

Degradation Kinetics of Potato Starch Paste under Ultrasonic Irradiation

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Abstract: The ultrasonic degradation of potato starch paste was undertaken in a reactor. The experimental results showed that the molecular weight and the intrinsic viscosity of potato starch paste decreased with ultrasonic irradiation time, and are approaching two limiting values respectively, below which no further degradation may take place. Ultrasonic degradation kinetics can be explained with the following equations: $M_t = 50.97 \times 10^4 + 572.77 \times 10^4 e^{-0.216t}$ or $\eta_t = 0.81 + 6.556 \times e^{-0.229t}$. The scission of chains in potato starch paste is random in the initial stage, and then non-random.

Key words: potato starch paste; ultrasonic; molecular weight; intrinsic viscosity; degradation kinetics

超声辐照马铃薯淀粉糊降解动力学的研究

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摘 要: 本文进行了超声辐照时间对超声辐照降解马铃薯淀粉糊的动力学的研究。研究表明, 淀粉糊重均分子量和特性粘度随辐照时间的延长而降低; 而且趋于一个极限值。在处理条件下, 超声降解动力学方程式为: $M_t = 50.97 \times 10^4 + 572.77 \times 10^4 e^{-0.216t}$, $\eta_t = 0.81 + 6.556 \times e^{-0.229t}$ 。马铃薯淀粉糊分子链剪切在初始阶段是随机的, 然后是非随机剪切。

关键词: 马铃薯淀粉; 超声; 分子量; 特性粘度; 降解动力学

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As the most abundant reserve polysaccharide in plants, starch consists of a mixture of two α -glucans containing mainly α -D-glucan. Amylose and amylopectin are two macromolecular components of starch granules. Amylose, a poly (1-4)- α -D-glucan, is essentially linear while amylopectin is branched and consists of linear (1-4)- α -D-glucan chains connected through (1-6)- α linkages. They also have different weight-average molar masses^[1]. Because of rapid increase in demand for starch, there is an urgent need for substitution of starch with other substrates for alcohol as well as various other industrial fermentations^[2].

In many of these applications specific molecular weight of polysaccharides is required because of their unique functional properties, such as thickening, film-formation, metal binding and antimicrobial activity^[3]. It has been reported that polysaccharides can be degraded by acidic hydrolysis^[4] or enzymatic treatment^[5]. However, in these methods further purification is necessary due to the presence of additions

used to initiate reactions and formation of side products. Sonodegradation is a free of initiator and side product. Therefore, it is a simpler and more environmentally friendly than conventional ones.

Ultrasound are mechanical waves with frequencies between 2×10^4 Hz and 10^9 Hz^[6]. Propagation of high intensity ultrasound is accompanied by generation of compression and shear waves at large intensities that in turn create shock waves^[7]. The abrupt decrease in pressure at the edge of the saw tooth in the negative pressure cycle of the ultrasonic shock wave spontaneously generates small cavities. These cavities collapse in the positive pressure cycle, produce highly turbulent flow conditions and extremely high pressures and temperatures; a process that is better known as cavitation^[8]. High-intensity ultrasonication produces cavitation, which generates hot spots of short lifetimes with intense local heating of $\sim 5000^\circ\text{C}$, pressures of ~ 1000 atm, and heating and cooling rates above 10^{10}K/s ^[9].

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Application of high-intensity ultrasound to dispersion of carbohydrates can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation^[10]. Cavitational thermolysis may produce hydroxyl radical and hydrogen atoms that can be followed by formation of hydrogen peroxide and, in the absence of oxygen, hydroperoxyl radical^[11]. These transient reactive species can subsequently react with carbohydrates^[12]. In addition, hydrolysis and cleavage due to strong mechanical forces have been reported for a variety of polysaccharides^[13]. Sonication of starch led to formation of shorter chain molecules and reducing sugars^[14] and sonication of pectins resulted in weaker gels to reduced molecular weights^[15]. Partially depolymerized dextrans, of great interest to the pharmaceutical industry, were produced via sonochemical, degradation of native dextrans^[16]. The homolytical-heterolytical mid-chain splitting of dextran together with a recombination of the fragments led to a narrower mass distribution.

Based on these results, it can be hypothesize that the ultrasound may offer an alternative, rapid method to degrade the molecular weight of starch paste. The specific objective of this study was to determine the influence of irradiation time on the molecular weight and the intrinsic viscosity of starch paste. The aim of this research was to set up a function of ultrasonic processing parameters for predicting the polymerization of the ultrasonicated product.

1 Materials and Methods

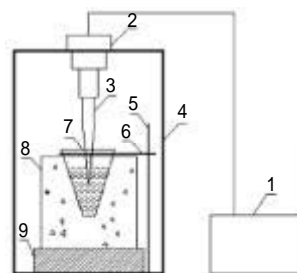
1.1 Materials and samples preparation

Potato starch use in this work was purchased from National Starch Company, America. Starch of 2.000g was suspended in 100 ml demineralized water and boiled for 30 min. After cooling to room temperature, the starch paste was subjected to sonication treatment.

