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Water redistribution during the recrystallisation of amylopectin in amylopectin/gelatin blends

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Abstract

The DMTA thermogram of 50:50:32 gelatin/amylopectin/water extrudates showed two main transitions: 24 and 52°C associated with the glass transition temperatures (T_gs) of gelatin and amylopectin, respectively. After storage (15 days, 60°C), amylopectin recrystallised to the A-polymorph. This was paralleled by a decrease of the T_g of gelatin to 1.5°C, which was explained in terms of water redistribution during the formation of amylopectin crystallites. A full analysis of water partitioning in the system is reported.

Keywords: Starch; Gelatin; Water redistribution

The effect of water on the functional properties of macromolecules is of major interest in many areas of polymer and biological sciences. These effects are better understood in the context of the glass–rubber transition where water acts as a plasticiser. The partitioning of water and other plasticisers in multicomponent systems and its relevance to their behaviour has rarely been addressed [9]. Furthermore, to the best of our knowledge, the redistribution of plasticisers in a mixed system upon the crystallisation of one of its components and the effects of this on the glass transition temperatures (T_gs) of the various components have not been investigated. This communication reports a study of the effect of amylopectin recrystallisation in a biphasic amylopectin–gelatin blend on water distribution between the components of the blend and the subsequent impact on their T_gs.

Non-expanded 1:1 amylopectin/gelatin extrudates containing 24.4% water wt/wt wet weight basis (wwb) were prepared as described previously [9]. The blends were analysed shortly after extrusion or after storage (15 days, 60°C) at constant water content.

The DMTA thermograms acquired in bending mode shortly after extrusion showed two main α-transitions which shifted to higher temperatures when the measurement frequency was increased from 1 to 5 Hz (Fig. 1(a)). In a related study on these blends, Mousia et al. [9] assigned these transitions to the T_gs of gelatin (tan δ peak at 24°C) and amylopectin (tan δ peak at 52°C). A third transition occurring at ~48°C, showing no frequency dependence and, therefore, seen as an overlap of the tan δ data, was observed. This transition was associated with the melting of the gelatin ordered regions. The nature of this transition, which is also observed at ~52°C after the ageing of the sample (Fig. 1(b)), was ascertained by DSC analysis (10°C/min) of the unaged system where a melting endotherm centred at ~44.5°C could be clearly seen (Fig. 2).

The wide-angle X-ray diffractogram (XRD) recorded on the freshly extruded blend showed a broad amorphous pattern (Fig. 3). Although the DSC results indicated that at room temperature gelatin is in the gel state, the crystalline order of the gelatin helical regions was not clear from the XRD. This could be due to the fact that: (i) the XRD peaks of crystalline gelatin (mainly at $2\theta = 7$ and 31°) are usually weak [1]; or (ii) the presence of amylopectin may have interfered with the long-range packing of the gelatin helical structure. However, these blends are highly phase separated [9] and the behaviour of the gelatin and amylopectin phases are to a large extent independent. Therefore, the first reason is the more likely explanation for the absence of crystalline gelatin contribution to the XRD spectrum.

After ageing at constant moisture content and a temperature of 60°C for 15 days, i.e. in conditions where the amylopectin is in the rubbery state, the XRD pattern showed sharp peaks typical of A-type crystalline starch (Fig. 3). The starch crystallinity index calculated using the method

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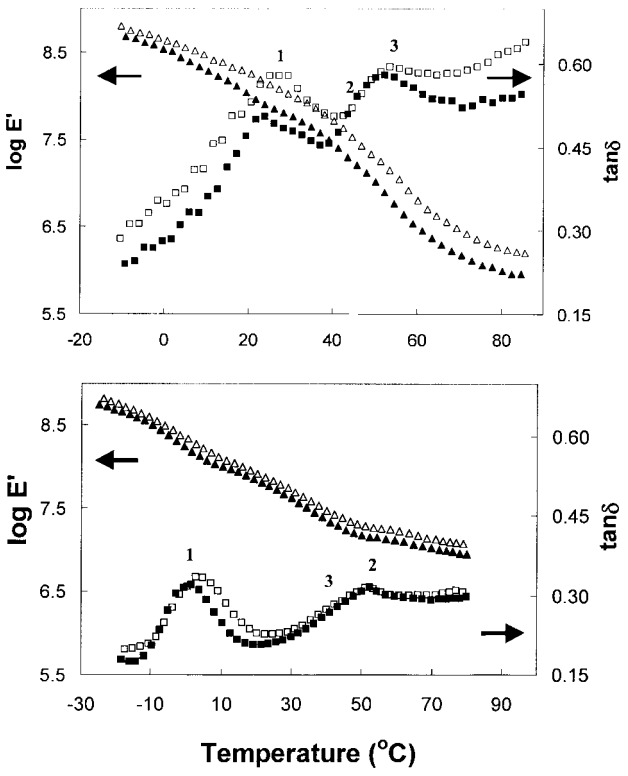

