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Thermally induced degradation of citrus pectins during storage – Alterations in molecular structure, colour and thermal analysis

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ABSTRACT

Commercial citrus pectins (17 samples from 3 different suppliers) were stored at 60 °C and 80% humidity for two weeks. Molecular parameters (galacturonan content, degree of methoxylation, intrinsic viscosity), colour and behaviour in thermal analysis (DSC and TG) were tested and the results were compared with those of model pectins prepared under laboratory conditions from a previous study. Whereas the molecular parameters and colour of both groups changed similarly, considerable differences in the thermal analysis were found not only between model pectins and commercial pectins but also between commercial samples from different suppliers. It seems that varying processing conditions between laboratory preparations and industrial processing as well as differences in industrial scale processing influence the pectin properties and their degradation during storage.

All commercial citrus pectin samples were strongly demethoxylated and depolymerised, former high-methoxylated pectins with degree of methoxylation (DM) > 50% became low-methoxylated with DM < 50% and some low-methoxylated samples afterwards had a DM close to pectic acid. As a result, also their gelation properties changed markedly. For pectin producing and applying companies it might be essential to check the properties of pectins after longer storage under unfavourable conditions. As a consequence, a variation of the gelation conditions for pectins after storage might be necessary.

1. Introduction

Pectins are branched heteropolysaccharides with a backbone of galacturonic acid and rhamnose molecules, side chains of neutral sugars are linked to rhamnose. The structure of pectins is well described and discussed in several review papers (Schols & Voragen, 2002; Lopes da Silva & Rao, 2006; Thakur, Singh, & Handa, 1997; Voragen, Pilnik, Thibault, Axelos, & Renard, 1995) and other publications (Rolin, Chrestensen, Hansen, Staunstrup, & Sorensen, 2010; Schols, Coenen, & Voragen, 2009; Vincken et al., 2003).

The process for the production of high-methoxylated citrus pectin (HMP) is well standardised and similar for different pectin suppliers. The companies adapt their products to special applications such as gelling and thickening agents using limited demethoxylation by enzymes or acids as well as amidation by ethanolic ammonia (Rolin, 2002; Rolin et al., 2010). The processing for the production of low-methoxylated pectins (LMP) or amidated pectin (LMP-AMID) can differ stronger from company to company, for instance with respect to the enzymes used, the temperature, time or pH for demethoxylation.

Pectins can be characterised by different molecular parameters; the most important is the *degree of methoxylation (DM)*. It describes the percentage of methoxylated C_6 atoms in the galacturonic acid backbone and strongly determines the gelling properties. The second important molecular parameter is the molecular weight. It is often characterised through the *intrinsic viscosity (IV)*, which is governed mainly by the chain length. The third important molecular parameter, the *galacturonan content (GC),* indicates the purity of the pectin. Pectins of comparable molecular parameters do not necessarily have comparable material and techno-functional properties, too. Recent works (Einhorn-Stoll, Kastner, & Senge, 2012; Kastner, Einhorn-Stoll, & Senge, 2012a) compared molecular, material and techno-functional properties of commercial citrus pectins and showed that samples with comparable molecular parameters significantly differed in colour, particle size and surface morphology as well as in their behaviour during thermal analysis (start of thermal degradation, sample homogeneity) and gelation behaviour. The authors concluded that these differences resulted from variations in pectin sources and processing conditions.

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Table 1
Molecular parameters, colour and results of thermal analysis of original 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, L = lightness, +a = red colour, +b = yellow colour, DSC = differential scanning calorimetry, DTG = differential thermogravimetry, T_p = peak temperature, PW = peak width, v_{max} = maximum degradation velocity.

