Effect water of content on viscoelastic properties of amorphous potato starch: DMA measurement

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Due to its mechanical properties and the absence of endogenous lipids, amorphous potato starch is offering promising prospects as shape memory material despite its sensitivity to water. Heating at a temperature higher than the glass transition temperature Tg is a stimuli of shape recovery of prestressed amorphous starches. Also, the absorption of water as a plasticizer of the starch decreases the Tg, thereby promoting shape recovery behaviour.

The linear viscoelastic behaviour of amorphous potato starch obtained by extrusion is investigated by dynamic thermomechanical analysis (DMA) in function of the temperature and moisture content with the aim to improve the knowledge of its thermal rheological properties. The extrudates were equilibrated for 3 weeks under different relative humidity to achieve levels of water content between 9.3 and 17.2% w.b. The samples were then covered with a thin layer of silicone grease to minimize dehydration during the DMA analysis which were performed using traction-compression mode, under a strain amplitude of 0.05 % and simultaneous sweep of frequency (0.1 - 40 Hz) and temperature (25 - 105 °C), with a heating rate of 3 °C / min. Water loss during DMA experiments was evaluated by performing a thermogravimetric analysis and via Tg measured by DSC. The storage and loss modulus (E '(ω) and E" (ω)) were obtained as a function of the actual water content in the range of studied temperatures. Examples of the storage and loss modulus are shown in Figure 1. The storage modulus is the stress in phase with the strain. It is a measure of energy stored and recovered per cycle [1], in other words the elastic part of the viscoelastic behaviour. It decreases with increasing temperature and increases with increasing frequency, see Figure 1. The loss modulus is the stress 90° out of phase with the strain. It is a measure of energy dissipated per cycle, which depends on the viscosity. The loss modulus of potato starch, see Figure 1, exhibits a maximum in dependence on temperature. Its dependence on frequency is rather complex; it increases with increasing frequency at the low and high temperatures whereas it decreases with increasing frequency at the middle temperatures.

The isotherms of storage modulus were obtained by curve fitting and interpolation of the results. The principle of time-temperature superposition [2], using the translation factor a_T (T) allowed us to obtain master curves of storage modulus. The stress relaxation modulus E(t) and storage modulus E'(ω) are both a measure of stored elastic energy. The results of a dynamic measurements at frequency ω are qualitatively equivalent to transient ones at t=1/ω. We used the generalized Maxwell model to calculate relaxation modulus E (t) from E'(ω). The results are shown in Figure 2a for selected values of water content at the reference temperature of 50 °C. Six relaxation times τ_i and the corresponding parameters of the generalized Maxwell model, see Table 1, make possible numerical simulations in the range (10^{-2}, 10^{4}s). The obtained translation factor a_T (T), see Figure 2b, allows us to compute E(t) at any temperature and, by interpolation, also its variation as a function of water content.

The determination of viscoelastic parameters of the amorphous starch will contribute to the modelling of its thermo-mechanical behaviour and promote the shape memory programming and applications.

