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Improved Method To Calculate Hansen Solubility Parameters Of A Copolymer INFINEUM SV 260

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Abstract

The global and partial solubility parameters and radii of interaction spheres of a copolymer INFINEUM SV 260 were determined from solubility data and intrinsic viscosities using 13 solvents both by the classical Hansen' s method and an improved one. The obtained results are in good agreement each other and with intrnisic viscosity data.

Key words: *copolymer solubility, Hansen solubility parameters, Radius of interaction sphere, intrinsic viscosity, mass center*

Introduction

Solubility parameters are the most used quantities for the selection of solvents for polymers and to predict their compatibility with some other compounds or materials.That is why the solubility parameters of a polymer must be accurately known.
The total solubility parameters, δ, defined by Hildebrand [1] as the square root of the cohesive energy density, CED:

$$\delta = (CED)^{1/2} = (\Delta E^V/V)^{1/2} \quad (1)$$

where ΔE^V is the energy of vaporisation and V – the molar volume, is a measure of all the intermolecular forces responsible for the compound cohesion.
Hildebrand postulated that interaction, such as solvation should be stronger when the solubility parameters of solvent and solute have equal or very close values.
It was found that it is necessary to describe not only the intensity of interactions, but also their nature.
The first step in differentiation of interactions types was made by Praunsnitz et al. [2, 3], who divided the cohesive energy in two components: one due to the dispersion (d) and the one due to all the other types of forces (a). Thus, the total solubility parameter can be written as:

$$\delta = (\delta_d^2 + \delta_a^2)^{1/2} \quad (2)$$

where δ_d and δ_a are corresponding partial solubility parameters.

But it is customary to distinguish three types of intermolecular interactions, which collectively produce the cohesive energy characteristic of the liquid state of phase of non-electrolytes: dispersion, polar (p), and hydrogen bond (h) interactions. Thus, δ_a was divided into its components [4, 5]:

$$\delta_a = (\delta_p^2 + \delta_h^2)^{1/2} \quad (3)$$

where δ_p and δ_h represent the partial solubility parameters due to polar (dipole-dipole and dipole-induced dipole) and hydrogen bonding forces, respectively, and the total solubility parameter is related to the partial ones by the relation:

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \quad (4)$$

The determination of the solubility parameters of many substances being a difficult and laborious undertaking, some correlation between solubility parameters and other physical properties were established [6 – 9].
A more accurate method to predict the solubility of a polymer into a solvent was developed using an elaborated equation taking account of entropy effects, polymer-polymer, polymer-solvent and solvent-solvent interactions [10 – 13]. The equation was also used for oligomers [13-16].
The object of this paper is to determine the partial and total solubility parameters of a copolymer produced and recommended – Infineum UK LIMITED. Both the Hansen' s method [4, 5] and an improved one [14] were used fot their determination.

Experimental Details

The following copolymer were used as: hydrogenated poly(isoprene-co-styrene) (Infieum UK LIMITED) – trade name INFINEUM SV 260 .
Solubility parameters were determined from solubility data using Hansen' s method [4, 5] as well as an improved, more accurante one [14].
The viscosities of the solvents and solution were determined using two Schott Ubbelohde- type viscometers (0a and Ia), selected according to the values of their constant, so that the margins of the uncertainty, inherent in the Hagenbach-Couette correction, does not exceed the error allowed for the measurements. Intrinsic viscosities were determined from the dependence of reduced viscosity on polymer concentration and their extrapolation to zero polymer concentration. Their normalisation at unity by dividing them to the highest value obtained was also necessary to apply the improved method.

Results and Discussion

Determination of the partial and global solubility parameters of a polymer by the classical (Hansen' s) method [4, 5] consists in testing polymer solubility in different solvents with known global and partial solubility parameters. Solvents that interact with the given polymer (dissolve or swell it) are represented as points in planes having as coordinates (δ_p, δ_h),
($2\delta_p$, δ_p) and ($2\delta_d$, δ_h) respectively. They are comprised into circles of radius R, which represents the radius of interaction or solubility sphere of the polymer. The coordinates of the centre of the spheres represent the partial or Hansen solubility parameters of the polymer. Any of the three planes can be considered first for drawing the circle, which results in different values for R and Hansen solubility parameters.
The solvents used, their solubility parameters , the intrinsic viscosities obtained and the normed ones are given in Table 1.

