
3 Design of Foods Using Naturally Structured Materials

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3.1 INTRODUCTION

Firstly, it is worth defining what will be covered in this chapter. The use of new insights from processing opportunities will be identified, such that an increased use of natural plant cell-wall materials (PCWMs) can be used in food production in a reproducible way. The area of natural structurants is a vast one, and most food ingredient suppliers might argue that their products are natural, or at least derived from natural sources. Plant cell-wall polymers (e.g. pectins), storage polymers from seeds, grains or tubers (e.g. locust bean gum, starch, xyloglucan), microbial exudate gums (e.g. xanthan, pullulan, curdlan, gellan) and chitosan from crustacean shells might all be identified as water-soluble polysaccharides, and all provide thickening and/or gelation properties, utilised in the structuring of the aqueous phase of food products. Similarly, the proteins commonly used in foods are also from natural origin (e.g. milk, soya, egg, potato). These aforementioned polymers are covered in significant detail in other publications (Phillips and Williams, 2009, 2011), and it is not the intention to review them, or their application through product design, as their use has already been introduced effectively (Norton and Frith, 2001; Norton and Foster, 2002; Foster, 2007).

It is worth considering their *origins*, however, as structuring materials in their own right. The polymers previously introduced are refined polymers, and in industrial use are often accompanied by very tight specifications, such as molecular weight, gel strength or viscosity at certain concentrations and under known environmental conditions (such as temperature), for certain lengths of time, colour, dry particle mess size and even defined fine structure content (e.g. degree of esterification of pectins or the galactose:mannose or guluronate:mannuronate

ratios of galactomannans or alginates, respectively). What is not as well understood, and therefore specifications remain undefined, is the designed use of less refined materials from PCWM. The properties of these materials are very dependent on the material origin. Harris and Smith (2006) describe them as either “outer” or “inner” fibres, typically derived from lignified secondary cell walls or non-lignified parenchyma walls, respectively. Broadly speaking, the “inner” fibres are able to modify texture, whereas “outer” fibres are currently sources of high insoluble dietary fibre. There is therefore a potential for greater use of these materials in foods. Indeed, Larrauri (1999) reviewed the opportunity for using high dietary fibre powders from fruit by-products for this purpose. At that time refining steps included only milling and screening or wet milling, washing, drying and dry milling. Some of the recommended properties identified for such fibres were to be: bland tasting; a balanced composition of soluble and insoluble fractions, and for health purposes to be associated with bioactive components, and be compatible with typical food processes. Larrauri (1999) also indicated certain process steps required to produce high dietary fibre products, which include: the use of alkaline hydrogen peroxide delignification; extrusion; encapsulation and enzyme modification. Work in understanding the capability and feasibility of the use of PCWM in foods was later reviewed by Foster (2011), who identified four main “conversion” routes for PCWM: the use of enzymatic, thermal, mechanical and chemical steps, along with combinations of these. All of these have effects on the constituent polymers within the PCWM, and a knowledgeable blending step post process might be the route for the provision for specification of these materials for controlled and, more importantly, reproducible food production.

Natural ripening events occurring *in vivo* are mediated by a host of enzymes working on the PCWM polymers. Pectin methylesterase, polygalacturonase and pectin lyase enzymes determine fruit softening and cell–cell debonding. Thermal (hot break) processing of such materials may control subsequent enzyme action upon pureeing/homogenisation of the material, providing control of material properties (Appelqvist *et al.*, 2002). Indeed, the processing without heating (cold break) of material at different stages of ripening e.g. tomato, show an increase in particle size and overall paste viscosity for less mature and more physically intact cell walls (Abson *et al.*, 2012). A number of studies (Belmar *et al.*, 1999a,b; Bayod *et al.*, 2007; Fischer, 2008; and Martins Silva *et al.*, 2010) have shown the effect of homogenising purees on the functionality of PCWM. Fischer (2008) shows that both water uptake and an increase in volume occupancy of a hydrated particle suspension of PCWM is dependent upon vegetal material type, with the more robust PCWM of cereals being less effective than

the softer fruit pulps. Current understanding is that homogenisation increases the viscosity of the paste due to an opening up of the PCWM structure and an increase in particle size and volume occupancy, whereas above certain homogenisation pressures, which will be tissue-type dependent, the viscosity is seen to decrease, with an accompanying decrease in particle size (Den Ouden and van Vliet, 2002).