Demineralized water from Milipore Milli-Q system was used for preparation of all solutions. Other chemicals used in this work were of analytical grade.

1.2 Sonochemical degradation

Sonochemical degradation was performed using UP 400 S Ultrasonic Processor, working at the frequency of 25kHz with output power 300W/cm². The starch sample of 100ml was placed in the middle of the reactor, 1mm above the surface of the transducer. Ultrasound irradiation time ranged from 0 to 60min, carried out in the air atmosphere. The average bulk temperature of sonicated paste was maintained at 20±2℃.



1. ultrasonic generator; 2. piezoelectric transducer; 3. horn; 4. soundproof box; 5. supporter; 6. iron clamp; 7. conical flask of samples; 8. breaker with ice-water; 9. pallet.

Fig.1 Schematic of reactor potato starch paste degradation under ultrasonic irradiation

1.3 Determination of the intrinsic viscosity of potato starch paste

The intrinsic viscosity of potato starch paste was determined following the ASTM (American Society for Testing and Materials, 2001) standard practice for dilute solution viscosity of polymers. The viscosity of serially diluted starch solution was measured and the reduced viscosity η_r was calculated by:

$$\eta_r = \frac{(\frac{\eta}{\eta_0} - 1)}{c} \quad (1)$$

where η is the viscosity of starch paste at the polymer concentration of c and η_0 is the solution viscosity at 1.002 MPa at 20.0℃ (Lide, 2004). The inherent viscosity η_i was calculated by:

$$\eta_i = \frac{\ln(\frac{\eta}{\eta_s})}{c} \quad (2)$$

The intrinsic viscosity $[\eta]$ of starch pastes was determined by the intercept of both η_r and η_i where c was near zero (Berth & Dautzenberg, 2002; Pa & Yu, 2001). Error analysis for intrinsic viscosity was conducted by calculating the partial differentials of Eq(1) and Eq(2) to obtain standard deviations of the reduced and inherent viscosity. The partial differentials was obtained from standard deviations of the replications of the viscosity measurements for each serial dilution.

1.4 GPC (gel permeation chromatography) analytical procedure

Potato starch paste samples were measured on GPC. GPC measurements were performed by Waters chromatograph equipped with 1525 Binary HPLC pump, CO-8020 column oven and RI-2414 refractive index detector. Two

Table 1 Effect of ultrasonic irradiation time on the weight average molecular weight and the intrinsic viscosity of potato starch paste (ultrasonic intensity: 300W/cm², concentration of potato starch paste: 2%, distance from probe tip: 1mm)

Irradiation time (min)	0	1	2	3	4	5	10	20	30	60
MW ($\times 10^4$)	593.12	549.45	448.37	360.48	280.84	220.84	111.2	77.8	52.12	50.68
$[\eta]$ (ml/g)	7.46	6.28	4.86	4.23	3.52	2.91	1.80	1.00	0.84	0.85

TSK gel PWXL columns in series (G 5000, G 3000) were used. 0.2mol/L KH₂PO₄ solution was used as solvent at a flow rate of 0.6ml/min. The columns were calibrated on the base of Dextran standards at a concentration of 0.2mg/ml.

2 Results and Discussion

2.1 Ultrasonic degradation of potato starch paste

In order to study the effects of ultrasonic irradiation time on the degradation of potato starch paste, the molecular weight and its intrinsic viscosity of degraded starch samples on the cross section at 1 mm from the probe were first investigated. The data were listed in Table 1. It can be clearly seen that the weight average molecular weight and the intrinsic viscosity of starch paste strongly depend on irradiation time. In the first 5 min of ultrasonic irradiation, potato starch paste undergoes great degradation, causing a significant decrease of the average molecular weight and the intrinsic viscosity. After 30 min of irradiation, the molecular weight and the intrinsic viscosity of potato starch paste almost keep unchanged and tend to a limiting value. The molecular weight corresponding to the peak value is 50×10^4 , namely the limiting molecular weight.

