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Starch Swelling and Its Role in Modern Ceramic Shaping Technology

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Summary: A microscopic real-time visualisation of potato starch swelling in aqueous media at 56 °C is performed. The viscosity increase of a starch-water mixture during the swelling step is documented by viscometric measurements. The mechanism of ceramic green-body formation in a new ceramic shaping process, called "starch consolidation", is discussed. In particular, the rheological changes during swelling and their concomitant structural background can explain certain discrepancies between model predictions and experimental findings observed in previous work.

Keywords: biopolymers; ceramic shaping technology; polysaccharides; starch; swelling

Introduction

In the last two decades, new ceramic shaping technologies have been developed that are able to overcome some of the limitations of classic shaping procedures. Most of these new techniques are based on the ability of organic substances (with or without water) to undergo phase transitions (chemically or thermally initiated) that allow the in-situ preparation of ceramic green bodies from ceramic suspensions. Starch is one of these substances. It is well known that starch granules, when exposed in excess water to moderately elevated temperatures, undergo a process of irreversible swelling and crystalline melting, called gelatinization.[1] Thus, the starch-water system was one of the possible media to prepare (porous) ceramic green bodies. Traditionally, starch was used as a pore-forming agent in classic ceramic shaping technologies (e.g. extrusion of ceramic pastes).

Starch is a native polysaccharide, a mixture of two D-glucose polymers (larger, branched amylopectin and smaller, linear amylose). Typical of biopolymers, starch granules have unique structures and microscopic features, their shape and size differ according to the botanical origin (e.g. rice, maize, corn or potato).[2]

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A few years ago, a new ceramic shaping method – starch consolidation[3] – was proposed, in which starch is used in the preparation of ceramics. This technique makes use of the ability of starch to swell in water at elevated temperature and to form a rigid ceramic green body from a ceramic suspension. At the same time, of course, starch serves as a pore-forming agent in the ceramic matrix. Consequently, this shaping method is appropriate only for preparing porous ceramics. In the meantime, starch consolidation has been successfully used to make alumina ceramics, zirconia ceramics and alumina-zirconia composites,[4] cordierite ceramics,[5] and bioactive calcium carbonate implants.[6]

Recently, a simplified geometric model of ceramic green body formation due to starch swelling was proposed, and its predictions were compared with experimental findings in real ceramic suspensions.[7-8] The model is based on an excluded-volume approach and can serve, in combination with independently measured data concerning the starch swelling kinetics, as a framework for predicting the kinetics of body formation. More precisely, it can deliver an estimate of the minimum time needed for the formation of a net-shaped green (i.e. unsintered) ceramic body from the starch-containing ceramic suspension in the starch consolidation process. In the present paper the process of starch swelling is studied by optical microscopy and viscometric measurements. Based on the qualitative findings of this work, the mechanism of the starch consolidation process is discussed.

Experimental

The microscopic real-time visualisation of potato starch (Solamyl, Natura, Czech Republic) swelling in excess water at elevated temperature (56 °C) was performed on a specially constructed optical flow-through cell connected to a thermostat (B3, Haake, Germany). The flow-through cell (closed heating circle) connected to the thermostat was used (instead of a heatable object holder) in order to keep the temperature of water on the transparent sample holder (with the starch suspension) at the required constant temperature (56 °C) during microscopic imaging. The stages of swelling were recorded every 25 s for a total time of 30 min using image-analysing software (Lucia G, Laboratory Imaging, Czech Republic). This computer-controlled imaging system allowed to monitor starch swelling as a continuous process and to observe the gradual growth of starch globules. Although in principle the software allows quantitative evaluation of microscopic features (e.g. the size distribution of the starch during the individual stages of swelling) this was not performed in the present work.

Concomitantly with swelling of the starch globules, supported by partial dissolution of the amylose and amylopectin units, the originally aqueous matrix is transformed from a purely viscous suspension to a viscoelastic gel. The viscosity increase of the starch - water mixtures was documented by viscometric measurements (coaxial cylinder system, Z-41, Haake, Germany) in the shear mode (RV-1, Haake, Germany) until the onset of the phase transition to a viscoelastic gel. The starch suspension (15 vol.%) was heated to 56 °C using a thermostat and the apparent viscosity (at a shear rate of 500 s^{-1}) was recorded during 1 h.

Results and Discussion

Figure 1 shows four selected stages (after 0, 5, 15 and 25 min) of starch swelling as observed by optical microscopy. The micrographs give a qualitative picture of the growth of starch globules in excess water at a temperature corresponding to that of ceramic body formation (56 °C). It can be seen that the growth of starch globules is a fast process (a few minutes) at the investigated temperature. Furthermore, it is evident that not all starch globules grow at the same rate. During growth, globules can be damaged by excessive water uptake, while others remain intact. A future quantitative study of the starch swelling process using image analysis should take these findings into account.