3.2 SO WHAT DOES THIS MEAN FOR FOOD PROCESSING?

Such effects of processing require a material/molecular understanding, with such an understanding ultimately re-designing/defining the optimal processing conditions required to produce well-defined materials for use in the food industry. Both Nawirska and Kwasniewska (2005) and Jarvis (2011) have begun to ascribe hierarchical descriptions of these phenomena, by describing the polymeric components of PCWM as supramolecular assemblies. By taking such an approach one can therefore consider how such assemblies are constructed by nature, and from a food processing perspective how such assemblies are controllably deconstructed for optimal/designed functionality. Seymour *et al.* (1990) showed that even after extraction of middle lamella pectins (washed with 1,2-cyclohexanediaminetetraacetic acid (CDTA)) and increasing intensity of alkali washing, pectic materials were still present in the insoluble cellulose fraction. Later, Foster *et al.* (1995), using solid-state NMR with magic-angle spinning to determine the qualitative composition and molecular motions of polymers within the PCWM structures, showed pectic galactans filling the cellulose–hemicellulose network pores. Additionally, the latter study showed commonality across both variety (onion, tomato, pea and tobacco) and tissue (fruit, stem and leaf), while also showing that the cellulose in the PCWM from different origin differed in non-crystalline content between 60–80%. Breakdown or removal of different fractions of the PCWM begins to show differences in the tissue type and structural origins of the mechanical properties. The extraction of pectinaceous material from apple (Redgwell *et al.*, 2008a; Sauvageau *et al.*, 2010) has shown hemicellulose–cellulose complexes in alcohol-insoluble and alkali-washed fractions, which were subsequently lost upon cellulase digestion of the hemicellulose–cellulose complex. Sequential extraction of polymers from cell wall fragments is another way of fingerprinting the characteristics of PCWM. Foster *et al.* (1995) used solid-state NMR, whereas direct visualisation, using AFM (atomic force microscopy) and TEM (transmission electron microscopy), shows a decrease in interfibre spacing from 26.2 to 11 nm, indicating shrinkage of the structure as the hemicellulose–cellulose

Table 3.1 Showing the proportions of different sugars in commercially available natural structurants, measured by gas chromatography after derivatisation, and crystallinity after curve fitting X-ray diffractograms (Janin and Foster, unpublished data).

Material	Proportion of Different Sugars					Cellulose Crystallinity (%)
	Glucose	Xylose	Mannose	Galactose	Arabinose	
Citrus Fibre	67.8	9.4	8.4	12.1	2.3	23
Natta de Coco	100	–	–	–	–	70
MCC	99.5	0.5	–	–	–	54
Powdered Cellulose	91.6	5.1	3.3	–	–	51

network is deconstructed and the swollen pectin network is removed (Kirby *et al.*, 2006). Table 3.1 shows a breakdown of the sugar composition and measured cellulose crystallinity of some current food grade materials.

Nata de Coco is a bacterial cellulose, entirely made from glucose, and has a high proportion of crystallinity, in line with expectation from such production protocols. Microcrystalline cellulose (MCC) contains very small amounts of alternative sugars, as expected from the acidic removal of amorphous cellulose regions within the cellulose microfibrils. Powdered cellulose contains traces of xylose and mannose from hemicellulose fractions remaining within the sample. The citrus fibre is the most interesting, because it contains a lot of residual PCW polymers, with galactose and arabinose indicative of residual pectin. From a food processing perspective this will promote the PCWM to be charged, imparting pH and salt dependencies.

Images of some of these samples (see Fig. 3.1) indicate that not only do the materials differ in polymer content, but also in their physical appearance. The dimensions of the citrus fibre (see Fig. 3.1a and c) and the powdered cellulose (see Fig. 3.1b and d) in the hydrated (see Fig. 3.1a and b) and dry (see Fig. 3.1c and d) state show differences in overall shape and aspect ratio.

