

Melt Rheology Affect Zein Foam Properties

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ABSTRACT

A foamable material must possess gas-retaining properties; these can be evaluated by rheological measurements. This paper presents how the concentration of plasticizer affect the rheological properties of the zein melt, and how this in turn affect the end-product foam in terms of porosity and microstructure.

INTRODUCTION

Today, large amounts of petroleum are used for disposables, packages and fuel. This runs counter an environmentally and climate friendly development, as petroleum is not a renewable resource. One alternative to petroleum based fuel is bio-ethanol made from cereals. In this process only the starch of the cereals is consumed, leaving cereal proteins, such as prolamins as by-products. In the U.S., ethanol biofuel is predominantly manufactured from maize, and hence the maize prolamin zein is left available. Zein has long been recognized as a potential resource for materials manufacturing¹.

Materials manufactured from zein have been extensively investigated and reported on. However, those reports and investigations almost exclusively deal with materials in the shape of films. In the present project, we are studying foamed zein, which is in contrast to previous studies. Theories regarding foaming of solid foams state that the pre-foam material must possess gas-retaining properties. These can

fortunately be evaluated by rheological measurements.

During foam formation, gas cells grow through biaxial extension at high strains and usually low extension rates. Low viscosity is necessary for bubble nucleation, but on the other hand, there is a lower viscosity limit under which the cell walls collapse during cell expansion. This, of course, causes failure of the foaming process. Extensional viscosity measurements of the pre-foam material can show whether it fulfils the requirements for foaming.

In this investigation zein resins were prepared, rheologically analyzed and foamed by solvent evaporation. The foams were then characterized with respect to structure and porosity. This paper hence offers an investigation of how foam properties are affected by the rheological properties of the zein resin, which in turn are controlled by the plasticizer contents.

EXPERIMENTAL

Resin and Foam Formation¹

Commercial zein (Z3625; Sigma-Aldrich, Schnelldorf, Germany) was defatted in n-hexane as described by Oom et al.². The protein content of zein was 92% (w/w), determined using the Dumas method and multiplying the nitrogen content by 6.25. Zein resins were then prepared by mixing 3.0 g (dry weight) zein powder with

oleic acid (as plasticizer, different concentrations) and 1.05 g aqueous ethanol (70% w/w). The mixtures were kneaded by hand for approximately one minute until resins were formed. A zein resin was placed in a vertically orientated cylindrical hole (20 mm diameter) in an aluminium block (width 62 mm, length 62mm, height 80 mm). The block with the resin was kept in an oven at 175 °C for 20 minutes. Thereafter, the block with the newly formed, cylindrical shaped foam was allowed to cool.

Dynamic Measurements

Dynamic measurements in small amplitude oscillatory shear were performed as described by Oom et al.² using a Stresstech HR Rheometer (Rheologica Instruments, Lund, Sweden) equipped with parallel plates of 15 mm diameter. Samples were applied between the plates with a gap of 3 mm and the periphery of the sample was covered with paraffin oil to prevent evaporation and oxidation. Time scans were performed on zein-resins using a constant frequency of 1 Hz and applying a constant stress, which was well within the linear viscoelastic region for the material. The shift in phase angle and the storage- and loss moduli were recorded during 8500 s. The mechanical spectra were obtained through a frequency scan between 10 and 0.01 Hz. The applied stress was well within the linear region. The Cox-Merz' rule was applied and data were fitted into the Power-law model for shear flow to obtain the Power-law index n and constant K needed for Hyperbolic Contraction Flow measurements. Analysis was performed at 22 °C.

Hyperbolic Contraction Flow

The extensional rheological properties of the resins were measured as described by Oom et al.² using a Hyperbolic Contraction Flow rig^{3, 4} mounted in an Instron 5542 Universal Testing Instrument (Instron Corporation, Canton, USA). The extensional strain rate used were 0.1 s^{-1} , as described by Wikström and Bohlin³. The transient

extensional stress was monitored until reaching a stable plateau value from which the maximum extensional viscosity was calculated. The total Hencky strain was 8.1 for the zein resins, and used for compensating for shear stress contribution to the total stress⁴. Measurements were performed at 22 °C.