Fig. 1. DMTA thermograms — open symbols, 1 Hz and solid symbols, 5 Hz — acquired on the gelatin/amylopectin 1:1 blend: (a) shortly after extrusion (adapted by Mousia et al. [9]); and (b) after storage at 60°C for 15 days. (1) T_g (gelatin); (2) T_m (gelatin); and (3) T_g (amylopectin).

reported by Hermans and Weidinger [4] was found to be approximately 40%. This result suggested that in the experimental conditions of water content and storage temperature, amylopectin recrystallisation (retrogradation) occurred within the storage period. This is in agreement with the findings of Farhat et al. [2] on the effect of water content and storage temperature on the kinetics of retrogradation of waxy maize starch and on the polymorphic form of the retrograded amylopectin.

The DMTA thermograms acquired after storage of the system reflected the effect of starch retrogradation of the mechanical properties of the blend (Fig. 1(b)). As expected, when comparing the viscoelastic behaviour of amorphous and semicrystalline polymers, the E' value of the third viscoelastic region, the rubbery plateau, increased from approximately 0.9×10^6 to 1.4×10^7 Pa (1 Hz) as a result of the recrystallisation of amylopectin.

Another major change in the DMTA thermogram was the shift of the tan δ peak associated with the T_g of the amorphous fraction of gelatin to lower temperatures (from 24 to 1.5°C). The changes in the viscoelastic properties of the blend on storage, particularly the temperature at which the transitions occurred, are interpreted in terms of: (i) the effect of amylopectin crystallisation on the distribution of water between the components of the blend; and (ii) the effect of

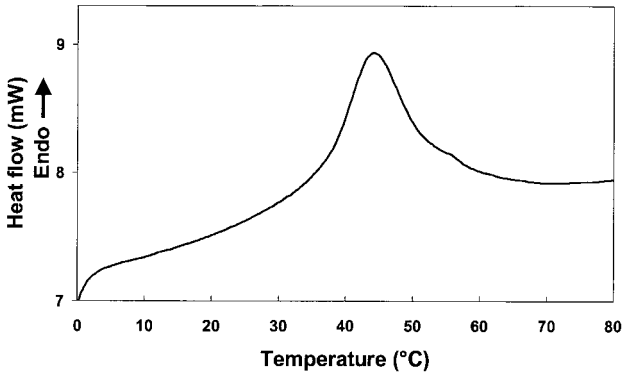

Fig. 2. DSC thermogram (10 K/min) of the unaged amylopectin/gelatin blend.

the degree of crystallinity of amylopectin on the glass transition of its amorphous fraction.

Mousia et al. [9] estimated the amount of water associated with gelatin and amorphous amylopectin in similar unaged blends using the water vapour sorption/desorption isotherms of the individual components. Furthermore, they were able, by feeding these values of water contents into the Gordon–Taylor [3] relationship of T_g versus water content obtained on pure gelatin and amylopectin systems, to predict successfully their T_g values in various blends. For example, based on their calculations, in the unaged blend (water content = 24.4%wwb) the water content of gelatin is approximately 29.5% (wwb), i.e. 14.8% on a total wwb of the sample (twwb). The moisture content of amylopectin in this same fresh blend would be 19.3%, i.e. 9.6%twwb (Table 1(a)). After storage, the glass transition of gelatin shifted to ~1.5°C. Using the same approach, for a T_g = 1.5°C the water content of gelatin estimated from the Gordon–Taylor equation is 35.5% (wwb), i.e. 17.8%twwb with the remaining water (6.6%twwb) associated with amylopectin. Since the crystal structure of the A-polymorph cell unit contains 12 anhydroglucose residues and only four

