



The Determination of the Hildebrandt Solubility Parameter of Polymethyl methacrylate by Infinite Dilution Inverse Gas Chromatography

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Solubility parameters are directly related to the cohesive energy density of a material. The latter is a measure of the strength of interaction between molecules or atoms, therefore, solubility parameters are related to stability and other physical properties. Inverse Gas Chromatography provides a fast and reliable route for the measurement of these parameters. This paper describes the determination of the Hildebrandt solubility parameter of PMMA and investigates the influence of different types of Chromosorb, which is used as a carrier for the coated polymer.

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 and other physical properties of a material. A common method of quantification uses the solubility parameter (sometimes also called cohesion 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 amorphous or partially amorphous macromolecules. 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].

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 [7,8]. The latter technique was implemented here.

In the current study solubility parameters have been determined for powdered polymethyl methacrylate (PMMA). For comparison PMMA films coated on different Chromosorb supports have also been investigated.

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 adsorption 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 V_N are computed using Eq. 1.

where T is the column temperature, F is the exit flow rate at 1 atm and 273.15K, m the sample mass, t_R is the retention time for the adsorbing probe and t_0 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 Ω at infinite dilution can be obtained:

$$\ln \Omega = \ln (273.15 \cdot R / (p_0 \cdot M_1 \cdot V_N)) - p_0 \cdot (B_{11} - V_1) / (R \cdot T) \quad (2)$$

where p_0 is the saturation pressure, M the molecular mass, B_{11} the second virial coefficient and V_1 the molecular volume of the probe molecule at column temperature. V_N is the net retention volume.

The next step is the calculation of the Flory-Huggins-parameter χ :

$$\chi = \ln \Omega + \ln (\zeta_1 / \zeta_2) - (1 - (V_1 / V_2)) \quad (3)$$

where ζ is the liquid density and V again the molecular volume.

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

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT} \right) \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{\chi_s}{V_1} \right) \quad (4)$$

In this equation δ_1 is the solubility parameter of the probe molecule, δ_2 the solubility parameter of the polymer, χ_s the entropic contribution to the Flory-Huggins parameter and V_1 the molar volume of the probe molecule. If the probe molecule is the variable a plot can be generated, where the term on the left-hand side versus δ_1 yields a linear relationship. δ_2 can then be determined from the slope.

Method

PMMA powders were packed into silanised glass columns (SMS standard column with 3mm ID and 30 cm length). The pure PMMA sample was purchased from Aldrich. Chromosorb supported PMMA samples were kindly provided by Huntsman, Belgium. Table 1 shows the different Chromosorb types and the PMMA loading.

Table 1. Different Chromosorb types and the PMMA loading.

Chromosorb Type	Loading (%)
'G' acid-washed	5.23
'W' non acid-washed	4.76
'W' acid-washed	2.99
'P' acid-washed	3.49

All solubility experiments were carried out on an SMS-iGC 2000. Measurements were performed with octane, butylcyclohexane, undecane, butyl acetate, dodecane, 1-pentanol, nonane and decane at 363 K and 0% RH with a probe molecule concentration of 0.03 p/po injection pressure. Before measurement a pre-treatment was done for 2 h at the measurement temperature. Methane was used as a tracer (deadtime correction) and helium as the carrier gas.

Calculations were performed by using the SMS-iGC Advanced Software v1.2 .

Results

Figure 1 shows a typical solubility parameter plot for PMMA coated on Chromosorb W acid-washed.

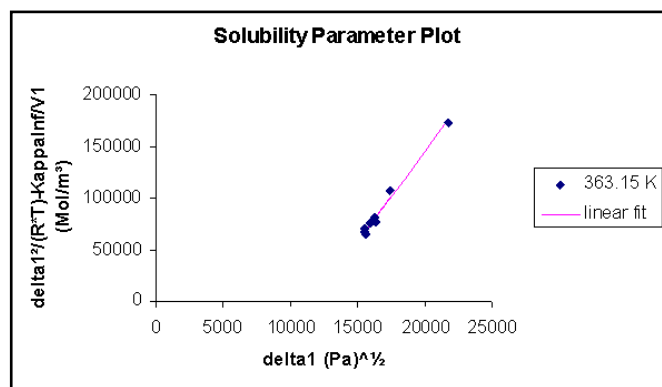


Figure 1. Solubility parameter plot for PMMA coated on Chromosorb W (acid-washed) at 363 K. The different experimental points represent the various probe molecules used (see above).