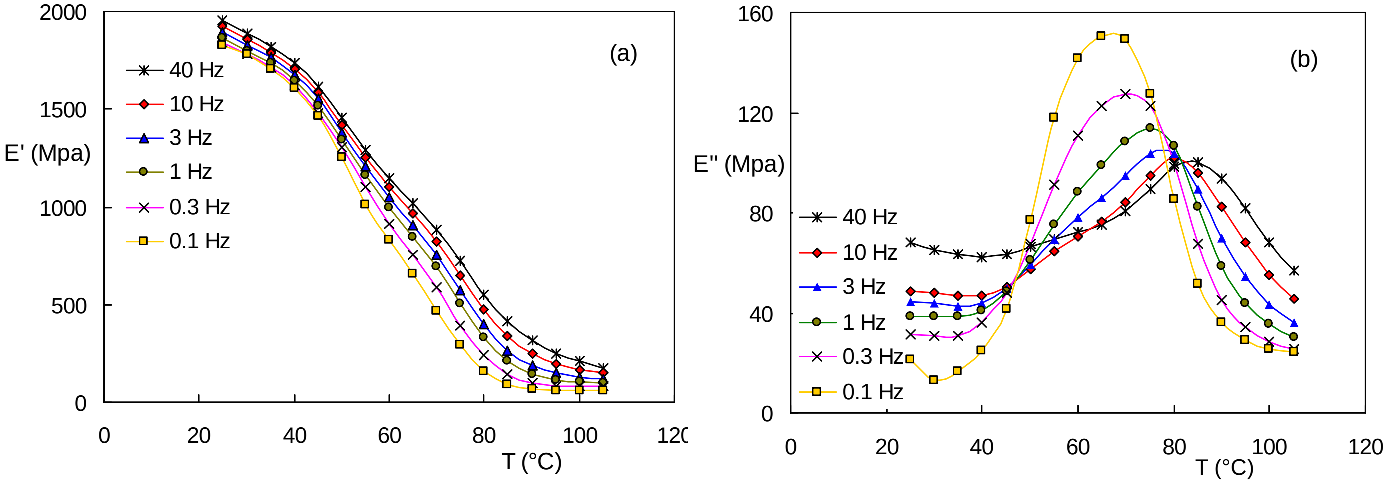

Figure 1*: Storage (a) and loss modulus (b) of extruded potato starch with a moisture content of 14.2% w.b.*

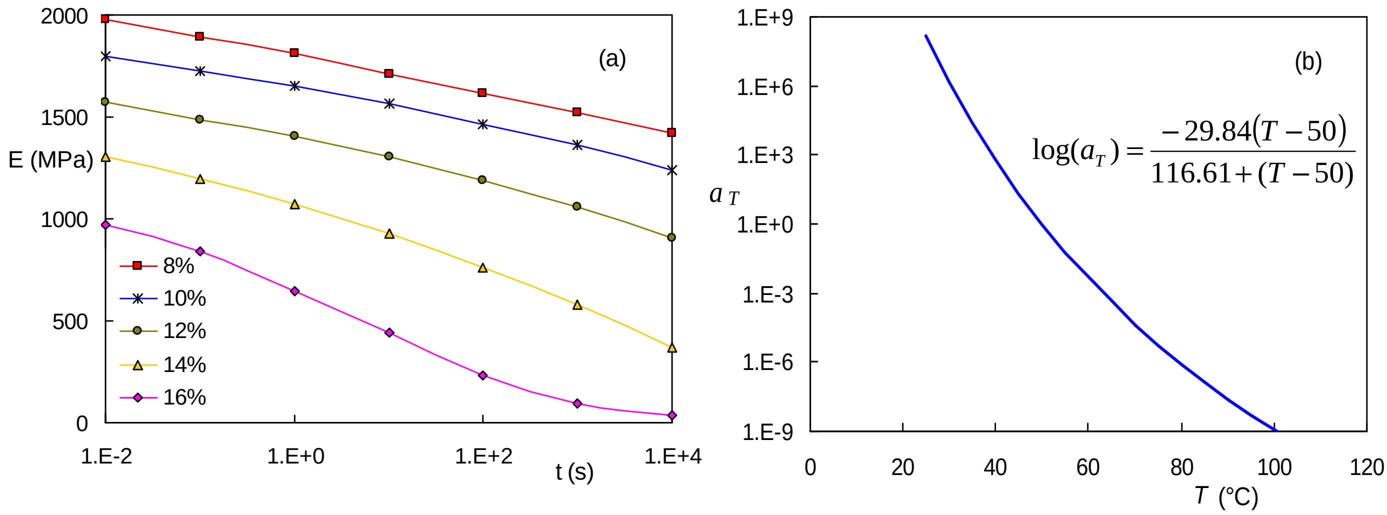

Figure 2*: Relaxation modulus at 50°C for selected moisture content (a) and translation factor a_T (b).*

Table 1*: Coefficients of the generalized Maxwell equation* $E(t) = E_0 + \sum_{i=1}^{6} E_i \exp(-t/\tau_i)$ *for selected water content at T=50°C.*

τ_i	w.c. (%)	8	10	12	14	16
	E_0	1370.3	1193.2	835.8	282.8	16.3
0.1	E_1	149.4	130.1	146.5	192.5	223.6
1	E_2	21	23.2	37.1	68.4	163.2
10	E_3	160	121.8	137.7	191.2	230.9
100	E_4	55.7	82.3	100.9	143.5	222.6
1000	E_5	107.4	122.7	145	202.8	92.1
10000	E_6	127.6	134.1	183.4	245.3	48.2

[1] J.D. Ferry, "Viscoelastic properties of polymers", John Wiley and Sons, (1980).
[2] M.L. Williams, R.F. Landel, J.D. Ferry, J Amer Chem Soc, 77 (1955) 3701.