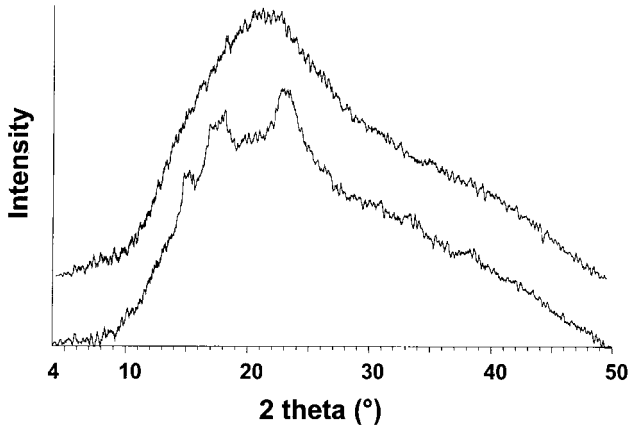

Fig. 3. XRDs ($\lambda = 0.154$nm) of the gelatin/amylopectin 1:1 blend measured before (top) and after (bottom) ageing.

Table 1
Water distribution and T_gs in the amylopectin/gelatin blend before and after ageing (twwb refers to the total wet weight basis of the blend and *W* refers to the water content of the individual phases and/or components)

(a) Fresh sample									
Water (%twwb)	Gelatin (%twwb)	Amylopectin (%twwb)	*W* (gelatin) (%twwb)	*W* (amyl) (%twwb)	T_g (gelatin) (°C) measured	T_g (amyl) (°C) measured	T_g (gelatin) (°C) calculated	T_g (amyl) calculated (°C)	
24.4	37.8	37.8	14.7	9.6	23.5	52	27.8	48.0	
(b) Aged sample									
Water (%twwb)	Gelatin (%twwb)	Amylopectin (%twwb)		*W* (gelatin) (%twwb)	*W* (amyl) (%twwb)		T_g (gelatin) (°C) measured	T_g (amyl) (°C) measured	
24.4	37.8	37.8		17.8	6.6		1.5	46	
Accounting for the degree of amylopectin crystallinity →		Amorphous (%twwb)	Crystalline (%twwb)		*W* (amorph.) (%twwb)	*W* (cryst.) (%twwb)			
		22.7	15.1		6.1	0.6			

molecules of water [5], i.e. approximately 3.7% (wwb), and knowing the degree of crystallinity of amylopectin (~40%), the water content of the amorphous fraction of amylopectin could therefore be calculated and a value of 21.1% (wwb) was found, i.e. 6.1%twwb (Table 1(b)).

For a water content of 21.1% (wwb), the expected T_g value of amorphous amylopectin is 36.2°C. The experimental value of T_g derived from the tan δ peak associated with the amorphous fraction of amylopectin in the aged sample is approximately 46°C. This is in agreement with the anticipated behaviour of most semicrystalline synthetic polymers (e.g. Refs. [6,8]) and with the findings of Kalichevsky et al. [7] and Mizuno et al. [10] where the T_g of partially crystalline, retrograded starches was found to exceed that of the fully amorphous systems. Within the context of this approach accounting for the partitioning of water between the components of the blend, the apparent decrease of the T_g of amylopectin on recrystallisation does not contradict the expected behaviour where an increase in T_g with increased degree of crystallinity due to the reduced motion of the amorphous phase when co-existing with a crystalline phase is anticipated.

This may also explain why the results of Kalichevsky et al. [7], where the T_g of amylopectin increased by between 10 and 20°C in retrograded samples with crystallinity indices between 2 and 11%, showed more systematically the effect of crystallinity on T_g, compared to the results of Mizuno et al. [10]. Indeed, in the former study, ignoring the issue of water partitioning is less serious due to the low weight fraction of the crystalline material.

This report clearly demonstrates the effects of the redistribution of water in a biopolymer blend, as a result of the recrystallisation of one of its components, on its viscoelastic properties. This could have major implications on the mechanical properties and the performance of the blend. Experiments where amylopectin is recrystallised to the A or the B polymorphs, which contain different amounts of water in their crystalline cell unit (4 and 36 water molecules, respectively), which would strengthen this study are envisaged. Furthermore, an extension of these ideas concerned with the relevance of the water redistribution during starch gelatinisation, which involves the melting of amylopectin crystallites, i.e. the reverse event of that studied here is in progress. This phenomenon is of major relevance to many food processes (e.g. baking) where the viscoelastic properties of the protein component gluten, which are water content dependent, are believed to change at the onset of starch gelatinisation.

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