Polym. Bull. (2012) 68:1053–1063
DOI 10.1007/s00289-011-0607-8

ORIGINAL PAPER

A new procedure for calculating Hansen solubility parameters of carbon nanotube/polymer composites

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Received: 4 December 2010 / Revised: 1 August 2011 / Accepted: 16 August 2011 /
Published online: 21 August 2011

Abstract In this article, a new modeling and optimization procedure for Hansen solubility parameters (HSP) is developed. HSP values and the radius of interaction sphere for a solute can be determined by using this method based on experimental data at room temperature. The newly developed method could fit the experimental data better and get smaller radius of interaction sphere compared with the classical Hansen's method. The HSP values of carbon nanotubes and polymer matrix are calculated to show the accuracy of the proposed approach. The physical affinity between the carbon nanotubes and polymer in the filler-polymer matrix system composite has been evaluated by their HSP spheres interaction.

Keywords Hansen solubility parameters · Multi-objective optimization · Goal attainment method

Introduction

Hansen [1, 2] solubility parameters are found widespread used in many fields, such as the paints and coating industry, evaluating surfaces of pigments and fillers like carbon nanotubes, selecting solvents, and predicting the adhesion to polymers.

The term of solubility parameter was first used by Hildebrand and Scott [3]. The Hildebrand solubility parameter is defined as the square root of the cohesive energy density (CED):

$$\delta = \sqrt{\text{CED}} = \sqrt{\frac{\Delta E}{V}} \tag{1}$$

where ΔE is the energy of vaporization and V is the molar volume.

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A widely used solubility parameter to predict solubility of the solute is proposed by Hansen [4]. Hansen's total cohesion parameter equals to the Hildebrand parameter. The total solubility parameter is related to the partial ones, which is defined as:

$$\delta = \sqrt{(\delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2)} \tag{2}$$

where δ_{d}, δ_{p}, δ_{h} are dispersive, polar, and hydrogen bonding solubility parameters, respectively. The Hansen solubility parameters are based on the fact that the total energy of vaporization of a liquid consists of the dispersive, polar, and the hydrogen bonding interactions. However, the results of the HSP for polymer and solute calculated by Hansen's model are still not fully satisfied.

The object of this article is to develop an accurate method which could determine the Hansen solubility parameters, as well as the radius of interactions sphere for a given solute with known HSP data of solvents. In this study, the proposed procedure is implemented in Matlab. A set of experimental data was provided for HSP calculation. The method could fit the data better comparing with the classical Hansen's method.

Procedure description

Modeling of problem

The problem characterized by Hansen is studied based on the experimental dispersion, according to the interaction degree between the solvents and solute. The solvents were divided into two groups: good solvents and bad solvents [5]. A sphere was located in the HSP space, the sphere includes the good solvents and excludes the bad solvents with minimum error via a computer program, as shown in Fig. 1. The data input to the program is the solvent number, "1" indicates a "good" solvent, while "0" stands for a "bad" solvent. The program systematically evaluates the input data by using the "desirability function" [6] to fit the data. The function is given as:

$$\textit{Data fit} = (A_1 * A_2 * A_3 \cdots A_n)^{\frac{1}{n}} \tag{3}$$

with

$$A_i = \mathrm{e}^{-(\text{error distance})} \tag{4}$$

where n is the number of solvents for which there is experimental data in correction. The *Data fit* is increasing and approaching 1 when the fit improves during the evaluation. The best and largest *Data fit* is 1, when all the good solvents are inside the sphere and all the bad ones are outside.

For a given good solvent within the sphere and a bad solvent outside the sphere, the A_i is equal to 1. The error distance is the distance to the sphere of the solvent either as being good solvent outside the sphere or bad one inside.