3.3 SO HOW DO THESE DIFFERENCES AFFECT FUNCTIONALITY?

The rheological properties of plant tissue, isolated cells and isolated PCWM from tomato fruit show that the mechanical spectra are similar to hydrocolloid gel networks, with $G' > G''$, almost independent of frequency, with a slope of complex viscosity (η^*) ~ -1 . Both isolated pericarp cells and whole tissue can be influenced by turgor, and flaccid deformable cells showed a decrease in G' of concentrated dispersions

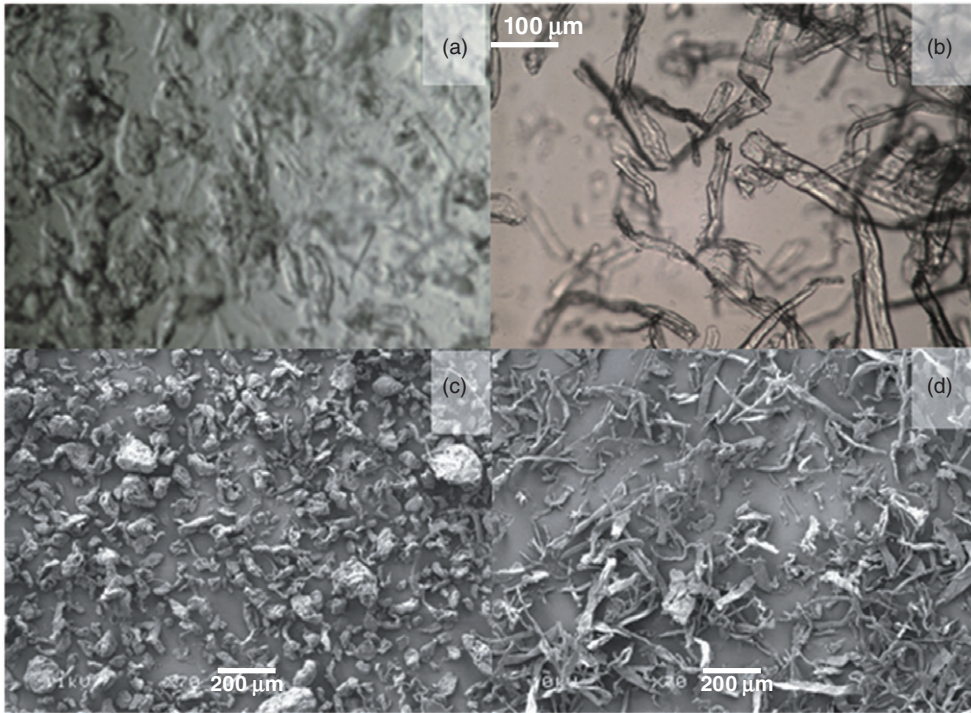


Fig. 3.1 Hydrated (a and b) and dry (c and d) of citrus fibre (a and c) and powdered cellulose (b and d). The scale bar in b is common for both hydrated micrographs and that in the dry sample in 200µm.

when compared, at constant dry weight, to fully turgid cells (Foster *et al.*, 1994). Cepeda and Gomes (2002) applied a modified Krieger–Dougherty model to describe the rheological characteristics of pimento puree, which included an electrostatic effect of the colloidal contribution to the zero shear-rate viscosity due to repulsion of particles. Indeed Abson *et al.* (2012) has shown that pureed material is also susceptible to influences of osmotic stress, where the properties are dependent upon the soluble solid levels. Redgwell *et al.* (2008b) has shown that the creation of structure through a suspension of either isolated cells or entangled/fragmented PCWM of shear-disrupted kiwi and tomato fruit samples is enhanced with an increase in the available surface area for particle–particle interactions, which were reduced in the presence of polyelectrolytes. The charge effects provided to such particles by the constituent pectinaceous material, therefore, also affect the interaction potential of particles, as found in the reported analysis of citrus fibre (see Table 3.1). Foster (2011) has discussed how particles which may