2.2 Ultrasonic degradation kinetics

On the basis of experimental results Yuntao^[17] concluded that the rate of sonochemical degradation for a molecule with degree the polymerisation degree of x , was proportional to the fraction of polymer chain, which exceeded a limiting degree of polymerisation, x_0 , i.e.:

$$-\frac{dy}{dt} = k(x - x_0) \quad (3)$$

where k is a general rate parameter, which depends on the polymer system under investigation. The cited author^[18] simplified the kinetic calculations in describing the degradation of potato starch paste average molecular weight, and its was expressed as:

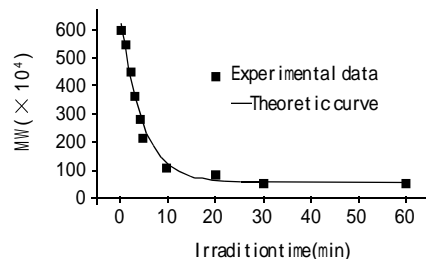
$$-\frac{d(M_t - M_\infty)}{dt} = k \left(\frac{M_t - M_\infty}{M_\infty} \right)$$

where M_∞ and M_t are the limiting and average molecular weights at irradiation time respectively.

By integrating and considering that at $t=0$, $M_t=M_0$

(where M_0 is the initial molecular weight), Eq (4) can be expressed as:

$$M_t = (M_0 - M_\infty)e^{-kt} + M_\infty \quad (5)$$



Ultrasonic intensity: 300 W/cm², concentration of potato starch paste: 2%.

Fig.2 Dependence of MW of potato starch paste on ultrasonic irradiation time

on designating the constant $M_0 - M_\infty = A$,

$$M_t = M_\infty + Ae^{-kt} \quad (6)$$

It can be seen from Fig.2 that the data of showed in Table 1 can be describes well with Eq(6). The equation of theoretic curve is as follows:

$$M_t = 50.97 \times 10^4 + 572.77 \times 10^4 e^{-0.216t} \quad (7)$$

where $M_\infty = 50.97$, which is well consistent with the experimental data of 50.68. The similar kinetics equation can also describe the dependence of the intrinsic viscosity of potato starch paste on irradiation time:

$$\eta_t = \eta_\infty + (\eta_0 - \eta_\infty)e^{-kt} \quad (8)$$

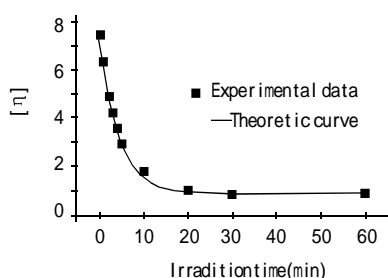
The theoretic curve showed in Fig. 3 is agreeable well with the experimental data. The theoretic expression is

$$\eta_t = 0.81 + 6.556 \times e^{-0.229t} \quad (9)$$

It can be seen from Fig.3 that the theoretic limiting intrinsic viscosity of potato is 0.81, very close to the experimental value of 0.84.

3 Conclusions

3.1 Ultrasonic degradation of potato starch paste occurs based on the mechanism of molecular relaxation of potato starch paste. In the initial stage, ultrasonic degradation is a random process, and the molecular weight distribution broadens. After that, ultrasonic degradation of potato starch paste is a nonrandom process, and the molecular weight distribution becomes narrows. Finally, molecular weight trends toward a limiting value.



Ultrasonic intensity: 300 W/cm², concentration of potato starch paste: 2%.

Fig.3 Dependence of $[\eta]$ of potato starch paste on ultrasonic irradiation time

3.2 The degradation kinetics of potato starch paste under ultrasonic irradiation obeys following equation: $M_t = 50.97 \times 10^4 + 572.77 \times 10^4 e^{-0.216t}$ or $\eta_t = 0.81 + 6.556 \times e^{-0.229t}$, where the limiting molecular weight or the intrinsic viscosity is 50.87×10^4 or 0.81, and the rate constant of degradation reaction is 0.21, 0.229 respectively.

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信息

加拿大研究员确定乳腺癌基因的致病机理

加拿大研究员表示,他们已经揭开蛋白酪氨酸磷酸酶 1 B 基因与乳腺癌发作之间的联系,大约有 40% 的乳腺癌与这种基因有关。这一发现为乳癌治疗带来了希望。

由麦吉尔大学的科学家实施的这项研究显示,中止易受特定癌症影响的老鼠体内的蛋白酪氨酸磷酸酶 1 B 基因的活性可减缓癌细胞的生长,从某种程度上预防了肿瘤。这项研究结果发表在《自然基因学》杂志上。

联合研究员兼麦吉尔肿瘤研究中心的主任迈克尔·特伦布莱说:“我们鉴定出的蛋白酪氨酸磷酸酶 1 B 基因,因其在糖尿病和肥胖症中扮演着重要角色而知名。在这项最新研究中,我们发现蛋白酪氨酸磷酸酶 1 B 基因在调节新陈代谢中所起的作用,与在促进癌细胞增生和转移中所起的作用同等重要。”

1999 年,这组研究员发现抑制由蛋白酪氨酸磷酸酶 1 B 基因产生的酶,使治愈 2 型糖尿病和肥胖成为可能。自此以后,已经有一大批药物公司研发新的抑制物,用来治疗这些疾病。特伦布莱说:“这些化学药物必须达到能处理乳癌的程度。”

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