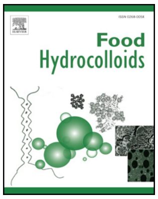
Food Hydrocolloids 87 (2019) 497–505

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd



Air bubbles in calcium caseinate fibrous material enhances anisotropy

Zhaojun Wang[a], Bei Tian[b], Remko Boom[a], Atze Jan van der Goot[a,*]

[a] Food Process Engineering, Wageningen University & Research, PO Box 17, 6700AA, Wageningen, the Netherlands
[b] Department of Radiation Science and Technology, Faculty of Applied Science, Delft University of Technology, Mekelweg 15, 2629JB, Delft, the Netherlands

ARTICLE INFO

Keywords:
Air bubble
Fibrous material
Microstructure
Mechanical property
Anisotropy

ABSTRACT

Dense calcium caseinate dispersions can be transformed into hierarchically fibrous structures by shear deformation. This transformation can be attributed to the intrinsic properties of calcium caseinate. Depending on the dispersion preparation method, a certain amount of air gets entrapped in the sheared protein matrix. Although anisotropy is obtained in the absence of entrapped air, the fibrous appearance and mechanical anisotropy of the calcium caseinate materials are more pronounced with dispersed air present. The presence of air induces the protein fibers to be arranged in microscale bundles, and the fracture strain and stress in the parallel direction are larger compared with the material without air. The effects can be understood from the alignment of the fibers in the parallel direction, providing strain energy dissipation. This study shows that creation of anisotropy is the result of interactions between multiple phases.

1. Introduction

A decade ago, an anisotropic calcium caseinate structure was created by a novel technique based on well-defined shear flow (Manski, van der Goot, & Boom, 2007b, 2007a), which is relevant for its structural resemblance to meat. Therefore, it has a potential to be a basis of new meat analogue products. The calcium caseinate dispersion was deformed by simple shear flow and concurrent crosslinking by transglutaminase. A typical fiber diameter of ∼100–200 nm was observed with scanning electron microscopy (Manski et al., 2007b). The formation of this fibrous morphology was attributed to the aggregation of caseinate micelles, which have mildly attractive interactions due to the divalent calcium ions (Manski, van Riemsdijk, Boom, & van der Goot, 2007c). The aggregates are susceptible to aligning in the shear flow and simultaneously solidifying with transglutaminase. The presence of calcium ions was shown to be essential; the anisotropic structure could not be formed with sodium caseinate, and the formation of the fibrous structure was blocked by the addition of sodium triphosphate, which exchanges the divalent calcium ions bound to the protein with sodium ions (Grabowska, van der Goot, & Boom, 2012).

Dispersed air was observed in these calcium caseinate fibrous materials (Manski et al., 2007b; Manski, van der Zalm, van der Goot, & Boom, 2008), and also in materials created with soy protein isolate with wheat gluten blend (Grabowska, Tekidou, Boom, & van der Goot, 2014) and soy protein isolate with pectin blend (Dekkers, Hamoen, Boom, & van der Goot, 2018). A more recent study revealed that such fibrous materials may contain up to 20% (v/v) air with an average bubble diameter of ∼100–400 μm (Tian, Wang, van der Goot, & Bouwman, 2018). The dispersed air provides an additional phase that influences the texture, microstructure, and functionality (Campbell & Mougeot, 1999; Zúñiga & Aguilera, 2009). During dough mixing, it was found that air entrapment affects the dough rheology. The rate of work input during dough mixing increased due to the presence of air bubbles while the resistance of dough to failure decreased under biaxial extension (Chin, Martin, & Campbell, 2005). A study on agar gel showed that an aerated gel is stronger than a gel without air (Ross, Pyrak-Nolte, & Campanella, 2006; Tiwari & Bhattacharya, 2011). Many natural porous composites, which are often hierarchically organized at multiple length scales (nano-, micro- and macroscale), have remarkable strength from the alignment of their fibers, crystals, or other structural elements, but have great toughness at low density (Gibson, 2012; Wegst, Bai, Saiz, Tomsia, & Ritchie, 2015); examples are bamboo and wood. The voids play a significant role in fracture toughening (Habibi & Lu, 2014; Lakes, 1993; Stanzl-Tschegg, Keunecke, & Tschegg, 2011; Wegst et al., 2015). For wood, the pores within the structure arrest cracks by the dispersion of stress over the surface of the pore after it has been compromised (Stanzl-Tschegg et al., 2011). This also occurs in synthetic cellular composite materials, such as honeycombs (Greil et al., 2002; Haghpanah, Oftadeh, Papadopoulos, & Vaziri, 2013) and foams (Andersons, Kirpluks, Stiebra, & Cabulis, 2015; Olurin, Fleck, & Ashby,

