The Determination of the Hildebrandt Solubility Parameter of Different Starch Types by Infinite Dilution Inverse Gas Chromatography

Surface Measurement Systems Ltd

Solubility parameters are directly related to the cohesive energy density of a material. The latter is a measure for the strength of interaction between molecules and atoms; therefore, the solubility parameter can be used to predict the stability of food ingredients, polymers, drugs or excipients. Inverse Gas Chromatography provides a fast and sensitive route for the measurement of this parameter. This paper describes the determination of the solubility parameter of starch measured by water at infinite dilution

Introduction

The cohesive energy of a material is a parameter, which quantifies the attraction that atoms or molecules have for one another. Thus it is directly related to the stability of a material. A common way to determine this property uses the solubility parameter, which represents the square root of the cohesive energy density. The solubility parameter was originally derived by Scatchard and Hildebrand for regular solutions [1]. However, its application can be extended to simple solid/liquid or solid/(condensed) vapour systems under the assumption that the investigated solid can be considered as a "supercooled liquid". This is often the case for highly amorphous materials. This means in practise a probe molecule is able to penetrate the bulk structure of a solid when the solubility parameters of the solvent and the material under investigation are similar. It is for this reason that solubility parameters have been successfully applied to various problems in drug delivery [2], cosmetic formulation [3], polymer blending [4], pigment dispersion [5] or solvent selection for nanoparticle preparation [6]. Correlations have been found between the solubility parameter and oral absorption of drugs [7] or particle adhesion [8] and agglomeration [6].

The retention volume measured by Inverse Gas Chromatography (iGC SEA) can be converted into an activity coefficient, which is used to calculate the Flory-Huggins interaction parameter. The solubility parameter can then be obtained from the Flory-Huggins interaction parameter by either varying the temperature or the probe molecule in the iGC SEA experiment [9,10] The former technique was implemented here.

In the current study Hildebrandt (1-D) solubility parameters have been determined for different starch samples with water.

Theory

Solubility effects can be studied by pulse inverse gas chromatography at infinite dilution. In this technique a small amount of an organic vapour is injected into a carrier gas stream. At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear sorption isotherm, which can be described by Henry's Law. In this case the experimentally obtained peaks are symmetrical (Gaussian) and the retention time in the peak maximum can be used to calculate the retention volume. The net retention volumes VN are computed using Equation 1.

$$V_N = j/m \cdot F \cdot (t_R - t_0) \cdot \frac{T}{273.15} \qquad (1)$$

where T is the column temperature, F is the exit flow rate at 1 atm and 273.15K, m the sample mass, tR is the retention time for the adsorbing probe and t0 is the mobile phase hold-up time (dead-time). j is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

After calculating the retention volume from the retention time the activity coefficient Ώ at infinite dilution can be obtained:

$$ln\,\Omega = \ln(273.15*R/(p_O*M_1*V_N)) - p_O*(B_{11} - V_1)/(R*T)$$
$$(2)$$

where po is the saturation pressure, M the molecular mass, B11 the second virial coefficient and V1 the molecular volume of the probe molecule at column temperature. The next step is the calculation of the Flory-Huggins-parameter χ:

$$\chi = \ln\Omega + \ln(\zeta 1/\zeta 2) - (1 - (V1/V2)) \qquad (3)$$

where ζ1 and ζ2 are the liquid densities and V1 and V2 the molecular volumes of probe molecule and sample respectively.

Now using the approach from DiPaola and Guillet [10] a linear equation can be formed:

In this equation δ1 is the solubility parameter of the probe molecule, δ2 the solubility parameter of the polymer and χS the entropic contribution to the Flory-Huggins parameter. If the probe molecule is the variable a plot can be generated, where the term on the left-hand side versus δ1 yields a linear relationship. δ2 can be determined from the slope.

An alternative is the approach from Benczedi [9]. If there are only a few probe molecules with an appropriate solubility, a temperature variation can be carried out with just one probe. This approach is expressed in a linear form:

The parameters have the same meaning as above. So if a plot is made of χ $\Box$/V1 versus 1/T the solubility parameter of the polymer can be obtained from the slope:

In this case the solubility parameter of the sample is assumed to be constant over the temperature range considered.