Sample	Type	Molecular parameters			Colour			Thermal analysis			
		GC (%)	DM (%)	IV (cm^3/g)	L	a	b	$T_{p\ DSC}$ (°C)	$T_{p\ DTG}$ (°C)	PW (K)	v_{max} (%/min)
1A	HMP	89.3	60.9	639	88.60	1.09	12.86	240.5	237.8	27.6	19.9
1B	HMP	85.5	59.6	598	89.67	1.06	10.85	239.4	236.1	25.8	22.2
2A	HMP	81.6	68.9	647	86.40	2.00	12.20	244.0	240.3	35.6	16.3
2B	HMP	87.7	55.1	492	87.70	1.60	11.40	245.0	240.7	34.5	16.2
2D	HMP	65.8	76.9	660	86.85	1.75	11.52	247.6	243.3	30.7	18.5
3A	HMP	80.9	69.8	554	89.90	1.40	11.00	249.8	246.1	24.3	22.2
3B	HMP	83.4	57.1	576	88.40	1.70	12.90	247.9	243.9	25.7	20.7
3C	HMP	81.5	63.6	608	88.50	1.80	14.00	249.6	245.8	24.7	21.4
1C	LMP-AC	94.0	25.5	301	89.97	1.54	16.89	239.1	234.9	25.6	19.6
1D	LMP-AC	75.8	36.4	421	85.14	2.43	14.50	241.5	236.1	37.5	14.6
2C	LMP-AC	90.5	30.1	358	81.20	3.40	24.00	246.7	241.0	33.5	15.8
2E	LMP-ENZ	67.6	31.7	500	83.44	2.12	12.23	235.5	232.6	24.4	19.6
3D	LMP-ENZ	84.8	32.8	363	87.70	1.10	13.00	230.9	228.4	29.3	17.2
3E	LMP-ENZ	81.5	30.2	336	84.00	2.70	20.10	234.1	231.6	28.0	17.8
3F	LMP-ENZ	78.5	27.7	327	86.90	1.50	15.00	233.9	231.4	28.2	15.6
2F	LMP-AMID	61.3	29.6	450	84.35	2.11	12.71	242.9	239.0	27.5	16.9
3K	LMP-AMID	68.4	32.2	382	89.04	1.34	13.53	238.3	235.7	24.8	17.2

In addition to the differences resulting from varying raw materials and processing conditions, the molecular parameters may undergo further changes during storage. Pectins are delivered from producers to food companies in big packages and stored there until use. The time of storage and the conditions can vary considerably, especially with respect to temperature and humidity. Only very limited studies on the effect of storage on molecular parameters and techno-functionality of pectins exist. An early study from Padival, Ranganna, and Manjrekar (1981) described alterations of dry model pectins, prepared on lab scale, during storage. These authors found pectin degradation and alterations in gelation and solubility after long term storage at room temperature for several months. Recently, the research group of the present study published results on changes occurring during storage of pectins, prepared in laboratory at well-defined conditions. These samples were stored at temperatures above 50 °C and humidity above 65% for two weeks (Einhorn-Stoll & Kunzek, 2009a). Changes in molecular parameters included demethoxylation, depolymerisation and formation of brown reaction products. The extent of these changes increased with increasing temperature and relative humidity, but not to a similar extent for all pectins. Demethoxylation was the dominating reaction and was associated with other changes such as browning and behaviour in thermal analysis. In addition, depolymerisation occurred to an unexpectedly high extent. The typical cleavage reactions of pectins in solution are acidic hydrolysis as discussed by Diaz, Anthon, and Barrett (2007) or Fraeye et al. (2007) and β-elimination as described for instance by Keijbets and Pilnik (1974), Kravtchenko, Arnould, Voragen, and Pilnik (1992) or Krall and McFeeters (1998). They could, however, not sufficiently explain these results. The well-known β-elimination requires the presence of methoxyl groups close to the reacting glycosidic linkages, which are only sparingly available in low-methoxylated pectins. An acidic hydrolysis requires a high water activity and only limited amounts of unsaturated oligogalacturonides, which cause brown colour (Ibarz, Garza, & Pagán, 2008; Voragen, Schols, & Pilnik, 1988), are formed. Thus, that reaction does not sufficiently explain the strong browning of the stored samples. Therefore, an additional cleaving mechanism was proposed (Einhorn-Stoll & Kunzek, 2009a) that would result in an increased number of unsaturated oligogalactoronides and possibly more and/or other browning components. However, the detailed reactions occurring and the structure of the final reaction products are not elucidated, yet.

The effects of storage on the model pectin degradation were tested by thermal analysis (TA) as combined DSC and TG. This method has been successfully used for the characterisation of pectins (Einhorn-Stoll & Kunzek, 2009b; Einhorn-Stoll, Kunzek, & Dongowski, 2007). The main information from TA for pectin studies are the shape of the DSC curves, the shift of the DSC and DTG curves (to the left = sample is more thermal sensible, to the right = more stable), the peak width (PW) of the DTG curve (broader peak = less homogenous sample) and the maximum degradation velocity (v_{max}). v_{max} is the maximum height of the DTG peak and often correlates with the peak width; the more homogenous the sample