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Pectin-water interactions: Comparison of different analytical methods and influence of storage

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ABSTRACT

Interactions of pectin with water are essential for nearly all pectin applications. It was assumed that these interactions strongly depend not only on chemical molecular parameters but also on physical powder material properties and that they might be affected by storage. This was examined with nine different pectin samples from three suppliers. Storage at 60 °C and 80% humidity for two weeks was used in order to simulate long term storage at moderate conditions. Material properties were tested by measuring solid density and BET surface and by mercury porosimetry and X-ray analysis. Pectin-water interactions were examined with two different methods, a modified sorption method at a_w around 1.0 and the capillary sucking method (Baumann method). After storage, the BET surface of the pectin samples was reduced, solid density was altered differently and crystalline structures became amorphous. It is assumed that storage at high heat and humidity caused particle surfaces softening, swelling and partly dissolution. The particle surfaces smoothed, small inter-particle voids were reduced or sealed and particles agglomerated. These alterations caused a reduced water uptake of stored pectins. In general, the accessibility of hydrophilic groups in pectin was more important for pectin-water interactions than their number. All applied methods for testing pectin-water interactions detected special sample properties and their combination allowed an extensive evaluation of the water binding properties.

1. Introduction

Pectins are important gelling and thickening food ingredients. Commercial pectins are mainly sold as dry powders and have to be dispersed or dissolved in water or watery systems in the food production process. Therefore, pectin – water interactions are crucial for the application and the water uptake velocity of powders might also determine the order of mixing dry components into water (Pilosof, Boquet, & Bartholomai, 1985). Despite of a high final solubility, the wetting and dissolution properties of pectins are often poor. A common phenomenon is the "fish-eye effect", the formation of sticky and partly "undissolved powder lumps" during pectin dissolution (Kurita, Miyake, & Yamazaki, 2012). Mixing with sugar or a strong mechanical energy input is often used to reduce this effect, but might not be possible for all applications (Hirata, Dacanal, & Menegalli, 2013). A better understanding of the specific interactions of pectins with water and their detailed examination is therefore highly relevant with respect to industrial applications.

The results of such investigations of pectin–water interactions strongly depend on the analytical methods. Most frequently, the examination by sorption isotherms is applied (Basu, Shivhare, & Muley, 2013; Bettelheim, Sterling, & Volman, 1956; Bettelheim & Volman, 1957; Galus, Turska, & Lenart, 2012; Kurita et al., 2012; Panchev, Menkov, & Denev, 2004; Panchev, Slavov, & Menkov, 2007; Panchev, Slavov, Nikolova, & Kovacheva, 2010; Tsami, Vagenas, & Marinos-Kouris, 1992; Wallingford & Labuza, 1983). Also the Baumann-method, a capillary sucking procedure, was applied for the characterization of the water uptake (Wallingford & Labuza, 1983). These two methods differ considerably with respect

List of abbreviations: HMP, high methoxylated pectin; LMP, low methoxylated pectin; LMP-AC, acidic demethoxylated pectin; LMP-ENZ, enzymatic demethoxylated pectin; LMP-AMID, amidated pectin; DM, degree of methoxylation; GC, galacturonan content; IV, intrinsic viscosity; PS, particle size; S, stored samples; WUS, water uptake by sorption; WUC, water uptake by capillary sucking; t_s, time of sucking measurement.

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to the water content in the system. Whereas during the investigation of sorption isotherms the samples adsorb only limited amounts of water from wet air by moisture transfer and diffusion, the Baumann-method offers much more water that can be sucked through a porous glass plate and may cause also swelling (Elizalde, Pilosof, & Bartholomai, 1996) and even dissolution (Wallingford & Labuza, 1983). Different types of water, associated more or less strongly with the sample, can be identified by a special DSC method. This has been recently applied for model pectins prepared in laboratory scale (Einhorn-Stoll, Hatakeyama, & Hatakeyama, 2012) and for commercial pectins (Einhorn-Stoll, Prinz, & Drusch, 2014). The results of the latter examination could not completely be explained by the chemical molecular parameters such as the number of hydrophilic groups. Therefore, it seems to be possible that also other factors such as physical material properties of the pectin powders affected the pectin-water interactions.

In general, food powder properties are strongly influenced by the bulk powder properties as well as the particle characteristics (Mathlouthi, 2001). Especially particle surface area, porosity and roughness are highly important for the wetting and dissolution behaviour, because the first contact between powder and water during wetting occurs at the particle surface (Fyfe et al., 2011; Murrieta-Pazos et al., 2012). Moreover, inter-particle voids and macro capillaries may affect this process. Water sorption in food powders can be described as a two-step process with (I) initial sorption on the particle surface at lower water content, followed by (II) the formation of "water clusters" in voids or capillaries when more water is available (Furmaniak, Terzyk, & Gauden, 2007). Typical processing steps during pectin production, such as chemical modification, precipitation, separation, drying or milling, can have a substantial effect on the final powder properties (Tsami, Krokida, & Drouzas, 1999). They can influence also pectin–water interactions because these powder properties can determine the accessibility of the hydrophilic groups (Tsami et al., 1992). Indeed, it was previously found (Einhorn-Stoll et al., 2012) that different chemical pre-treatments modified the pectin powder material properties and had an effect on the pectin–water interactions.