On the viscosity-time curve, Figure 2, three regions can be distinguished: The first corresponds to a purely viscous suspension with a viscosity almost constant in time, i.e. a system of individual starch globules and water with no or only a few swelling starch particles. This situation prevails until a time of approx. 4 min from the start of the experiment. The second region (minutes 4 - 11) shows a steep increase in the shear viscosity corresponding to the stage of fast swelling of starch globules by water uptake. At this stage, the effective increase in the starch volume fraction is the main reason for the viscosity increase. At the end of the second stage, the transition from purely viscous to viscoelastic behavior is the main effect. This region, of course, cannot be adequately measured by steady-shear viscometry alone (tests in the oscillatory mode would be needed to quantify viscoelastic behavior). In the third region, the structure of polymers is altered and single chains change their spatial conformations. The increase in shear viscosity with time is notably slower in this region until a point is reached where the shear viscosity becomes immeasurable and undefined.

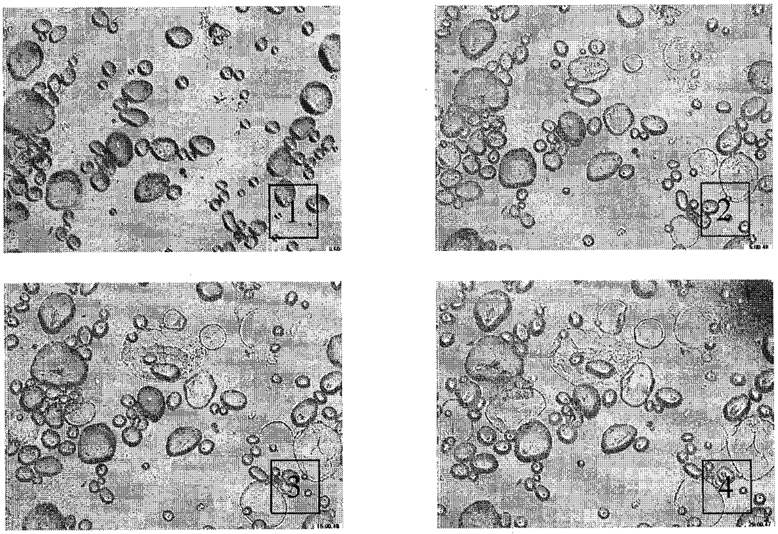

Fig. 1. Micrographs of swelling starch globules in excess water at 56 °C after 0, 5, 15 and 25 min (see pictures 1, 2, 3, and 4, respectively).

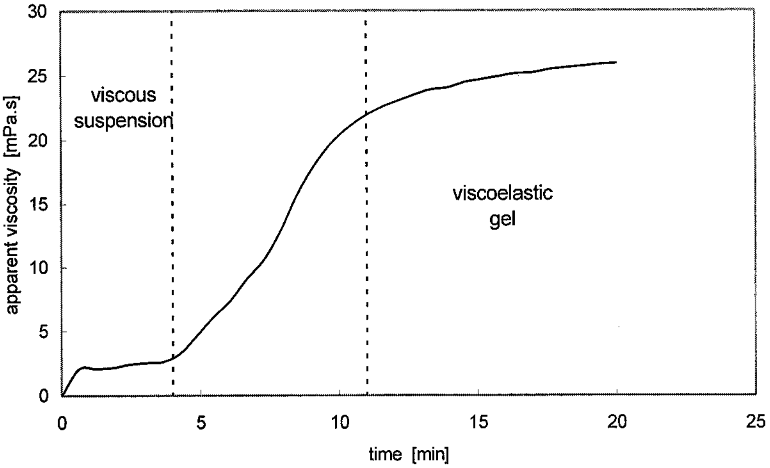

Fig. 2. Increase in apparent viscosity of starch suspension with time measured, at constant shear rate ($\gamma = 500\ s^{-1}$) in steady shear mode.

The results underpin some of the hypotheses made in connection with our previous results.[7-8] In these studies, a simplified geometric model of the system starch-water-oxide ceramic powder was proposed to predict the minimum time necessary to form a ceramic green body from suspension. The time evolution of the particle size distribution of starch heated in excess water was measured by low-angle laser light scattering, and the swelling kinetics of starch was quantified by drawing the arithmetic-mean equivalent diameters of the (volume-weighted) particle size distribution versus heating time. The determined swelling kinetics was fitted by empirical models and could be used to predict minimum body formation times. For an alumina suspension with 15 vol% starch, the thus predicted body formation time (prediction based on a purely geometrical "excluded volume" model without consideration of rheological aspects) was approx. 8 min while experimental findings indicated at least 12 min. This discrepancy can be attributed to changes in the structure and rheology of the starch-water system, when the body formation process in space is already finished.

Conclusion

Starch swelling and its role in a modern ceramic shaping method, starch consolidation, were discussed. Swelling of starch globules was observed by optical microscopy. Their growth is quite fast, but the growth rate is not the same for all starch globules. During growth, some globules cracked, while others retained their integrity. The viscometric measurements showed that the viscosity of the system increased as a result of starch swelling. The fastest increase in shear viscosity occurs in the time interval between minutes 4-11 from the beginning of the experiment. After this increase, a transition to a viscoelastic gel proceeds, which cannot be adequately characterized by steady shear viscometry and which is accompanied by structural changes in the starch - water system, leading to the formation of a rigid gel network. This underpins our previous hypotheses concerning the reason why a longer time is needed for the body formation than predicted from the simplified ("excluded volume") geometric model.

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