



# Processing surface sizing starch using oxidation, enzymatic hydrolysis and ultrasonic treatment methods—Preparation and application



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## ABSTRACT

The surface application of starch is a well-established method for increasing paper strength. In surface sizing, a solution of degraded starch is applied to the paper. Two procedures have proved valuable for starch degradation in the paper mill: enzymatic and thermo-oxidative degradation. The objective of this study was to determine achievable efficiencies of cavitation in preparing degraded starch for surface application on paper. It was found that ultrasonic-assisted starch degradation can provide a starch solution that is suitable for surface sizing. The molecular composition of starch solutions prepared by ultrasonic treatment differed from that of starch solutions degraded by enzymes or by thermo-oxidation. Compared to commercial degradation processes, this resulted in intensified film formation and in greater penetration during surface sizing and ultimately in a higher starch content of the paper. Paper sized with ultrasonically treated starch solutions show the same strength properties compared to commercially sized paper.

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## 1. Introduction

The use of ultrasonic cavitation to modify substances in liquid systems has been the subject of numerous publications (Price, West, & Smith, 1994; Sauter, Emin, Schuchmann, & Tavman, 2008; Weiss, Kristbergson, & Kjartansson, 2011). A general explanation of the phenomenon is that sonication generates ultrasonic cavitation, i.e. the formation of micro bubbles in the liquid caused by a rapid drop in local pressure below the vapour pressure of the liquid. In addition, there are more limiting conditions necessary like the presence of a nucleus or a suitable magnitude of static pressure in the liquid (Brennen, 1995; Sauter et al., 2008). If the local pressure exceeds the vapour pressure, the reduction in bubble volume can lead to a violent collapse of the bubble. This violent collapse means an enormous compression of the bubble content (in aqueous systems mostly a mixture of vapour and gas) and is accompanied by a high local temperature of up to 1000 K and a pressure of several 100 MPa (Philipp & Lauterborn, 1998; Suslick & Flannigan, 2008).

In aqueous systems, cavitation causes the formation of substances such as H<sub>2</sub>O<sub>2</sub> or radicals that can initiate secondary

reactions (Manickam & Rana, 2011; Suslick, Mdleleni, & Ries, 1997). Furthermore, there are two mechanical effects associated with the collapse—the formation of shock waves and the formation of high-speed liquid jets during a non-spherical collapse (transient cavitation), (Brujan, Nahen, Schmidt, & Vogel, 2001; Lindau & Lauterborn, 2003; Tomita & Shima, 1990).

The occurrence and extent of cavitation is linked to various parameters of the ultrasonic field such as frequency, sound wave amplitude or intensity (Neppiras, 1980; Lauterborn & Ohl, 1997). The cavitation bubble in an ultrasonic field oscillates in a stable, spherical shape corresponding to the oscillating pressure (Brennen, 1995). The bubble grows to a critical size as a function of time due to non-linear gas diffusion (rectified diffusion) (Neppiras, 1980). This critical bubble size depends on the frequency of the oscillating pressure and thus in turn on the ultrasonic frequency. Lower frequencies result in larger bubbles and thus in a more vigorous collapse. Cavitation can break both non-covalent and covalent bonds in polymers. However, there is no fundamental knowledge as to whether the mechanical or the chemical effects induce the breakage (Weiss et al., 2011).

Ultrasonic degradation in aqueous solutions has been investigated for many synthetic polymers like poly(acrylamide), poly(acrylic acid), poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethylene oxide) and polysaccharides like dextrans, pullulans, agarose, chitosan, starch, and carboxymethyl cellulose as referred to by Koda, Taguchi, and Futamura (2011). They concluded from this work that the degradation of water-soluble polymers in

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aqueous solutions occurs by midpoint scission of the polymer chain as a result of the mechanical effects induced by the ultrasound. Furthermore, it is a well-known fact that ultrasonic irradiation of an aqueous solution results in the production of OH and H radicals, especially at high frequencies (Riesz & Kondo, 1992), which enhance the degradation of polymers in solution. The physical modification of the starch structure and functionality by ultrasound has been summarized and discussed elsewhere (Radosta, Kiessler, Vorweg, & Brenner, 2015). In the latter study, the ultrasonic degradation of starch polysaccharides in solution was employed to prepare degraded starch as a surface sizing agent.

