Data Article

Water vapor sorption and glass transition temperatures of phase-separated amorphous blends of hydrophobically-modified starch and sucrose

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A B S T R A C T

This article contains water vapor sorption data obtained on amorphous blends of octenyl succinic acid-modified (denoted as hydrophobically modified starch; HMS) and sucrose (S) in the anhydrous weight HMS/S ratios between 100/0 and 27/75. The water vapor sorption data was obtained gravimetrically. The amorphous state of the blends was confirmed by X-ray diffraction. The glass transition temperatures of the phase-separated blends are listed; the blends show phase separation into a sucrose-rich phase and a HMS-rich phase, the composition of which varies with the blend ratios. The sucrose-rich phase is characterized by a glass transition temperature $T_{g,\text{lower}}$ that is 40 to 90 K lower than the glass transition temperature $T_{g,\text{upper}}$ of the HMS-rich phase.

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## Specifications table

| Subject area | Physical chemistry |
|-------------|-------------------|
| More specific subject area | Hydrocolloids, carbohydrate polymers, phase transitions |
| Type of data | Table (Water vapor sorption, glass transition data), figure (X-ray diffraction, Water vapor sorption isotherms) |
| How data was acquired | Water vapor sorption data (gravimetric analysis); X-ray diffraction data (Phillips X'pert Pro diffractometer (Panalytical)); Differential Scanning Calorimetry (Discovery DSC, TA Instruments) |
| Data format | Analyzed data |
| Experimental factors | Spray-dried blends of Octenyl succinic acid-modified starch and sucrose in the anhydrous weight ratios 100/0, 90/10, 80/20, 60/40, 45/55 and 25/75. |
| Experimental features | Spray-dried blends were water activity-equilibrated at water activities 0.11, 0.22, 0.33, 0.43, 0.54, 0.68 and 0.75 ($T = 298$ K). Water vapor sorption was determined gravimetrically until equilibrium was achieved (1200 hours). Water activity-equilibrated samples were analyzed for eventual crystallinity by X-ray diffraction and for the glass transitions of the phase separated blends (sucrose-rich and modified starch-rich phases) by Differential Scanning Calorimetry. |
| Data source location | NA |
| Data accessibility | NA |
| Related research article | D. J. Hughes, G. Badolato Bönisch, T. Zwick, C. Schäfer, C. Tedeschi, B. Leuenberger, F. Martini, G. Mencarini, M. Geppi, M. A. Alam, J. Ubbink, Phase separation in amorphous hydrophobically-modified starch - sucrose blends: Glass transition, matrix dynamics and phase behavior, Carbohydrate Polymers (in press) |

## Value of the data

- We present a broad set of water vapor data on blends of hydrophobically modified starch and sucrose with a systematic variation in composition. The water vapor data are obtained in the range between 0.11 and 0.75 at $T = 298$ K.
- Data on the glass transition temperatures of the phase-separated blends is valuable in the context of the understanding of the phase behavior of amorphous phase-separated systems.
- These data allow the exploration of the effect of composition on water vapor sorption behavior in the glass transition range.

## 1. Data

Spray-dried blends of hydrophobically-modified starch and sucrose were water activity-equilibrated at water activities 0.11, 0.22, 0.33, 0.43, 0.54, 0.68 and 0.75 ($T = 298$ K). Water vapor sorption was determined gravimetrically until equilibrium was achieved (1200 h); the data is reported in Table 1. Water activity-equilibrated samples were analyzed for eventual crystallinity by X-ray diffraction (Fig. 1) and for the glass transitions of the phase separated blends (sucrose-rich and modified starch-rich phases) by Differential Scanning Calorimetry (Tables 3 and 4).
The water vapor sorption data in Fig. 2 are fitted by the GAB equation (Fig. 2):

\[ Q_{w} = \frac{K C W_{m} a_{w}}{(1 - K a_{w}) \cdot (1 - K a_{w} + K C a_{w})} \]

where \( K \), \( C \) and \( W_{m} \) are fitting coefficients [3].

### 2. Experimental design, materials, and method

HMS-S blends were prepared by spray drying aqueous dispersions with well-defined ratios of HMS and S [2]. The blends were then equilibrated at a range of water activities \( (a_{w}) \) at \( T = 298 \) K in desiccators containing saturated salt solutions \( (a_{w} \text{ (salt)}) = 0.11 \) (LiCl), 0.22 (CH₃COOK), 0.33 (MgCl₂), 0.43 (K₂CO₃), 0.54 (Mg(NO₃)₂), 0.75 (NaCl). The pure spray-dried HMS \( (Q_{S} = 0.0) \) was also equilibrated at \( a_{w} = 0.68 \) (KI). The water activities are given by Greenspan [1]. Water sorption was followed gravimetrically for 1200 h. In this time, all samples reached their equilibrium water content. The water content of the blends was determined from the weight loss/gain upon water activity equilibration and the initial water content of the blends. These initial water contents were determined by dehydration in a laboratory oven for 27 h at 253 K at a pressure below 25 mbar and under a slight flow of dry nitrogen. Powder diffraction patterns were collected using a Philips X’pert Pro diffractometer (Panalytical) operating at 40 kV and 30 mA utilizing Cu Kα radiation \( (\lambda = 0.154 \text{ nm}) \). Scans were performed at 298 K under local atmospheric humidity over the 2θ range 5–35° with a step size of 0.02° and a data acquisition time of 2 s at each step. Glass transition temperatures were determined from the 2nd heating ramp of experiments carried out by Differential Scanning Calorimetry (DSC) as described by [2]. The midpoint glass transitions were extracted from the thermograms by deconvolution assuming the presence of multiple glass transitions each characterized by a Gaussian line shape of the first derivative of the heat flow curve [2].
Table 3

