

Interfacial phenomena in starch/fumed silica at varied hydration levels

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Abstract

Hydrated powders of non-gelatinised starch and hydrogels of gelatinised starch alone or with addition of modified nanosilica (with grafted aminopropylmethylsilyl groups substituting one-third of surface silanols) were studied using broadband dielectric relaxation spectroscopy (DRS), thermally stimulated depolarisation current (TSDC) method and ¹H NMR spectroscopy with layer-by-layer freezing-out of bulk and interfacial waters. The ¹H NMR and TSDC techniques with the use of Gibbs–Thomson relation for the freezing point depression allow us to calculate: (i) the thermodynamic parameters of interfacial water weakly and strongly bound to polymer molecules and nanoparticles; (ii) size distributions of pores filled by structured water; (iii) surface area and volume of micro-, meso- and macropores. The DRS and TSDC results for hydrogels and hydrated powders with starch/modified fumed silica show that the β - and γ -relaxations of starch are strongly affected by water and functionalised silica nanoparticles which slow down both low- and high-frequency and low- and high-temperature relaxations.

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1. Introduction

Starches of different origin are widely used in food industry as thickening agents, and their swelling and solubilisation properties depend on temperature [1]. Fumed silica (especially modified one such as studied here) can also be used as a thickening agent [2]. Therefore, a mixture of starch with modified fumed silica can be of interest as a complex thickening agent. The double-helix structure of starch consisting of essentially linear poly(1,4- α -D-glucan) (amylose, molecular weight $M_w \approx 0.1$ – 1.0 MDa) and branched amylopectin ($M_w \approx 0.01$ – 1.0 GDa) with 1,4- α -D-glucan chains connected through 1,6- α linkages depends on biological origin, amounts of water and temperature [3–6]. In the case of potato starch (studied here) having hexagonal unit cell ('B' type) of the space group $P6_1$, content of amylose is 17–20% (apparent amylose $\sim 23\%$) [3,4]. Gelatinisation of starch is accompanied by several processes such as swelling, leaching of amylose, loss

of crystallinity, increase in the viscosity, solubilisation of the macromolecules, etc. [7,8]. Some of these effects lead to a decrease in the mobility of the macromolecules and bound water molecules and influence dielectric and other properties of the starch–water systems [9,10] dependent on water content, starch gelatinisation and temperature [10–14]. Generally, the dielectric constant and the loss factor increase with increasing water content in the starch systems [12,15], and on its gelatinisation [7].

Different relaxation processes characteristic for modified and unmodified starches were studied by the dielectric relaxation spectroscopy (DRS) method over wide temperature and frequency ranges [4,16–20]. Majumder et al. [16] observed two α -relaxations (gelatinisation corresponds to α -relaxation [4]) and two γ -relaxations in starch depending on hydration, with excess of water able to unravel the double-helix structure. Subsequently, relaxation processes associated with collective helical motions depend on water concentration. Additionally, several kinds of phases, such as inter-crystalline and liquid crystalline, were identified depending on water content and temperature. The total activation energy of relaxations increased with increasing water content. Einfeldt et al. [17–19] observed three relaxations for starch/water: the β -relaxation associated with the local chain

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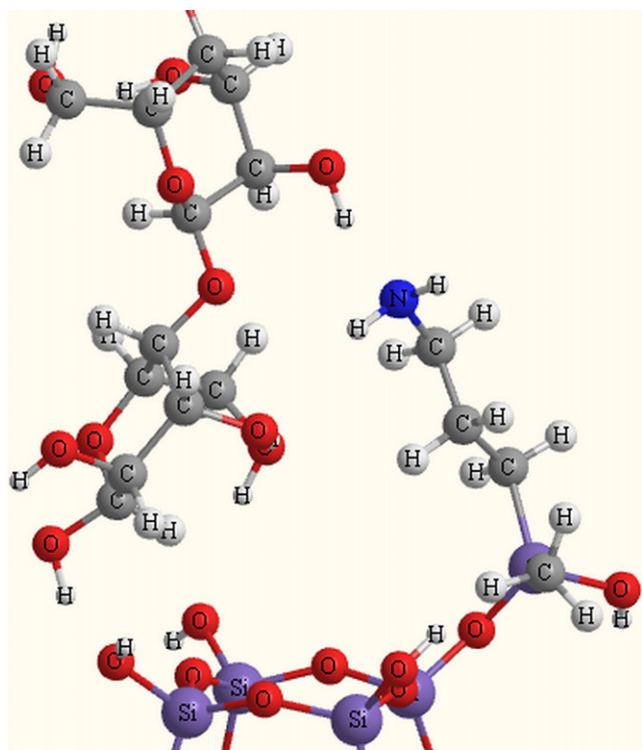


Fig. 1. Hydrogen bonding of a starch fragment to a modified silica surface.