Method

Different starch types were packed into silanised glass columns (SMS standard column with 2mm ID and 30 cm length). Starch samples used in this study were commercial rice starch supplied by Fluka and wheat starch supplied by Aldrich. Extruded potato starch was provided by Firmenich. All experiments were carried out on an SMS-iGC 2000. Measurements were done with water between 378 and 413 K at 0% RH. Before measurement a pre-treatment was done for 10 h at the initial temperature. Methane was used as a tracer and helium as the carrier gas.

Calculations were performed by using the SMS-iGC Standard and Advanced Analysis Software v1.1 .

Results

Figure 1 shows a typical solubility parameter plot for a temperature variation. In this particular case a measurement was carried out with extruded potato starch between 378 K and 413 K with water as probe molecule.   .
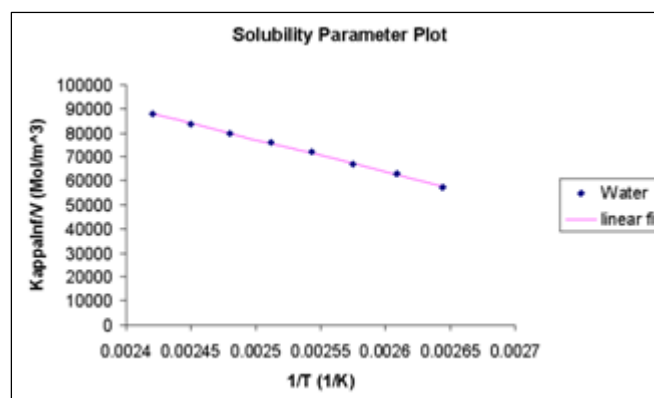

Figure 1. Solubility parameter plot for extruded potato starch measured between 378 K and 413 K with water as probe molecule

The straight line fit is excellent and a result of 14.4 MPa1/2 was obtained. A measurement at the same conditions on rice and wheat starch gave solubility parameters around 5 MPa1/2.

A comparison with the literature showed that low molecular sugars with structures related to starch have a solubility parameter around 37 MPa1/2 [7]. Therefore, a similar value was expected before experiments were undertaken. Benczedi et al published a value of 36.8 MPa1/2 for potato starch, measured between 373 K and 433 K [9] but recalculation of these experimental values showed 22.6 MPa1/2 to be the true result.

One explanation for the underestimation of the solubility parameter of a polymer system such as starch can be its crystallinity. As discussed before, experience has shown that the solubility concept is only valid for materials with a considerable amorphous content. Moreover, even if the system is amorphous, bulk penetration must be sufficiently fast to reach equilibrium during the interaction with the probe molecule. This latter assumption is not always valid since bulk absorption is usually a slow, diffusion controlled process. In this case, the temperature becomes a crucial variable. With increasing temperature, molecular motion will increase and the solubility should reach a maximum close to the glass transition point. Since Benczedi et al measured at higher temperatures it explains why their solubility parameter was higher although it didn't reach the value for low molecular weight sugars. The commercially available rice and wheat starch, however, did appear to be too crystalline to apply the approach used in this study.

Besides the possibility of working at temperatures close to the glass transition, frontal iGC SEA provides the potential to improve results. The benefit of the frontal experiment is that of continuous measurement, so that equilibrium is always attained. In this case slow bulk diffusion will not affect the results and the maximum solubility should be achieved with materials of considerable amorphous content.

However, the results obtained in this study are still interesting with regard to stability issues of partly amorphous materials. Although equilibrium solubility parameters should only have a small temperature dependence, the adsorption kinetics and therefore "non-equilibrium" solubility parameters, determined by pulse chromatography, can be used to predict storage stability since they seem to be a sensitive indicator for the influence of temperature and amorphous content.

Conclusion

iGC SEA provides a fast and easy way to measure the Hildebrandt (1-D) solubility parameter. Commercially available samples of rice and wheat starch showed a value for the solubility parameter close to 0 due to their high crystalline content. Extruded potato starch showed a value of 14.4 MPa1/2 below and 22.6

MPa1/2 close to the glass transition temperature. Lower molecular weight materials with similar structure showed a solubility parameter around 37 MPa1/2. The difference can be explained by the limited access of the probe molecule (water) into the bulk structure of the macromolecules.

Acknowledgement:

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