In Fig. 1, R_{o} is the interaction radius of the solute sphere and R_{a} is the distance from a given solvent to the centre of the sphere. R_{o} is one of the main results for the

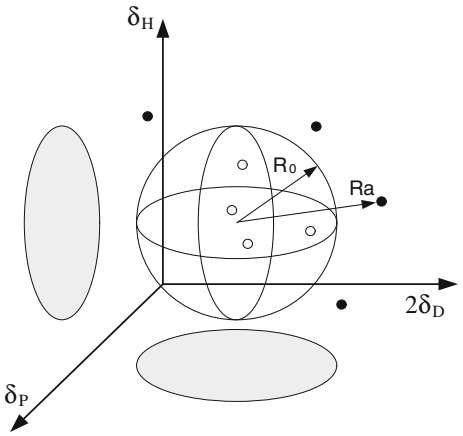

Fig. 1 Classical method for Hansen solubility parameters

program to calculate. The smaller the radius of the sphere is, the more accurate the result is. R_a is calculated using the Eq. 5, where the δ_{D1}, δ_{P1}, δ_{H1} are the centre point of the solute sphere calculated by program, the δ_{D2}, δ_{P2}, δ_{H2} are the solvent coordinates according to the centre point.

$$(R_a)^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (5)$$

For good solvent outside the sphere, Eq. 4 is transformed to Eq. 6, for bad solvent inside the sphere, the formation turns to Eq. 7.

$$A_i = e^{-(R_a - R_o)} \quad (6)$$

$$A_i = e^{-(R_o - R_a)} \quad (7)$$

$$\text{RED} = R_a/R_o \quad (8)$$

The relative energy difference (RED) value has been defined according to Eq. 8, for good solvents the RED is normally below 1.0, and for bad ones the RED will be over 1.0.

Goal attainment method

Hansen's calculation is based on a pseudo optimization, while in some cases the *Data fit* sometimes could not reach 1 and R_o may be not small enough.

Our method for calculating the HSP is different from Hansen's method. In order to get the maximum *Data fit*, and simultaneously obtain the minimum radius of the solubility sphere and the HSP values, we use an optimization toolbox of Matlab, the goal attainment optimization algorithm [7], to implement the proposed method. We define the objective function as:

$$f(R_o, \delta_d, \delta_p, \delta_h) = 1 - \textit{Data fit} \quad (9)$$

The goal attainment method solves the multi-objective optimization problem which is defined as:

$$\min_{X\in\Omega} f(\mathbf{X}) \tag{10}$$

$$\min_{X\in\Omega} R_o \tag{11}$$

where $\mathbf{X}$ is the vector of design variables, $\mathbf{X} = \{R_o, \delta_d, \delta_p, \delta_h\}$. Ω is the feasible parameter space. The optimization problem is converted into the following nonlinear programming problem:

$$\min_{X,\lambda\in\Omega} \lambda \tag{12}$$

Subject to the constraint:

$$f_i - \omega_i\lambda \le g_i \quad i = 1, 2 \tag{13}$$

where the design objectives $f_1 = f(\mathbf{X}), f_2 = R_o$. g_i is the optimization goal for f_i, g_1 is the goal for Eq. 10, so $g_1 = 0$; g_2 is the goal of Eq. 11, while the value is expected as small as possible. $\omega_i \ge 0$ are weights, which can be adjusted according to the objective function. The minimization of the scalar λ leads to the finding of a non-dominated solution which under or over attains the specified goals to a degree represented by the quantity $\omega_i\lambda$.

The program routine

The fitting of the sphere to the data sets has been considered as an optimization problem. The problem has been defined as finding a sphere of minimum radius with the constraints that the good solvents should lie inside the sphere and bad solvents outside the sphere.

The Matlab's optimization toolbox "fgoalattain" function is used for the implementation of the optimization. This function uses nonlinear programming to minimize the multivariable objective function within the given constraints.

The routine of the program is illustrated in Fig. 2. Input to the computer program included every liquid for solubility parameters, and interaction data were selected from published works [2, 4]. Then, the computer program proceeds to locate the HSP and R_o parameters which give the best *Data fit*. A perfect fit of data would have a "*Data fit*" of 1.0. This is found for correlations of affinities for the tested material.

In this program, the average value of δ_d, δ_p, δ_h of the good solvents, and the radius of 0 were chosen as the start point. Through the calculation, the output data of the program are the HSP values, the interaction radius R_o of the solute, and the RED values of the solute to each solvent.

When the optimized results are found, it is compared with the Hansen's method to evaluate its improvement.