Water content and parameters associated with the glass transition fitting, as described in Section 2.4 of [2], for water activity equilibrated HMS-S blends. Q’s is the weight fraction of sucrose in the HMS-S blends (on anhydrous basis), Qaw is the weight fraction of water in the matrices, \( \Delta C_{g,lower} \) and \( \Delta C_{g,upper} \) are the changes in heat capacity associated with the lower and upper glass transitions, \( T_{g,lower} \) and \( T_{g,upper} \) are the glass transition temperatures and of the sucrose-rich and the HMS-rich phases, respectively, and \( \Delta T_{g,lower} \) and \( \Delta T_{g,upper} \) are the widths of the two glass transitions.

| Qw [dimensionless] | aw [dimensionless] | Qaw [dimensionless] | \( \Delta C_{g,lower} \) [J g\(^{-1}\) K\(^{-1}\)] | \( \Delta T_{g,lower} \) [K] | \( \Delta C_{g,upper} \) [J g\(^{-1}\) K\(^{-1}\)] | \( \Delta T_{g,upper} \) [K] |
|-------------------|-------------------|---------------------|----------------|-----------------|----------------|----------------|
| 0                 | 0.11              | 6                   | –              | –               | 0.16 ± 0.01    | 405 ± 1        |
|                   | 0.22              | 7.7                 | –              | –               | 0.16 ± 0.01    | 388 ± 1        |
|                   | 0.33              | 9.1                 | –              | –               | 0.17 ± 0.01    | 377 ± 1        |
|                   | 0.43              | 10.4                | –              | –               | 0.17 ± 0.01    | 366 ± 1        |
|                   | 0.54              | 11.7                | –              | –               | 0.17 ± 0.01    | 357 ± 1        |
|                   | 0.68              | 14.1                | –              | –               | 0.19 ± 0.01    | 337 ± 1        |
|                   | 0.75              | 15.9                | –              | –               | 0.19 ± 0.01    | 325 ± 1        |
| 0.1               | 0.11              | 4.7                 | 0.41 ± 0.04    | 330 ± 2         | 84 ± 6         | 0.16 ± 0.01    |
|                   | 0.22              | 6                   | 0.44 ± 0.03    | 322 ± 2         | 80 ± 5         | 0.16 ± 0.01    |
|                   | 0.33              | 7.1                 | 0.43 ± 0.03    | 312 ± 2         | 76 ± 5         | 0.19 ± 0.01    |
|                   | 0.43              | 8.3                 | 0.42 ± 0.03    | 305 ± 2         | 70 ± 5         | 0.20 ± 0.02    |
|                   | 0.54              | 9.7                 | 0.44 ± 0.03    | 295 ± 2         | 70 ± 4         | 0.22 ± 0.02    |
|                   | 0.75              | 15.1                | 0.54 ± 0.03    | 270 ± 1         | 69 ± 3         | 0.18 ± 0.01    |
| 0.2               | 0.11              | 3.3                 | 0.51 ± 0.03    | 327 ± 1         | 65 ± 3         | 0.12 ± 0.02    |
|                   | 0.22              | 4.6                 | 0.50 ± 0.03    | 313 ± 1         | 59 ± 3         | 0.17 ± 0.02    |
|                   | 0.33              | 5.7                 | 0.50 ± 0.02    | 303 ± 1         | 54 ± 2         | 0.19 ± 0.02    |
|                   | 0.43              | 7.4                 | 0.49 ± 0.01    | 291 ± 1         | 48 ± 1         | 0.19 ± 0.01    |
|                   | 0.54              | 9.2                 | 0.51 ± 0.01    | 284 ± 1         | 47 ± 1         | 0.18 ± 0.01    |
|                   | 0.75              | 17                  | 0.53 ± 0.01    | 245 ± 1         | 37 ± 1         | 0.21 ± 0.01    |
| 0.4               | 0.11              | 2.4                 | 0.52 ± 0.01    | 320 ± 1         | 28 ± 1         | 0.11 ± 0.01    |
|                   | 0.22              | 3.9                 | 0.55 ± 0.01    | 304 ± 1         | 25 ± 1         | 0.13 ± 0.01    |
|                   | 0.33              | 5.5                 | 0.55 ± 0.01    | 290 ± 1         | 22 ± 1         | 0.16 ± 0.01    |
|                   | 0.43              | 7.9                 | 0.81 ± 0.02    | 278 ± 1         | 17 ± 1         | 0.03 ± 0.01    |
|                   | 0.54              | 10.5                | 0.70 ± 0.04    | 262 ± 1         | 15 ± 1         | 0.06 ± 0.01    |
|                   | 0.75              | 19.6                | 0.85 ± 0.02    | 232 ± 1         | 15 ± 1         | 0.09 ± 0.01    |
| 0.55              | 0.11              | 2.3                 | 0.58 ± 0.01    | 302 ± 1         | 16 ± 1         | 0.13 ± 0.01    |
|                   | 0.22              | 4.4                 | 0.68 ± 0.01    | 286 ± 1         | 11 ± 1         | 0.13 ± 0.01    |
|                   | 0.33              | 6.4                 | 0.72 ± 0.02    | 269 ± 1         | 11 ± 1         | 0.10 ± 0.01    |
|                   | 0.43              | 9.2                 | 0.75 ± 0.02    | 259 ± 1         | 11 ± 1         | 0.12 ± 0.01    |
|                   | 0.54              | 12                  | 0.81 ± 0.02    | 247 ± 1         | 11 ± 1         | 0.12 ± 0.01    |
|                   | 0.75              | 22.9                | 0.68 ± 0.03    | 216 ± 1         | 9 ± 1          | 0.09 ± 0.01    |
| 0.75              | 0.11              | 1.9                 | 0.72 ± 0.02    | 301 ± 1         | 9 ± 1          | 0.09 ± 0.01    |
|                   | 0.22              | 4.2                 | 0.72 ± 0.02    | 286 ± 1         | 8 ± 1          | 0.09 ± 0.01    |
|                   | 0.33              | 6.2                 | 0.72 ± 0.03    | 273 ± 1         | 7 ± 1          | 0.09 ± 0.01    |
|                   | 0.43              | 7.6                 | 0.85 ± 0.02    | 258 ± 1         | 9 ± 1          | 0.12 ± 0.01    |
|                   | 0.54              | 11.8                | 0.61 ± 0.07    | 246 ± 1         | 8 ± 1          | 0.09 ± 0.01    |
|                   | 0.75              | 24.2                | 0.80 ± 0.04    | 214 ± 1         | 7 ± 1          | 0.18 ± 0.01    |