---

* Corresponding author.
E-mail addresses: zhaojun.wang@wur.nl (Z. Wang), B.Tian-1@tudelft.nl (B. Tian), remko.boom@wur.nl (R. Boom), atzejan.vandergoot@wur.nl (A.J. van der Goot).

https://doi.org/10.1016/j.foodhyd.2018.08.037
Received 23 May 2018; Received in revised form 20 August 2018; Accepted 20 August 2018

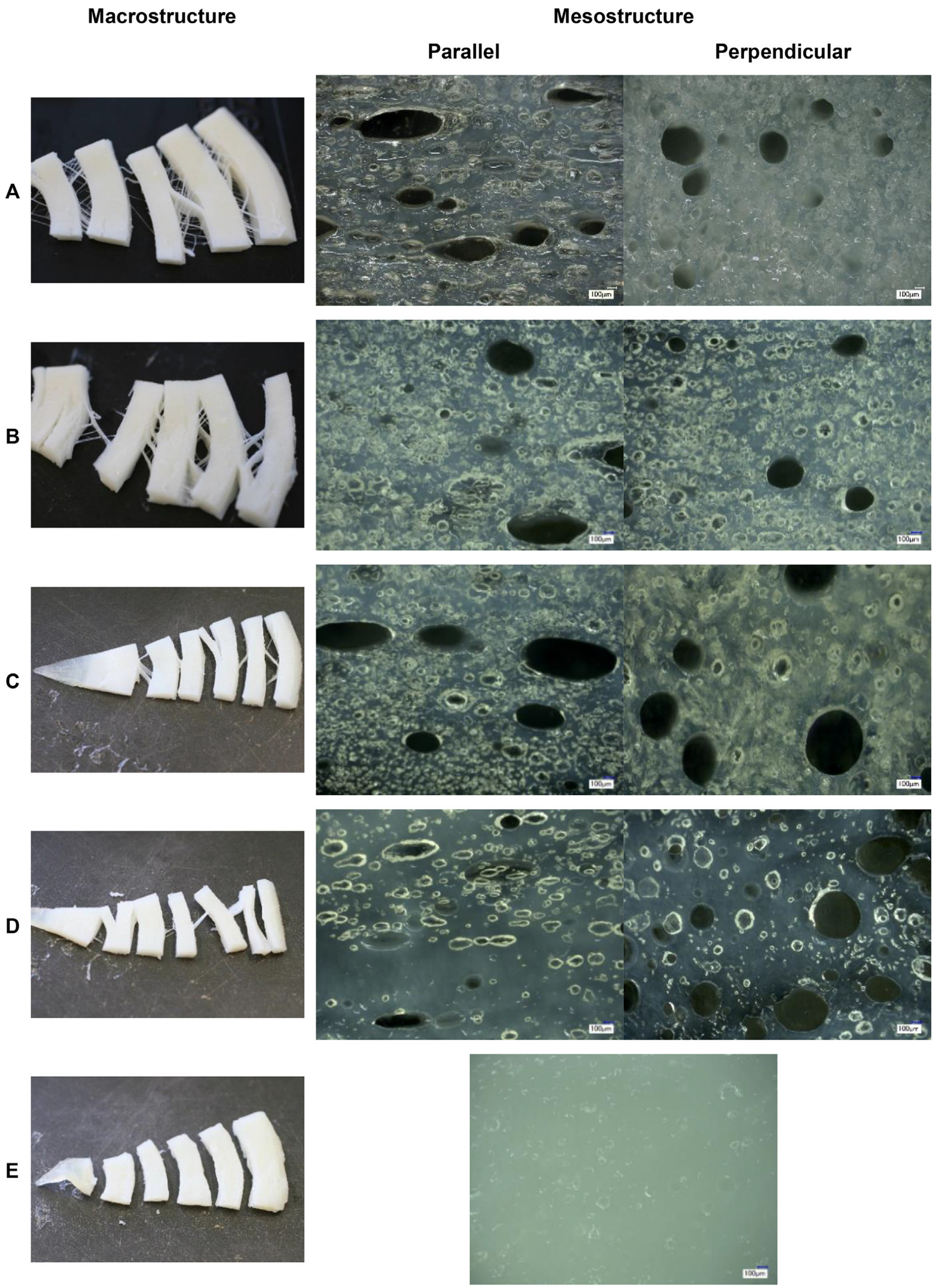


Fig. 1. Macrostructure and light microscopy images of 30% w/w calcium caseinate materials prepared with the different premixes A–E. The scale bars in the light microscopy images denote 100 μm.

2001).

The entrapment of air can introduce an extra separate phase into the calcium caseinate material (Manski et al., 2008), and may well lead to different mechanical properties. In this paper, we investigate the role of air bubbles on the microstructure and mechanical properties of the material structure. The morphology of entrapped air was studied with reflective light microscopy and X-ray tomography. Scanning electron microscopy was used to study the protein structure in the vicinity of air bubbles. Differences in mechanical properties were revealed with tensile analysis.