have the tendency to entangle differ from alternative particulate structurants, whereby a plateau in the elastic modulus of the fluid gel sample is apparent at around 3% dry weight, whereas the homogenised and un-homogenised fruit paste samples show a continual increase in modulus, indicating entanglement and particle–particle interactions. Day *et al.* (2010) have indicated network formation of particles below critical volume fraction, obeying a power-law relationship, in a similar way to that found by Frith *et al.* (2002) for irregularly shaped fluid gel particles. At higher packing volumes the complex modulus (G^*) can be modelled using equations employed to describe concentrated emulsions and elastic particle dispersions, with properties dominated by particle deformability (Den Ouden and van Vliet, 1997; Adams *et al.*, 2004). Sato and Cunha (2009) indicated that particle size distribution (PSD) of jaboticaba pulp, is an additional compounding factor in determining rheological-structure behaviour, with a broader PSD giving less viscous suspensions, due to improved packing efficiency at matched particle:serum ratio.

3.4 RECENT DEVELOPMENTS

The mechanical processes mentioned so far, such as pureeing and homogenisation have intimated an opening up of the cellular structure for improved water uptake and binding. A mechanistic view of this might be to unfold the clusters of cellular structures. However, there is an increasing volume of publications indicating that such processes have impact, at the molecular level, not only on the pectin and hemicellulose fractions, but also on the (previously believed) insoluble cellulose itself. Work in the early 1980s by Turback *et al.* (1983) and Herrick *et al.* (1983) introduced the concept of microfibrillated cellulose (MFC), whereby several passes through a homogeniser promotes dispersions of cellulose fibres to give gel-like consistencies. Chinga-Carrasco (2011) describes a gradual transition from inhomogeneous mixtures of elementary cellulose fibrils and native micro-/macrofibrils to homogeneous dispersions of more fibrillated cellulose upon more severe homogenisation. This is accompanied by a subsequent increase in transparency of the MFC. There is also an indication that homogeneous fibril qualities are facilitated by either enzymatic (Paakko *et al.*, 2007) or chemical (Saito *et al.*, 2006) pre-treatments.

Therefore, typical food processes may produce heterogeneous fibrillation, but in the case of systems possessing significant levels of hemicelluloses, the complexity of previously described insoluble and soluble material is clearly increased. Chinga-Carrasco (2011) also states that

an appropriate level of elementary nanofibrils has a major influence on mechanical, optical and barrier properties. Indeed, when poorly fibrillated fibres are filtered away, the remaining homogeneous nanofibrils produce transparent and high gas-barrier films. Kaushik and Singh (2011) have shown that nanofibrils can be produced from wheat straw using alkaline steam explosion followed by chemical and high shear treatment, with a removal of lignin and hemicellulose and an increase in thermal stability of the cellulose material. Acciaro *et al.* (2011) also describe the use of temperature-responsive cellulose microgels for controlled release, and Kolakovic *et al.* (2012) spray dried MFC for micro-particulate creation for sustained drug release. Chemical modification of MFC to produce carboxymethyl MFC allows MFC gels to be created with either a decrease in pH or an increase in ionic strength (Fall *et al.*, 2011).

Another emerging use of these materials is as surface active materials for emulsion and foam stabilisation. Hydrochloric acid hydrolysis of bacterial cellulose, post sonication, produces nanocrystals which stabilise 4µm oil droplets for several months (Kalashnikova *et al.*, 2011). Hydrophobised nanofibrils, either as single dispersed fibrils or network-like aggregates stabilised water-in-toluene emulsions (Xhanari *et al.*, 2011). Murray *et al.* (2011) reports cellulose:ethylcellulose as an emulsion and foam stabiliser. The cellulose component is fibrillated in a hammer mill and a cryogenic freezer mill, with ethylcellulose precipitated onto the fibrils through solvent exchange. They show that, in combination with protein, interfaces are stabilised against coalescence at lower protein concentrations than those required for stabilisation using protein alone.

Additional recent developments have been made to alter cellulosic systems using a ball mill. Paes *et al.* (2010) have reported the extent of ball milling on the de-crystallisation and re-crystallization of cellulose. Avolio *et al.* (2012), in a similar study, show not only a decrystallisation, but also a significant change in the morphology of the cellulose, from an initial fibre length of 200µm to 12µm, forming amorphous cellulose microparticles. Zhang *et al.* (2012), using back pressure-equal channel angular pressing have been able to process amorphous ball-milled cellulose into bulk plastic materials without using any additives.