Storage and long transport can influence the pectin quality, too. Their duration and conditions, especially temperature and moisture, can vary considerably. As a result, water vapour can condense on pectin particles and soften their surface as described by Matveev, Grinberg, and Tolstogusov (2000). It can even cause partial surface dissolution (Basu et al., 2013) or particle swelling (Vasquez, Braganza, & Coronella, 2011). Such alterations may affect pectin techno-functionality in mixing and dissolution steps.

In a recent study, long term storage of commercial pectins was simulated and accelerated by treatment in a climate chamber at 60 °C and 80% relative humidity (Einhorn-Stoll, Kastner, & Drusch, 2014). Pectins became demethoxylated and depolymerized, similar to model pectins prepared in laboratory scale in a previous study (Einhorn-Stoll & Kunzek, 2009). These chemical molecular alterations possibly also could have an influence on pectin-water interactions: Water is bound to hydrophilic groups of the pectin molecules (hydroxylic, carboxylic and, in case of amidated pectin, also amino groups) and the number of these groups increased considerably by demethoxylation (-COOH) and depolymerisation (-OH) during storage.

Possible alterations of pectin powder properties after storage can be tested by different methods. The powder solid density allows insight into particle packing and macro pores, in which water can be immobilized. The BET surface measurement gives information about the total surface of the pectin particles; an increased surface area allows more efficient sorption of water. The mercury porosimetry, mainly used for quantifying particle pores or interior voids, indicates also changes in inter-particle voids by determination of the most frequent pore diameter. A powder with more or bigger inter-particle voids should be able to bind more water by immobilization and inclusion. Another indicator of altered material properties are physical state transitions as measured by X-ray analysis. Materials in an amorphous state show a more efficient water uptake than crystalline samples (Lewicki, 2004; Matveev et al., 2000; Murrieta-Pazos et al., 2012) because less energy is necessary for water intrusion into amorphous structures.

The influence of storage on pectin chemical (molecular) parameters (Einhorn-Stoll, Kastner, et al., 2014) as well as on special pectin-water interactions in DSC measurements (Einhorn-Stoll, Prinz, et al., 2014) has already been reported in recent studies. It was found by DSC that altered physical (material) properties significantly contributed to differences in water uptake. It remains to be elucidated, to which extent alterations of chemical molecular parameters, such as the increased number of hydrophilic groups, as well as possible changes in the physical material properties contribute to the influence of storage on pectin-water interactions.

The aim of the presented study is it therefore: (I) to investigate the influence of alterations during storage of pectin powders on their physical material properties, (II) to test the water binding ability of original and stored pectin with other methods than DSC and (III) to compare and evaluate the different methods for the investigation of pectin-water interactions.

2. Materials and methods

2.1. Materials

Four types of commercial food grade citrus pectin from three different suppliers were used in the present study. Three samples

Table 1
Molecular parameters of original and stored pectins. HMP = high methoxylated pectin, LMP-AC = acidic treated low methoxylated pectin, LMP-ENZ = enzymatic treated LMP, LMP-AMID = amidated pectin, GC = galacturonan content, DM = degree of methoxylation, IV = intrinsic viscosity, PS = particle size. 0 = original samples, *S* = stored samples. The previous names refer to the publication in which the properties were determined. ↑/↓ = increase/decrease of the parameter.

Sample name	Pectin type	Prev. name	GC 0 (%)	GC *S* (%)	↑ (%)	DM 0 (%)	DM *S* (%)	↓ (%)	IV 0 (cm^3/g)	IV *S* (cm^3/g)	↓ (%)	Median PS (μm)
1H	HMP	1B	85.5	93.2	9.0	59.6	51.2	14.1	598	398	33.4	178
2H	HMP	2D	65.8	82.7	25.6	76.9	39.6	48.5	660	348	47.3	118
3H	HMP	3A	80.9	87.6	8.2	69.8	43.7	37.4	554	260	53.1	101
1L	LMP–AC	1C	94.0	99.9	6.3	25.5	15.4	39.7	301	180	40.2	110
2L	LMP–AC	2C	90.5	90.7	0.2	30.1	12.1	60.0	358	171	52.2	82
2LE	LMP–ENZ	2E	67.6	84.4	24.8	31.7	17.2	45.7	500	290	42.0	119
3LE	LMP–ENZ	3E	81.5	90.7	11.3	30.2	18.2	39.9	336	255	24.1	149
2LA	LMP–AMID	2F	61.3	68.6	12.0	29.6	21.7	26.7	450	323	28.2	125
3LA	LMP–AMID	3K	68.4	75.9	11.0	32.2	21.1	34.4	382	223	41.6	93

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