are easily absorbed where charge and energy is transferred to the hydrogen atom through collision of $\text{Ar}^{\text{e-}}$ with hydroxyl group (Fig. 2I). At the same time, the effect of the plasma electric field induces a further polarization of O–H bonds of

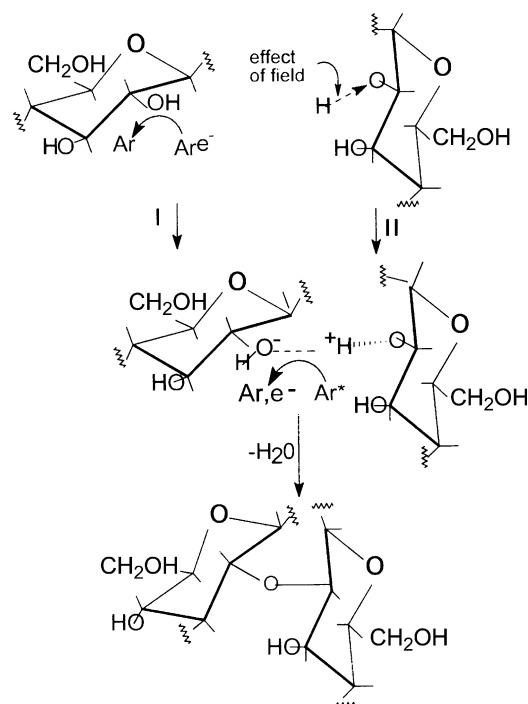


Fig. 2. Proposed mechanism for the cross linking of starch by glow discharge plasma.

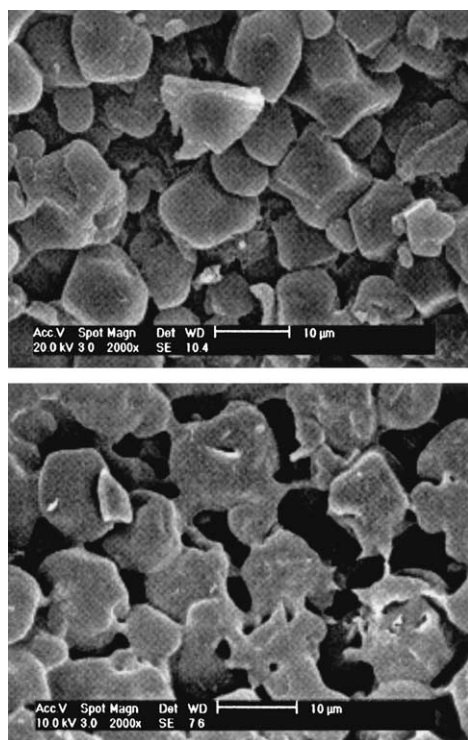


Fig. 3. SEM photographs of native (A) and plasma-modified (B) starch.

some hydroxyl groups and the covalent bond becomes electrovalent to some degree (Fig. 2II). With the energy transformed by Ar^* via another collision, two kinds of OH groups tend to dehydrate with large possibility, causing the crosslinking of two α -D-glucose units. This reaction is not reversible as helical channel of starch is hydrophobic. It is believed that the C-2 site is the most active position for crosslinking among three carbon sites in the pyranose (Whistler, Bemiller, & Paschll, 1987). Taking this into account, the degree of crosslinking is as high as 80.6% of the C-2 hydroxyl groups.

SEM photographs (Fig. 3) show that a network is formed between the regular native starch granules, illustrating the granules are linked to each other as a built of the glow discharge plasma treatment. X-ray diffraction patterns (Fig. 4) of the modified starch retains

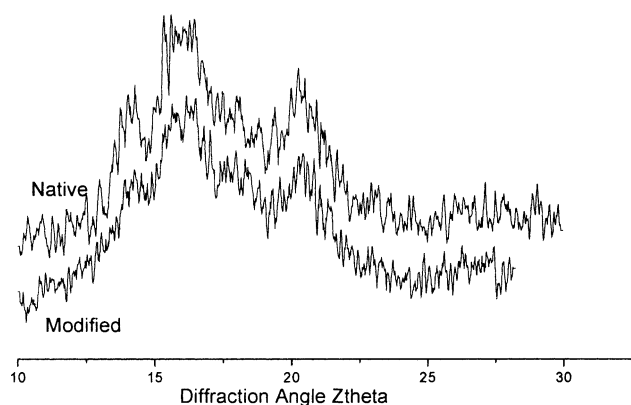


Fig. 4. X-ray diffraction patterns of native and plasma-modified starch.

the A-type X-ray diffraction with little change. Although the details of starch granule structure remain a matter of debate, the composite model of amorphous growth ring and crystalline grow ring is generally recognized (Tang, Brum, & Hills, 2001; Thomsa et al., 1997; Calvert, 1997). It can be concluded that the crosslinking inside the starch granule mainly occurs in the amorphous zone and the crystalline structure is not distorted, probably because the amorphous ring is more flexible and available for cross linking.

4. Conclusions

In this study, a new process for starch modification by plasma treatment is established. Characterizations indicate that the plasma-modified starch is highly crosslinked. This process is simply, but very effective. Plasma, instead of a chemical agent, functions as the reaction media, avoiding the possible formation of by-products and wastes. Since many gases can be ionized or decomposed into active species in the plasma, many reactions difficult in conventional chemistry will be easily carried out in this way. It is expected that a series of starch modifications like oxidation and substitution can be realized in this way, if an appropriate gas is used as discharge gas.

Acknowledgements

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