A good review of sources of natural materials, how they might be processed and potential sustainable uses is provided by Khalil *et al.* (2012) and builds upon work by Mohanty *et al.* (2002) who summarised opportunities and challenges in the use of sustainable biocomposites. Therefore, so far we have investigated what opportunities may occur in the future. However, it worth considering the current competitive landscape in the availability of “natural” structurants.

3.5 EXAMPLES OF COMMERCIAL SAMPLES AND THEIR USE

Table 3.2 shows typical food products in which commercially available “natural” structurants are used. It can be seen that the span of product type is broad, from wet emulsions to dry baked goods/pastas, and from dairy to use in meat products. The properties provided are mainly associated with efficiency in the ability of the fibrous structures to swell and retain water. This can be seen directly in both “increased moisture” and “syneresis control”. Such water binding also plays a role in reducing the need for excessive amounts of fat, where structurally it is replaced with naturally structured water (Van Ruijven *et al.*, 2009), which also promotes creaminess perception. In the past, crosslinked starches and gel particles have been used to provide such properties (e.g. Bialek *et al.*, 2000), but Fig. 3.2 shows the structural similarities between PCWM, starch and gel particles, and when treated as particulate dispersions the mechanical properties are similar (Foster, 2011).

Table 3.2 Showing the use of commercially available natural structurants and their functional uses. Citri-Fi and Herbacel AQ Plus are examples of citrus fibres and Solka-Floc of powdered cellulose.

Product types	Properties provided	Example ingredient
Baked goods	Increased moistness	Citri-Fi
Crème fillings	Fat reduction	Hydro-Fi
Dairy products	Reduced trans/saturated fat	Herbacel AQ Plus
Fibre drinks	Egg reduction	Herbapekt LV / APE
Dressings / sauces	Syneresis control	Avicel MCC
Pasta	Cholesterol lowering	Solka-Floc
Nutrition bars	Appetite regulation	JustFiber
Meat products	Stimulating bowel function	NutraFiber
	Calorie reduction	
	Increase creaminess	
	Opacity	

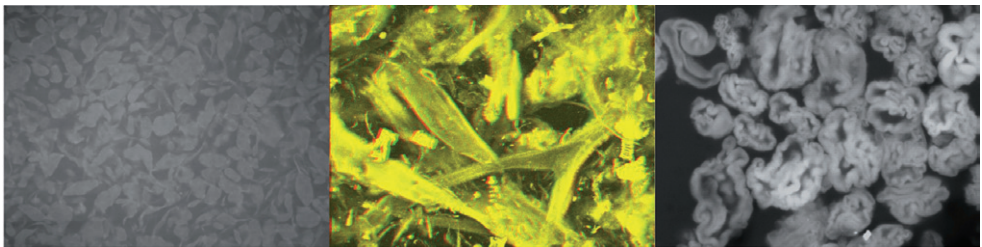


Fig. 3.2 A comparison of the structures of gel particles using CSLM (confocal scanning laser microscopy) (left), PCWM (centre) and crosslinked maize starch (right). Each image width is 200µm.

The list of commercial samples introduced is not exhaustive, but provides comparisons of products with different constituents (see Table 3.1), shape (see Fig. 3.1) and properties. All of these samples are potentially amenable to modification in current and future process functionalisation, as indicated in the previous section.

The properties of MFC, for example, are beginning to be described as a function of orientation linked to the Young's Modulus of fibrous networks (Supachok Tanpichai *et al.*, 2012) and in the presence of other polymer networks (Agoda-Tandjawa *et al.*, 2012). The effect of food processes, such as freezing, has also been evaluated (Agoda-Tandjawa *et al.*, 2010).