Structure Analysis

Foam cylinders were cleaved in two and scanned with a Canon CanoScan N1240U scanner (Canon Inc., Tokyo, Japan).

Porosity was calculated according to:

$$P = 1 - \frac{d_f}{d_s} \quad (1)$$

where P is the porosity, d_f is the density of the foam and d_s is the density of solid bulk zein.

RESULTS AND DISCUSSION

Extensional viscosity of resins with different plasticizer concentrations are shown in Fig. 1. It is evident that increasing plasticizer content leads to decreasing extensional viscosity.

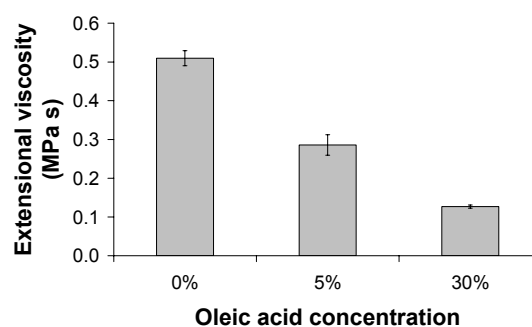


Figure 1. Extensional viscosity of zein resins with different plasticizer contents.

Foam from resin without oleic acid (Fig. 2) has a typical cell diameter from 1 – 2 mm. It is clear to see that under current conditions, addition of plasticizer (oleic acid) affects the creation of a regular foam structure negatively.

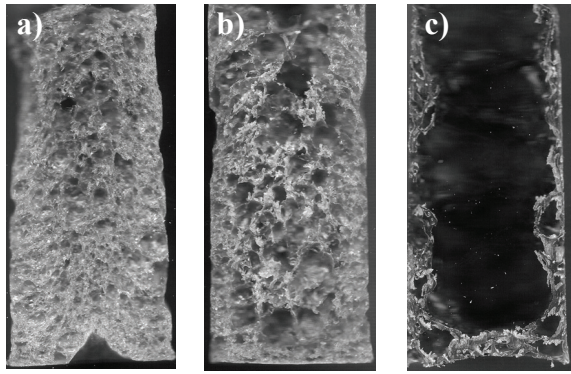


Figure 2. Zein foam with a) 0% plasticizer, b) 5% plasticizer and c) 30% plasticizer. The cylinder width is approximately 20 mm.

An addition of 5% oleic acid makes the foam structure more irregular, and adding 30% oleic acid results in an empty cylindrical shell, instead of a cylindrical foam. Consequently, the porosity (Fig. 3) is also decreased with increased plasticizer content. The porosity of the 30% oleic acid sample could not be measured, since this resin did not foam properly.

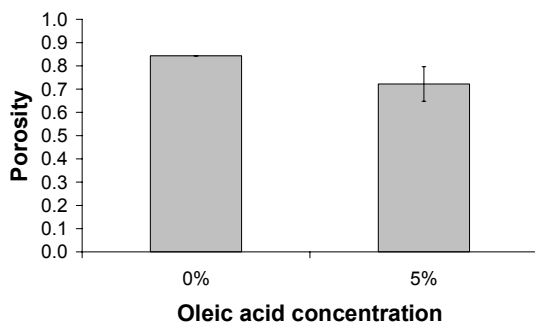


Figure 3. Porosity of zein foams made from resins with different plasticizer contents.

It is likely that the decreased extensional viscosity was too low for the resin to resist the strain of expanding bubbles. The cell walls therefore rupture when the strain gets too high, and the gas leaks out. However, since the resin is heated up from the outside and in, the aqueous ethanol likely evaporates from the periphery of the resin cylinder first. This decreases the plasticization of the resin, and thereby the extensional viscosity is increased. In turn, this leads to a greater gas

retaining capacity. The result is the shell seen in Fig. 2c). Even 2a) and 2b) show a more regular foam structure near the edges of the cylinder, than in the middle.

CONCLUSION

Rheological measurements can predict the foamability of a zein resin. This is likely also applicable on other resin-similar materials, e.g. resins from other biopolymers. Future studies will determine the upper extensional viscosity limit for bubble nucleation in zein resins, and also investigate the strain hardening properties of these materials.

ACKNOWLEDGMENTS

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