The use of degraded starch derivatives as surface sizing agents to increase paper dry strength is a widespread method used throughout the papermaking process. Surface application is carried out in a size or film press in most cases. These devices are located in the rear portion of the paper machine drying section. Surface application requires the adjustment of the molecular composition of the degraded starch in such a way as to achieve the desired low viscosity of the starch solution at the processing concentration. For this purpose, native starch from potato, wheat or corn is used in most cases. The starch slurry in a concentration of about 15–30% is degraded to the desired solution viscosity by enzymes or by a thermal-oxidation process. Degradation is carried out continuously in a jet cooker (JC) or batchwise in a reactor. The increase in paper strength by the surface application of degraded starch is achieved in two different ways. Especially small starch molecules penetrate into the fibre web, thus adding internal strength to the paper. Larger molecules are able to form a film on the fibre web surface, thus also contributing to paper strength. Strong starch degradation results in low molar mass, allowing high solution concentrations and high penetration at a defined viscosity. On the other hand, however, the binding power of the starch polysaccharides decreases with increasing degradation. So the challenge is to find the optimal molecular composition of the starch solution to yield low viscosity at a high concentration with an optimal ratio between penetration and surface film formation. Preferably, a high content of dry matter is pursued for economic reasons. Both industrially used degradation processes for preparing sizing starches, enzymatic and thermo-oxidative degradation, can be controlled very well, and have both advantages and disadvantages. (Radosta & Kiessler, 2008)

The objective of these studies was to determine achievable cavitation efficiencies in order to prepare degraded starch for surface application on paper. The cavitation process was compared to conventional preparation processes for sizing starch with regard to the molecular and rheological properties of starch solutions, the resulting strength properties of surface sized paper and an efficiency analysis. During the study with acoustically and hydrodynamically generated cavitation, it was found that treatment with acoustic (ultrasonic) cavitation only led to suitable results with respect to a decrease in starch solution viscosity. For this reason, hydrodynamic cavitation will not be included in this paper. The method focused on was the use of acoustically generated cavitation. In particular, the impact of cavitation on the molecular composition of the degraded starch and its application for surface sizing were considered.

## 2. Materials and methods

### 2.1. Materials

The starch used was native corn starch. The corn starch was purchased from Tate & Lyle (The Netherlands).

The corrugated paper used was based on recycled fibres from recovered paper grades 1.02.00 and 1.04.00 according to EN 643:2014 with a grammage of 100 g m<sup>-2</sup> without surface starch.

The mechanical book paper used was based on virgin fibres with a grammage of 90 g m<sup>-2</sup> without surface starch. Sample O represents the reference sample and is paper without the surface application of a starch solution.

The oxidizing agent used for the thermo-oxidation jet cooking process was ammonium persulphate purchased by Rhein-PerChemie rpc GmbH (Germany).

The enzyme alpha-amylase Warozym A152 produced by Woellner GmbH & Co. KG (Germany) was employed in the enzymatic jet cooking process.

### 2.2. Analytical methods

#### 2.2.1. Starch solution viscosity

The viscosity of the starch solution was determined using a Brookfield viscometer RVDV-I+ version 5.0 at 100 rpm, 50 °C and with spindles RV1-RV3 purchased from Brookfield Engineering Laboratories, Inc. (United States of America).

#### 2.2.2. Molecular characterization of the starch products

The analysis of molar mass distribution, the determination of the iodine absorption spectra, and the debranching analysis for the degraded starch products have been described elsewhere (Radosta et al., 2015).

#### 2.2.3. Starch content of surface sized papers

In order to determine starch content, approximately 2 g of surface sized paper was cut into small pieces and dispersed in about 10 mL of de-ionised water. After a swelling time of 30 min at 60 °C, the samples were repulped. The pulp samples thus formed were adjusted to a pH of 4.6 using aqueous acetic acid and an acetate buffer. The starch content in the pulp samples was determined by the enzymatic hydrolysis of starch to form glucose using amyloglucosidase purchased from Roche Diagnostics GmbH (Germany). The amount of glucose was determined quantitatively using a Super GL easy biosensor made by Müller Gerätebau GmbH (Germany). The starch content was calculated from the glucose content by a factor of 0.9. The amount of starch coming from the corrugated paper was determined separately and subtracted from the starch content measured after surface application.

#### 2.2.4. Paper properties

The surface sized paper was air conditioned for 24 h at a temperature of 23 °C and a relative humidity of 50% before determining the paper properties.

The grammage of the paper was determined according to EN ISO 536:2012. The paper properties were determined by the prescribed standard specifications: tensile strength according to DIN EN ISO 1942-2:2009 and bursting strength according to DIN EN ISO 2758:2003.

### 2.3. Pilot-scale studies

#### 2.3.1. Preparation of starch solutions by jet cooking

The preparation of starch solutions were plotted in Fig. 1. The starch was cooked in a pilot jet cooker (Cavitron-v. Hagen & Funke Verfahrenstechnik GmbH, Germany) which had a rated maximum capacity of 50 L.

The starting starch solutions for high-power ultrasonic treatment were produced by jet cooking starch slurries with a solids content of 75 g L<sup>-1</sup> (sample 0-UL1) and a solids content of 85 g L<sup>-1</sup> (samples 0-UL2, 0-UL3) without adding any enzyme or oxidizing agent. The temperature during the cooking process was 130 °C for samples 0-UL1 and 0-UL2 and 100 °C for sample 0-UL3 with a retention time of 40 s. The solution concentration after JC was 52 g L<sup>-1</sup> for sample 0-UL1 and 62 g L<sup>-1</sup> for samples 0-UL2 and 0-UL3. These

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