Results and discussion

Hansen's program finds the HSP of the polymer in the neighborhood of the answer region, and Hansen did not recommend that *Data fit* must be unity. This condition

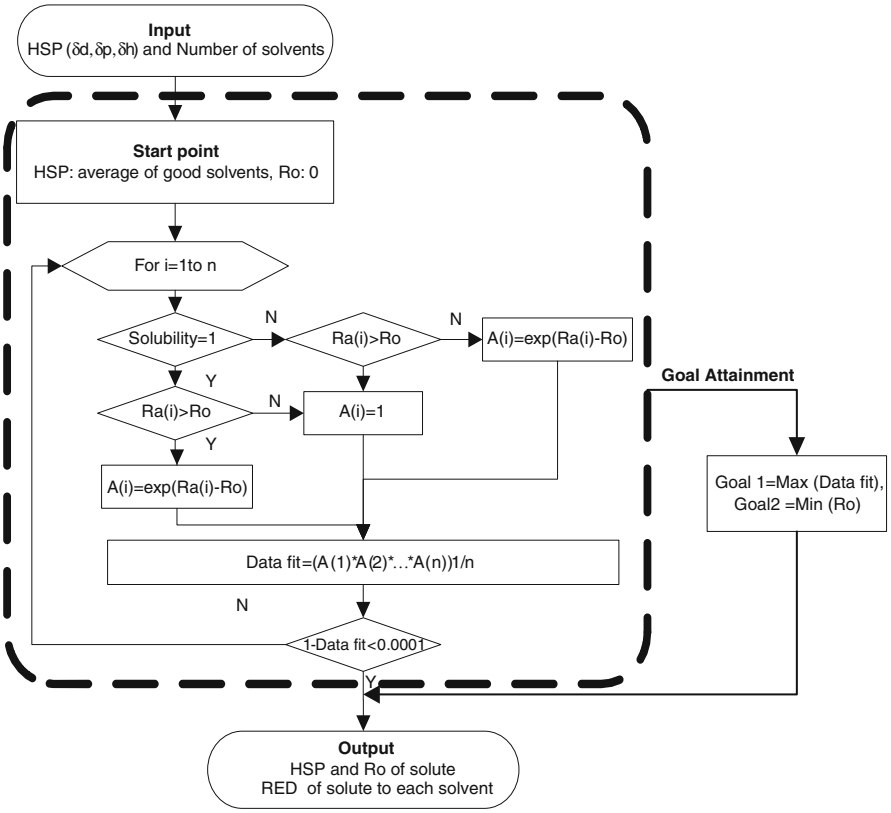

Fig. 2 The flowchart of the program

influences the calculated values of the polymer HSP and radius of the solubility sphere.

With reduced *Data fit* some error situations may happen, such as good solvents lies outside of the sphere, but it should be inside, bad solvents lies inside the sphere where it should be not.

The modified program was tested for several polymers, and the *Data fit* of the calculated HSP of the polymers are improved compared with Hansen's program. For the detail illustration, an example of poly (ether sulfone) (PES) which was illustrated by Hansen [2], 41 solvents were tested for this polymer, the results are shown in Table 1. In this study, the Hansen solubility parameters δ_d, δ_p, δ_h, and R_o were obtained, and the *Data fit* of Hansen's method is 0.999. These parameters were calculated with our method with the value of 1 for *Data fit*. As shown in Table 1, the HSP and R_o are $\delta_d = 18.8$, $\delta_p = 11.2$, $\delta_h = 7.9$, R_o=5.4, respectively. All these values are different from Hansen's values. However, our method could obtain smaller R_o and bigger *Data fit* comparing with Hansen's.

When the RED value is below 1.0, the corresponding solvent could dissolve the polymer, while when the RED is above 1.0, the solvent could not dissolve the