Spray-dried particles, particles produced through homogenisation of nanofibril:microfibril mixtures and aggregated cellulose whiskers provide a range of physical properties such as foam and emulsion stabilisation. In the absence of specific surface activity, this can be achieved through the production of thixotropic gel systems and, in the case of particles, plugging to inhibit film drainage between close-packed air cells/oil droplets. The Hydro-Fi is a blend of citrus fibres with more conventional, refined polymers. Further work needs to be carried out to attain control of food design using such natural structurants when combined with commonly used food ingredients. The work to date tends to have been observational, carried out with ketchup formulations (Sahin and Ozdemir, 2004, and Koocheki *et al.*, 2009), using guar, xanthan and carboxymethylcellulose (CMC). Sahin and Ozdemir (2004) showed that tomato paste dilution of at least 10% total soluble solids and 0.5% hydrocolloid provides optimal consistency. Koocheki *et al.* (2009) observed an increase in yield point and apparent viscosity with increasing hydrocolloid content. Recent work by Hemar *et al.* (2010) provides better formulation understanding in the addition of xanthan in the range 0.1–1% to low dispersed volume (10%) PCWM dispersions. Analogies can be drawn with recent work by Lad *et al.* (2010), where competition for water of hydration and swelling in mixtures of hydrocolloid and swellable particulates is hypothesised. This provides unexpected effects when the hydrocolloid is xanthan gum. However, much more fundamental understanding of the “blending” of PCWM and conventional hydrocolloids is required.

3.6 UNDERUTILISED POLYMERS WITH NATURAL CONNOTATIONS

As mentioned in the introduction, there are many polymers used as structurants in the food industry. One group of polymers is yet to make its mark as a commonly used ingredient, that being β -glucans. With the

advent of some of the new process opportunities highlighted in this chapter, the β -glucans may become much more accessible and therefore the potential for use increased. They are becoming well-characterised materials with excellent reviews by Lazaridou and Biliaderis (2007a); Izydorczyk and Dexter (2008) and Ahmed *et al.* (2012). A major focus for β -glucans in food use has been on the nutritional benefit of decreasing serum cholesterol levels (Bell *et al.*, 1999), potentially through binding of bile acids (Kahlon and Woodruff, 2003) and glycaemic and insulin responses (Brennan and Cleary, 2005), with recent reviews on clinical trials (Smith and Tucker, 2011) and physical property implications for digestion (Shelat *et al.*, 2011) providing increased evidence for functionality. The physical properties of β -glucans is becoming well characterised, particularly for the mixed-linkage cereal β -glucans. Aggregation and (cryo-)gelation is found with lower DP3:DP4 ratios (the degree of [polymerisation between the β -1,3 linkages) (Lazaridou and Biliaderis, 2004; Johansson *et al.*, 2008; Li *et al.*, 2011), with higher ratios promoting more rigid polymer chains (Li *et al.*, 2006, 2011) and lower molecular weight (Mw) (Doublier and Wood, 1995).

Additional β -glucans with potential include curdlan (Zhang *et al.*, 2002; McIntosh *et al.*, 2005), mushroom (Han *et al.*, 2010; Nitschke *et al.*, 2011) and spent yeast (Bell *et al.*, 1999).

Food applications have already been identified in fat replacement in mayonnaise (Worrasinchai *et al.*, 2006), milk gels (Kontogiorgos *et al.*, 2006; Lazaridou and Biliaderis, 2007b; Lazaridou *et al.*, 2008), controlling pasting properties in baked produce (Kim *et al.*, 2011; Liu and White, 2011; Sayar *et al.*, 2011) and as an emulsifier in liquor distillation (Dikit *et al.*, 2010). Izydorczyk and Dexter (2008) indicate a mechanism for functionality in baked products is a competition of soluble fibre for available water, limiting starch swelling and gelatinisation. While this would require precise validation, the similarities with the discussion provided earlier ensures that the functionality of natural structurants, aided by developments in process opportunities, is still very much in the early stages of enabling food product design.

3.7 CONCLUSIONS

It is becoming increasingly apparent that previously underutilised, mildly refined PCWM may have significant and novel use in food products. The enabling technologies are those of increased process control, to provide molecular level impact on functionality of the PCWM composites. In taking such an approach the greater availability of molecules retained within natural fibres, e.g. β -glucans, can be used to provide natural and healthy food ingredients.

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