The results obtained for the different measurements are shown in Table 2.

Table 2. Measured solubility parameters for different PMMA samples and dispersive surface energies of the pure Chromosorb supports.

Chromosorb Type	Sol. Param. (MPa ^{1/2})	γ_d (mJ/m ²)
No support	17.6	-
'G' acid-washed	25.3	45.3
'W' non acid-washed	26.9	66.8
'W' acid-washed	26.3	48.0
'P' acid-washed	28.5	61.4

The measured solubility parameters are average values based on two columns and two runs. They are in the range of numbers reported in other publications [8]. All differences can be considered as significant with exception of the two "W" samples where the differences lie within the error margin found for these measurements (<2%).

A comparison of the solubility parameters indicates that the samples with a Chromosorb support show much higher values than the unsupported PMMA powder. The samples with Chromosorb P has the highest solubility parameter, followed by the 'W' materials and the 'G' sample. These results suggest that the different Chromosorb supports have a significant influence on the retention behaviour as there is some considerable interaction of the probe molecules with the support and not only with the coating, which also affects the solubility parameters.

To gain a better understanding of the Chromosorb influence on the results solubility parameters obtained in this study were correlated with dispersive surface energies of the pure Chromosorb materials reported in an earlier application note [1]. These values can also be found in Table 2. It becomes obvious that the two samples with the highest solubility parameters (with Chromosorb W non acid-washed and P acid-washed) have the two supports with the highest surface energies. Moreover, it is known that acid-washing decreases the surface energy of Chromosorb [1] and this also may have a small influence on the retention volume measured and therefore on the solubility parameters.

The polymer loading appears to be another factor influencing the results. When Chromosorb W non acid-washed and P acid-washed are compared it can be seen that the 'P' sample has the higher solubility parameter but a slightly lower support surface energy than 'W'. This may be explained by the fact that 'W' has a much higher PMMA loading, allowing less interaction of the probe molecule with the Chromosorb surface. To obtain a more detailed understanding of these influences further systematic studies would be necessary.



Conclusion

IGC SEA provides a fast and easy way to measure solubility parameters. Values obtained in this study are in the same range as numbers reported in literature. Chromosorb supported samples show significantly higher solubility parameters than pure PMMA powder. The surface energy of the Chromosorb support as well as the PMMA loading seem to have a significant influence on the final results. It can be concluded that the choice of the Chromosorb support has a drastic impact on the solubility parameters measured. This dependence is more significant the lower the polymer loading due to an increasing interaction of the probe molecules with the support surface. These findings suggest that Chromosorb materials with low surface energies should be selected as supports for polymer coatings and that the polymer loading needs to be sufficient to provide a proper coating which allows the measurement of solubility parameters of the pure polymer coating.

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References

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- [1]Conder, J.R. and Young, C.L., Physicochemical Measurement by GasChromatography, John Wiley and Sons, Chichester, 1979.
 - [2]Lhoest, G., Pharm. Acta Helv. 48 (1973), 549.
 - [3]Vaughan, C., J. Soc. Cosmet. Chem. 36 (1985), 319.
 - [4]Small, P., J. Appl. Chem. 3 (1953), 71.
 - [5]Nara, M., Cosmetics and Toiletries 94 (1979), 23.
 - [6]Duclairon, C. et al, Macromolecules 31 (1998), 3062.
 - [7]Benczedi, D. et al, Macromolecules 31 (1998), 3062.
 - [8]DiPaola-Baranyi, G. and Guillet, J., Macromolecules 11 (1978), 228.
 - [9]Butler, D., SMS Application Note 209, 2003

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