\(^a\) Parameters of a third resolved glass transition in the Q’s = 0.2, aw = 0.75 HMS-S blend.
Table 4
Water activity and parameters associated with the glass transition fitting, as described in Section 2.4 of [2], for the oven-dried HMS-S blends. Q’s is the weight fraction of sucrose in the HMS-S blends (on anhydrous basis), $a_w$ is the water activity of the matrices, $\Delta C_{p,\text{lower}}$ and $\Delta C_{p,\text{upper}}$ are the changes in heat capacity associated with the lower and upper glass transitions, $T_{g,\text{lower}}$ and $T_{g,\text{upper}}$ are the glass transition temperatures and of the sucrose-rich and the HMS-rich phases, respectively, and $\Delta T_{g,\text{lower}}$ and $\Delta T_{g,\text{upper}}$ are the widths of the two glass transitions.

| $Q’S$ [dimensionless] | $a_w$ [dimensionless] | $\Delta C_{p,\text{lower}}$ [J g$^{-1}$ K$^{-1}$] | $T_{g,\text{lower}}$ [K] | $\Delta T_{g,\text{lower}}$ | $\Delta C_{p,\text{upper}}$ [J g$^{-1}$ K$^{-1}$] | $T_{g,\text{upper}}$ [K] | $\Delta T_{g,\text{upper}}$ |
|-----------------------|-----------------------|------------------|----------------|----------------|------------------|----------------|----------------|
| 0                     | 0.014                 | –                | –              | –              | 0.16 ± 0.01      | 449 ± 4        | 15 ± 1         |
| 0.1                   | 0.01                  | 0.31 ± 0.05      | 390 ± 7        | 140 ± 20       | 0.08 ± 0.01      | 430 ± 1        | 15 ± 1         |
| 0.2                   | 0.013                 | 0.40 ± 0.02      | 361 ± 1        | 74 ± 3         | 0.09 ± 0.01      | 396 ± 1        | 16 ± 1         |
| 0.4                   | 0.031                 | 0.46 ± 0.01      | 331 ± 1        | 33 ± 1         | 0.08 ± 0.01      | 357 ± 1        | 19 ± 1         |
| 0.55                  | 0.112                 | 0.53 ± 0.01      | 310 ± 1        | 20 ± 1         | 0.11 ± 0.01      | 342 ± 8        | 27 ± 3         |
| 0.75                  | 0.163                 | 0.60 ± 0.01      | 301 ± 1        | 13 ± 1         | 0.07 ± 0.01      | 350 ± 1        | 20 ± 2         |

Fig. 1. Normalized powder X-ray diffraction profiles of spray-dried HMS/S blends equilibrated at selected water activities. Q’s is the weight fraction of sucrose in the HMS/S blends on anhydrous basis.
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Transparency document. Supporting information

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