Table 1 Calculated solubility sphere for PES

Solvent	δ_d[a]	δ_p[a]	δ_h[a]	S[b]	RED1[c]	RED2[d]
Acetone	15.5	10.4	7	0	1.371	1.251
Acetophenone	19.6	8.6	3.7	1	0.955	0.962
Benzene	18.4	0	2	0	2.129	2.355
1-Butanol	16	5.7	15.8	0	1.777	2.070
Butyl acetate	15.8	3.7	6.3	0	1.741	1.814
Gamma-Butyrolactone	19	16.6	7.4	1	0.998	1.000
Carbon tetrachloride	17.8	0	0.6	0	2.301	2.510
Chlorobenzene	19	4.3	2	0	1.576	1.687
Chloroform	17.8	3.1	5.7	0	1.483	1.606
Cyclohexanol	17.4	4.1	13.5	0	1.467	1.761
Diacetone alcohol	15.8	8.2	10.8	0	1.321	1.363
o-Dichlorobenzene	19.2	6.3	3.3	0	1.204	1.257
Diethylene glycol	16.6	12	20.7	0	2.101	2.514
Diethyl ether	14.5	2.9	5.1	0	2.183	2.284
Dimethyl formamide	17.4	13.7	11.3	1	0.915	0.940
Dimethyl sulfoxide	**18.4**	**16.4**	**10.2**	**0**	**0.996**	**1.059**
1,4-Dioxane	19	1.8	7.4	0	1.493	1.751
Ethanol	15.8	8.8	19.4	0	2.077	2.448
Ethanolamine	17	15.5	21.2	0	2.241	2.674
Ethyl acetate	15.8	5.3	7.2	0	1.547	1.574
Ethylene dichloride	19	7.4	4.1	0	1.007	1.002
Ethylene glycol	17	11	26	0	2.837	3.420
Ethylene glycol monobutyl ether	16	5.1	12.3	0	1.563	1.746
Ethylene glycol monoethyl ether	16.2	9.2	14.3	0	1.395	1.579
Ethylene glycol monomethyl ether	16.2	9.2	16.4	0	1.618	1.888
Formamide	17.2	26.2	19	0	3.044	3.502
Hexane	14.9	0	0	0	2.745	2.929
Isophorone	16.6	8.2	7.4	0	1.094	1.001
Methanol	15.1	12.3	22.3	0	2.575	3.009
Methylene dichloride	18.2	6.3	6.1	1	0.99	1.000
Methyl ethyl ketone	16	9	5.1	0	1.368	1.238
Methyl isobutyl ketone	15.3	6.1	4.1	0	1.782	1.761
Methyl-2-pyrrolidone	18	12.3	7.2	1	0.655	0.385
Nitroethane	16	15.5	4.5	0	1.58	1.453
Nitromethane	15.8	18.8	5.1	0	1.899	1.866
2-Nitropropane	16.2	12.1	4.1	0	1.387	1.210
Propylene carbonate	20	18	4.1	0	1.429	1.501
Propylene glycol	16.8	9.4	23.3	0	2.457	2.969
Tetrahydrofuran	16.8	5.7	8	0	1.237	1.270
Toluene	18	1.4	2	0	1.978	2.146

Table 1 continued

Solvent	δ_d[a]	δ_p[a]	δ_h[a]	S[b]	RED1[c]	RED2[d]
Trichloroethylene	18	3.1	5.3	0	1.485	1.611

[a] The δ_d, δ_p, δ_h are in units of $MPa^{1/2}$ [2]

[b] S stands for the solubility [2]

[c] Obtained with classical Hansen's program [2] ($\delta_d = 19.6$, $\delta_p = 10.8$, $\delta_h = 9.2$, $R_o = 6.2$, *Data fit* $= 0.999$)

[d] Obtained with our modified program ($\delta_d = 18.8$, $\delta_p = 11.2$, $\delta_h = 7.9$, $R_o = 5.4$, *Data fit* $= 1$)

polymer, and the interaction between the solvent and polymer is weak. As seen in Table 1, the solvent Dimethyl sulfoxide is bad solvent for PES ($S = 0$), while the RED2 (1.059) calculated by our method could indicate this point. However, the RED1 (0.996) calculated by Hansen's classical method could not. As illustrated in Table 1, the values of HSP for PES are greatly affected by the values of *Data fit*. The difference between the values of *Data fit* in Hansen's work and our work is 0.001, but this small difference affects the HSP values and R_o of polymer considerably.

In Fig. 3, it can be seen that the optimization method affects the location of the solute spheres. The centre (δ_d, δ_p, δ_h) of the sphere A (by modified method) is different from that of sphere B (by classical method). As the *Data fit* of the classical method does not reach 1, some of the good solvents are outside or some of the bad solvents are inside sphere B. However, as the *Data fit* equals to 1, the sphere A calculated by the modified method includes all the good solvents and excludes all the bad ones. The radius of the sphere A is smaller than the sphere B, which means that the prediction of the compatibility by using the modified method is more accurate. As mentioned by Hansen [2], the output of the calculation is for the smallest radius with the maximum *Data fit*.

