HANSEN SOLUBILITY PARAMETERS
AND SWCNT COMPOSITES

R.Mikael.Larsen
Associate professor, Ph.D.
Department of Mechanical Engineering- Aalborg University
Pontoppidanstraede 101, DK 9220 Aalborg SÖ, Denmark
rml@ime.aau.dk

SUMMARY

In this study purified and modified SWCNT are embedded in epoxy and polycarbonate (PC) and the strain transfer from the matrix is evaluated by monitoring the G' Raman band shift of the carbon nanotube as strain is applied to the composite. Hansen solubility parameters are use to explain the varying degree of strain transfer.

Keywords: carbon nanotubes, modification, composites, interfacial strength, Raman, dispersion

INTRODUCTION

Polymeric composites with carbon nanotubes have still not explored the potential expected from the excellent mechanical properties of the carbon nanotubes and their large aspect ratio. Dispersion of the nanotubes within the polymeric matrix is difficult. SWCNTs agglomerates in bundles and a good dispersion of carbon nanotubes within the polymeric matrix is crucial in order to receive the optimal properties of the composite. A good dispersion will assure a better transfer of strains to the carbon nanotubes, because of an improved aspect ratio and higher compressive stresses on the CNT from the surrounding matrix. These compressive stresses will increase the friction force between the matrix and the nanotube. The compressive stresses come from the thermal contraction of the polymeric matrix when cooling below the melting point or the glass temperature [1].

The idea in this paper is to use the Hansen solubility parameters to predict the dispersion state of purified and modified carbon nanotubes during the processing of the nanotube composites and in the final composites. The strain transfer will be examined by monitoring the G' Raman band shift of the carbon nanotubes when applying a mechanical strain the composite [2].

HANSEN SOLUBILITY PARAMETERS (HSP)

HSP give information on the compatibility of the involved substances and are widely used to predict solvents for organic substances [3]. HSP can quite easily be provided by dispersing carbon nanotubes in different solvents with known solubility parameters as described by H. Launay et al [3]. For a good dispersion the solubility parameters for the

solvent or polymeric matrix should lie close to the CNT-material. The criterion for a good dispersion in the final polymer probably requires that the CNT material is dispersed well in both the solvent used during the manufacturing process and the polymer. In this paper the composite material is manufactured by ultrasonically mixing the nanotubes in a solvent then adding the polymer and finally evaporating the solvent and for the epoxy eventually adding the hardener.

Solubility parameter and thermodynamics of polymer-solvent mixing

HSP is an extension to the original Hildebrand solubility parameter. The original Hildebrand solubility parameter (δ) is derived from the Cohesive Energy Density (CED) [4,5]

$$\delta^2 = CED = \frac{\Delta U_{vap}}{V}$$

ΔU_{vap} is the energy of evaporation or the cohesive energy and V the molar volume.

To form a solution the thermodynamic laws require that the Free energy of mixing is less than zero.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

According to Flory-Huggins theory the entropy of mixing of a polymer in a small molecule solvent can be written as [6]

$$\Delta S_{mix} = -R\left(\frac{\varphi_1}{X_1}\ln\varphi_1 + \frac{\varphi_2}{X_2}\ln\varphi_2\right) = -R(x_1\ln\varphi_1 + x_2\ln\varphi_2)$$

φ_i is the volume fraction, X_i is number of monomer units in each of the polymers, x_i the molar fraction.

Flory-Huggins expressed the Free energy of mixing as

$$\Delta G_{mix} = -RT(\chi\varphi_1\varphi_1 + x_1\ln\varphi_1 + x_2\ln\varphi_2)$$

where χ represents the enthalpic term and is known as Flory-Huggins chi parameter.

This enthalpic term has later been revised and is now considered being a Gibb's free energy term, where ΔG_{mix} can be expressed by $\Delta G_{noncomb}$ and ΔS_{comb}. $\Delta G_{noncomb}$ is the free energy excluded the combinatorial entropy of solution ΔS_{comb}, which is equal to the Flory-Huggins entropy of mixing.

$$\Delta G_{mix} = \Delta G_{noncomb} - T\Delta S_{comb}$$

To correct for this chi is divided into an enthalpic and an entropic part

$$\chi = \chi_H + \chi_S$$

The enthalpic part of the chi-parameter was expressed by Hildebrand using the solubility parameters

$$\chi_H = \frac{V_{mix}}{RT}(\delta_1 - \delta_2)^2$$

And the entropic part (X_S) is many times considered to have a constant value of 0.34 but can vary a lot [7,8]. Using Hildebrand solubility parameters Gibb's free energy of mixing can thus be expressed as

$$\Delta G_{noncomb} = \varphi_1 \varphi_2 V_{mix} (\delta_1 - \delta_2)^2 + RT(\varphi_1 \varphi_2 \cdot \chi_S + x_1 \ln \varphi_1 + x_2 \ln \varphi_2)$$

φ_n is the volume fraction, V the molar volume ($V_{mix} = x_1 V_1 + x_2 V_2$) and δ is Hildebrandt solubility parameter [5].