motion, the δ -relaxation with an unknown molecular origin and the β_{wet} -relaxation with the motions of a water/starch mixing phase. They showed that the mixing of wet starches with vacuum grease did not affect the polymeric dynamics, and the type of starch had also no great influence on the polymeric dynamics. In addition, starches demonstrated a similar dynamic behaviour like other pure polysaccharides, because the main point for the characterisation of the segmental motion is the type of the glucosidic linkage and not its position and orientation at the repeating unit [17–19]. The water content has the most important influence on the time–frequency position of the relaxations because its impact as a plasticizer. According to Butler and Cameron [4], two relaxations are observed in starch at ~ 153 K because of small motions of the chain backbone and the rotations of methylol groups (with the latter process activated at lower temperatures than the former). Around ambient temperature a relaxation proposed to be the glass transition was observed (this transition assuming as β -relaxation is observed over a broad temperature range for different starches from 273 to 333 K [4]) and, in granular starch only, gelatinisation (it is observed for potato starch at 332 K) caused a relaxation around 333–353 K. Thus, the structure of strongly swelling polymers such as starch in wetted powders and hydrogels depends on hydration, treatment temperature and other conditions [3–6,21–23].

There are several methods utilized to estimate the structural characteristics (e.g. pore size distributions, PSD) of wetted powders or hydrogels on the basis of a specific behavior of pore liquids: (i) cryoporometry [24–30] using the ^1H NMR measurements at $T < 273$ K and the Gibbs–Thomson melting point depression of confined liquids; (ii) relaxometry [24,27] based on the enhanced relaxation of molecules at a pore surface depending

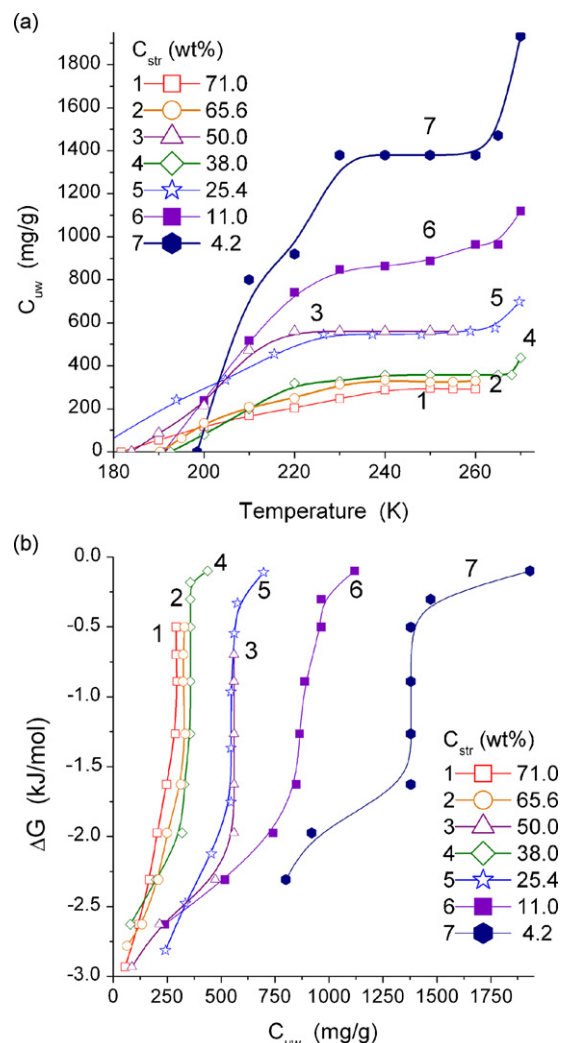


Fig. 2. (a) Temperature dependence of the amounts of unfrozen water (C_{uw}) bound in the starch powders (non-gelatinised) and hydrogels (gelatinised starch) at different concentration of starch (C_{str}). (b) The relationship between the amounts of unfrozen water and changes in the Gibbs free energy of the interfacial water layers.

on the pore size; (iii) thermoporometry based on the calorimetric technique for characterising pore structure from the melting or freezing point depression of a liquid confined in pores by reason of the added contribution of surface curvature to the phase-transition free energy [25,28]; (iv) cryoporometry with the thermally stimulated depolarisation current (TSDC) method based on the dependence of the dipolar relaxation of water affected by the size of confined space (pores) [29]. Notice that in the case of rigid porous polymers, their swelling and subsequent freezing can result in significant irreversible changes in the pore structure [31]. Previously it was shown [29,32] that interaction of polar polymers, proteins and microcrystalline cellulose with nanosilica affects hydration and structure of the macromolecules. A similar effect could be expected on interaction of starch with nanosilica.

The starch structure was well studied and documented [3–6,15,23,33–38]. However, detailed changes in the starch structure at different hydration levels are complex, espe-

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