The carbon nanotube could be used as reinforcement for polymer to improve the mechanical, electrical, and thermal properties; however, it is very difficult to get good dispersion of carbon nanotube in polymer and good surface adhesion between carbon nanotubes and polymers. One practical application of the HSP method is to infer the interaction between two materials, the compatibility between the carbon nanotube and polymer and hence the properties of the composite could be predicted by HSP. In order to illustrate one example for the prediction, and compare the results for the accuracy of the prediction, the example of epoxy and carbon nanotube is illustrated.

The HSP of the epoxy resin and carbon nanotubes obtained by the two methods are listed in Table 2. Comparing the values obtained by the two methods based on the same experimental data, the modified method also gets the *Data fit* of 1, and much smaller R_o values.

The HSP and R_o are in units of $MPa^{1/2}$. The *Data fit* should be 1.000 for all good solvents (G) out of a total number of solvents (T) having R_a less than R_o.

Figure 4 presents the region of the interaction of epoxy resin and the carbon nanotubes calculated by the modified method. The spheres of the carbon nanotubes

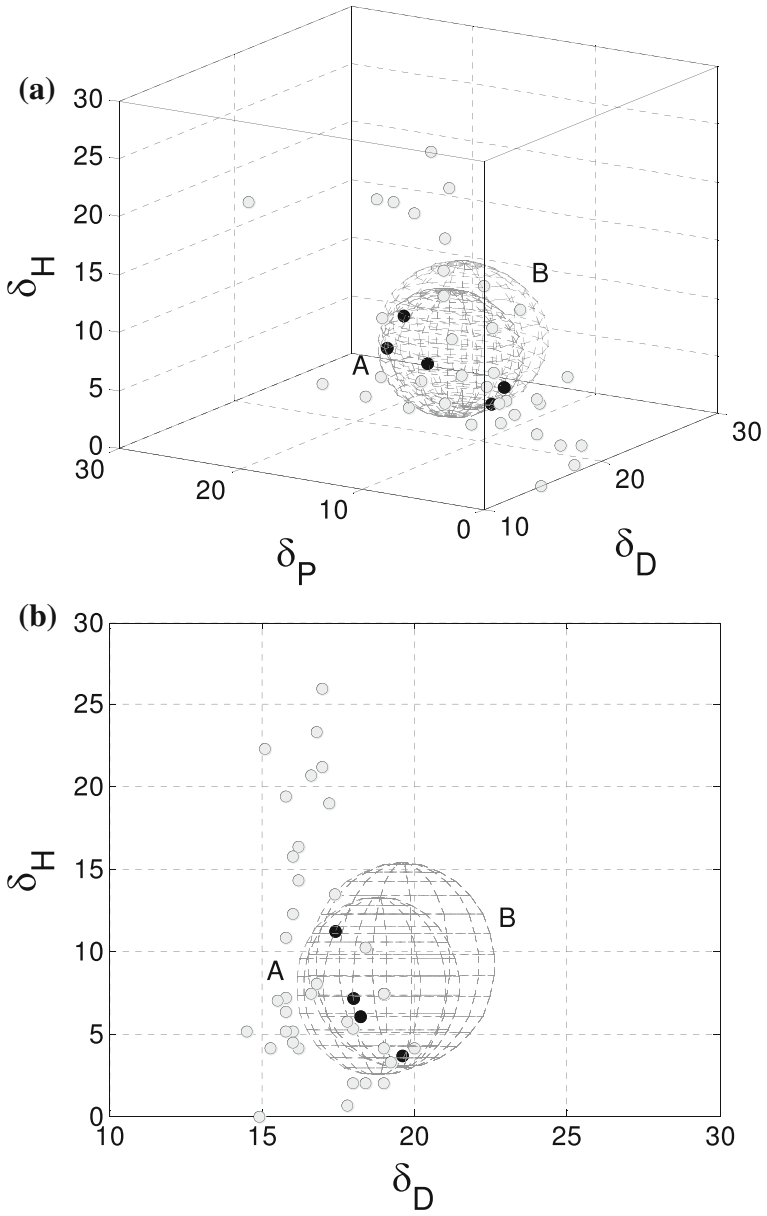

Fig. 3 The three-dimensional and two-dimensional plots of the PES spheres *A* (by modified method), *B* (by classical method), and the solvents (*black circles* good solvent; *gray circles* bad solvent) used for calculation

and the epoxy resin are partly superposed. If we take epoxy resin as a solvent in the composite, the RED value between epoxy resin and carbon nanotubes equals to 0.39 differs from 0.5 calculated by the classical method, which is far below 1, indicating