Table 1. The solvents used, their global and partial solubility parameters, intrinsic and normed viscosities at 25°C

Solvents	**δ, (MPa)$^{1/2}$**	**δ_d, (MPa)$^{1/2}$**	**δ_p, (MPa)$^{1/2}$**	**δ_h, (MPa)$^{1/2}$**	**[η], dl/g**	**[η]'$_i$**
n-Heptane	15.3	15.3	0	0	0.7903	0.3190
Cyclohexane	16.8	16.8	0	0.2	2.4767*	1.0000
Benzene	18.6	18.4	0	2.0	0.4923	0.1988
Toluene	18.2	18.0	1.4	2.0	0.6836	0.2760
o-Xylene	18.0	17.8	1.0	3.1	0.8310	0.3355
Metyl-ethyl-cetone	19.0	16.0	9.0	5.1	-	-
Cyclohexanone	19.6	17.8	6.3	5.1	-	-
Chloroform	19.0	17.8	3.1	5.7	1.4131	0.5705
Ethane dichloride	18.4	16.6	8.2	0.4	-	-
Triclorethylene	19.0	18.0	3.1	5.3	2,2608	0.9128
Carbon tetrachloride	17.8	17.8	0	0.6	2.0413	0.8240
Benzene chloride	19.6	19.0	4.3	2.0	0.7777	0.3140
Ethyl acetate	18.2	15.8	6.3	5.1	-	-

*The maximum value of intrinsic viscosity at which normation was made.

The improved method considers that good and limiting solvents of a polymer can be represented into the three-dimensional space of coordinates δ_d, δ_p, δ_h as a system of material points with different weighs [14]. The intrinsic viscosity, [η], being a measure of polymer-solvent interaction (the higher the interactions, the greater the value of intrinsic viscosity), was taken to weight the partial solubility parameters [14]. The coordinates of the mass centre of the system of material points represent the Hansen solubility parameters of the polymer.
The equations of the coordinates of the mass centre are [14]:

$$\delta_d = \sum (\delta_{di} \times [\eta]'_i) / \sum [\eta]_i \quad (5)$$

$$\delta_p = \sum (\delta_{pi} \times [\eta]'_i) / \sum [\eta]_i \quad (6)$$

$$\delta_h = \sum (\delta_{hi} \times [\eta]'_i) / \sum [\eta]_i \quad (7)$$

where $[\eta]'_i$ is the intrinsic viscosity of the polymer in solvent i normalised to unity. Normalisation to unity was made by dividing the intrinsic viscosities in the solvents given in table 1 by the maximum value obtained. Once the coordinates of the mass centre of the system of material points was determined, the distances separating the centre from the points was corresponding to good and limiting solvents, R_i, are computed. The highest value of R_i is considered the radius of interaction sphere. The equation used to compute R_i is the well-known Hansen' s relation:

$$R_i = [4(\delta_{di} - \delta_d)^2 + (\delta_{pi} - \delta_p)^2 + (\delta_{hi} - \delta_h)^2] \quad (8)$$

INFINEUM SV 260 has the highest intrinsic viscosity in cyclohexane, followed by trichlorethylene and carbon tetrachloride and the lowest value in benzene.
The Hansen solubility parameters obtained using the two method are given in Table 2.

Table 2. The Hansen solubility parameters obtained by the classical and the new method

Method	δ, $(MPa)^{1/2}$	δ_d, $(MPa)^{1/2}$	δ_p, $(MPa)^{1/2}$	δ_h, $(MPa)^{1/2}$	R, $(MPa)^{1/2}$
Classical	17.4	17.3	1.2	1.2	4.8
new	17.8	17.6	1.4	2.4	3.7

Conclusions

The method presented in the paper determines more accurately the Hansen solubility parameters and the radius of interaction sphere of a polymer, due to the combination of intrinsic viscosity data (used to determine the Hildebrand solubility parameters) with Hansen solubility parameters and an improved mathematical method.
The method is simple, uses literature data on solvents and polymers, and can be easily imlpemented on a computer.
The equations used to determine Hansen parameters are simple and do not imply special processing.

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Determinarea parametrilor de solubilitate prin metodă hansen şi o metodă îmbunătăţită pentru copolimerul INFINEUM SV 260

Rezumat

În acest articol sunt prezentate doua metode de determinare a parametrilor de solubilitate pentru copolimerul bloc INFINEUM SV 260. Atât metoda Hansen cât şi metoda nouă dau rezultate apropiate pentru parametrii de solubilitate parţiali cât şi global.