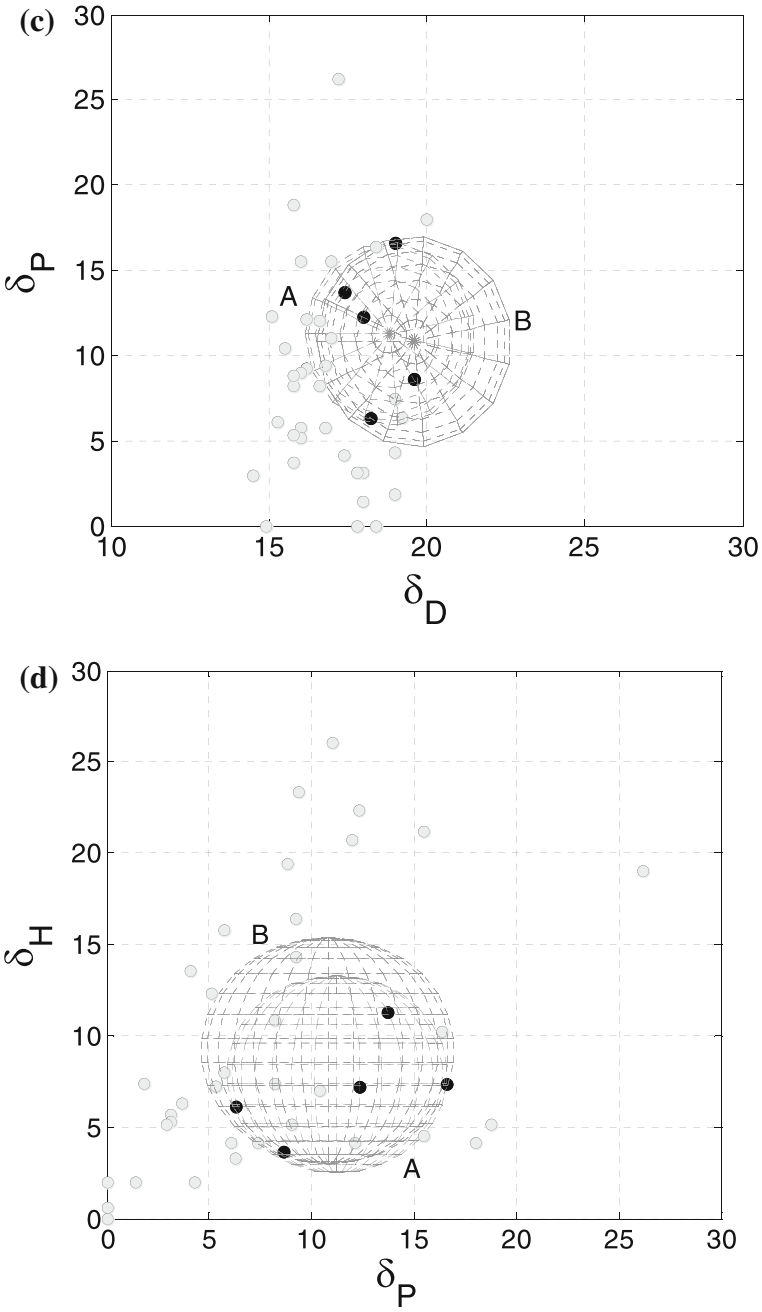

Fig. 3 continued

Table 2 HSP and R_o values for polymer and carbon nanotube obtained by classical and the modified method

Material	δ_d	δ_p	δ_h	R_o	*Data fit*	*G/T*
Epoxy resin (classical method)[a]	20.0	10.0	8.0	9.0	1.000	7/18
Epoxy resin (modified method)	19.1	9.4	8.4	7.4	1.000	7/18
Carbon nanotubes (classical method)[b]	21.3	5.7	11.3	12.4	1.000	12/19
Carbon nanotubes (modified method)	20.2	6.2	10.2	10.9	1.000	12/19

[a] Launay et al. [8]

[b] Ham et al. [9]

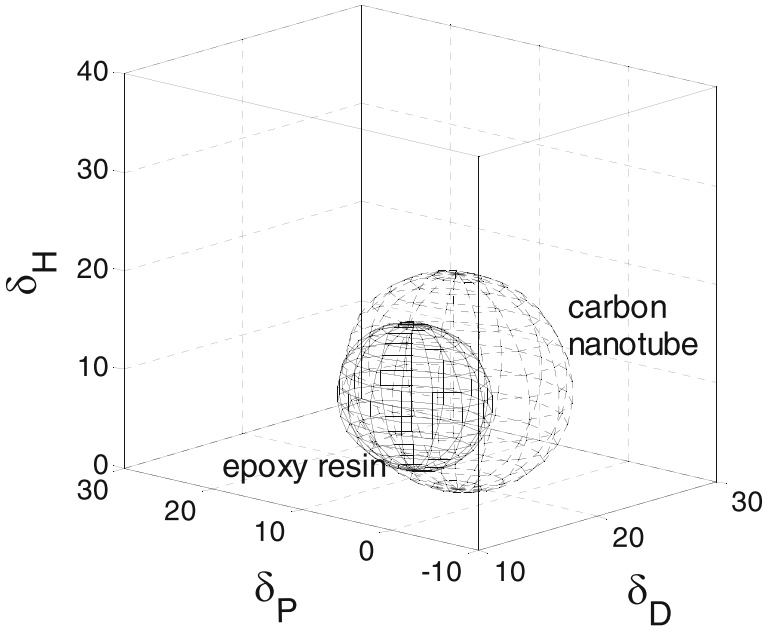

Fig. 4 The three-dimensional plot of the epoxy resin sphere, carbon nanotube sphere calculated by the modified method

that the carbon nanotubes should be soluble in epoxy resin, the carbon nanotubes and epoxy resin should have very high affinities.

In the same way, the interaction and physical affinities in composites between the carbon filler-polymer matrix systems could be studied by this model.

Conclusions

In this article, a new modified method of calculating Hansen solubility parameter by utilizing Goal attainment optimization algorithm was presented. This method could be used to determine more accurate Hansen solubility parameters and smaller radius

of interaction sphere of a solute in various solvents with known HSP compared with the classical HSP method.

The physical affinity between the carbon nanotubes and epoxy resin was investigated by using this modified method. This method could be applied for the estimation of the interaction and physical affinities in composites between the carbon filler-polymer matrix systems.

References

1. Hansen CM (1967) The three dimensional solubility parameter and solvent diffusion coefficient. Their importance in surface coating formulation. Thesis, Danish Technical Press
2. Hansen CM (2007) Hansen solubility parameters: a user's handbook, 2nd edn. CRC Press, Boca Raton
3. Hildebrand JH, Scott RL (1950) The solubility of nonelectrolytes. American Chemical Society. Monograph series, vol 17, 3rd edn. Reinhold Pub Corp., New York
4. Barton AFM (1991) CRC handbook of solubility parameters and other cohesion parameters, 2nd edn. CRC Press, Boca Raton
5. Hansen CM (2000) Hansen solubility parameters: a user's handbook. CRC Press, Boca Raton
6. Harrington EC (1965) The desirability function. Ind Qual Control 21(10):494
7. Gembicki FW, Haimes YY (1975) Approach to performance and sensitivity multiobjective optimization—goal attainment method. IEEE Transactions on Automatic Control 20(6):769–771
8. Launay H, Hansen CM, Almdal K (2007) Hansen solubility parameters for a carbon fiber/epoxy composite. Carbon 45(15):2859–2865. doi:10.1016/j.carbon.2007.10.011
9. Ham HT, Choi YS, Chung IJ (2005) An explanation of dispersion states of single-walled carbon nanotubes in solvents and aqueous surfactant solutions using solubility parameters. J Colloid Interf Sci 286(1):216–223. doi:10.1016/j.jcis.2005.01.002