The combinatorial entropy of mixing ($\Delta S_{comb} = -R(x_1 \ln \varphi_1 + x_2 \ln \varphi_2)$) is normally very small for polymer-solvent solution due to the large polymer chains. If the values of Hildebrand solubility parameter for the solvent-solute pair are close $\Delta G_{noncomb}$ will be small and ΔS_{comb} will assure that ΔG_{mix} will be less than zero. Hildebrandt solubility parameter works well for non-polar species without hydrogen bondings. For such species Hansen solubility parameters can be used.

In this case the cohesive energy is divided into three contributions, one from the dispersive forces, one from the polar bindings and one from hydrogen bindings [8].

$$E = E_D + E_P + E_H$$

$$\frac{E_T}{V} = \frac{E_D}{V} + \frac{E_P}{V} + \frac{E_H}{V}$$

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

Using Hansen solubility parameters to express the chi parameter it is possible to omit the entropic part [8].

$$\chi = \frac{V_{mix}}{RT} \left[(\delta_{D1} - \delta_{D2})^2 + 0.25(\delta_{P1} - \delta_{P2})^2 + 0.25(\delta_{H1} - \delta_{H2})^2 \right]$$

The factor of 0.25 is mainly determined from empirical data and the theoretical foundation does not seem to be well established.

For a graphical representation Hansen normally uses this equation

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

where R_a is the distance between the solvent and the material. The solute is tested against solvents with known Hansen solubility parameters and in this way the Hansen solubility parameters of the solute together with a R_0 distance can be found. Solvent which are closer than R_0 will likely be a good solvent. The ratio between R_0 and R_a is called the relative energy difference (RED)

$$RED = R_a / R_0$$

Good solvent normally have RED less than 1.0 and will be found inside the HSP sphere, which is shown in figure 1.

Figure 1. 3D plot of the HSP sphere
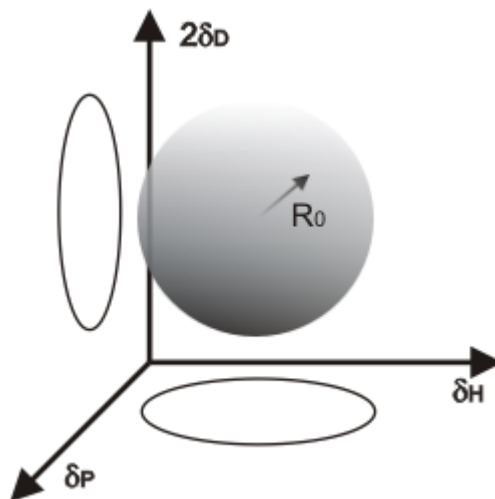
The theoretical background for the solubility parameters concerns large molecules dissolved in a solvent with small molecules. However Hansen solubility parameters are successfully being used to judge the compatibility between polymers and polymers additives like pigments and additives [9].

EKSPERIMENTAL

SWCNT material (Carbolex grade A) was purified by oxidation in air at 300°C followed by 6M HCl reflux to remove catalyst particles. After purification two different modifications were applied. At first the SWCNT was treated with 5M HNO_3 adding carboxylic groups to the nanotubes. Some of the HNO_3 modified SWCNT was melted with octadecylamine to add hydrocarbon chains to the nanotube leading to the ODA modified SWCNT. The purification and modification are more fully described in a previous paper [10]. Determination of Hansen solubility parameters was done by sonication small amounts of the CNT-material in 17 different solvent with known HSP. These solvents are shown in table 1. The solvents and the CNT were placed in a test tube and were sonicated in an ordinary ultrasonic bath. After sonication for 24 hours the SWCNT was in most cases dispersed. Some sedimentation took place during the first 24 hours and hereafter very little change in the dispersion state was observed. The dispersion state was determined 72 hours after the sonication. The solvents were separated in "good" and "bad" solvents depending on the dispersion state for the CNT. A computer program described by H.Launay et al. was used to determine the HSP [3].

Table 1. HSP for the solvents used for determining HSP for the materials

	δ_d	δ_p	δ_h	δ_t
Methanol	15.1	12.3	22.3	29.6
Ethanol	15.8	8.8	19.4	26.5
2-propanol	15.8	6.1	16.4	23.5
Acetone	15.5	10.4	7.0	19.9
Tetrahydrofuran	16.8	5.6	8.0	19.4
Cyclohexanone	17.8	6.3	5.1	19.6
Ethyl acetate	15.8	5.3	7.2	18.2
Acetonitrile	15.3	18.0	6.1	24.4
N,N-dimethylformamide	17.4	13.7	11.3	24.8
Triethylamine, N,N-Diethylethenamine	14.6	3.7	1.9	15.2
Dicloromethan, methylenchlorid	18.2	6.3	6.1	20.3
Chloroform	17.8	3.1	5.7	19.0
Tetrachloromethane	17.8	0	0.6	17.8
Hexane	14.9	0	0	14.9
Decahydronaphthalene	18.8	0	0	18.8
Benzene	18.4	0	2.0	18.6
Xylol, o-xylene, 1,2-dimethylbenzene	17.8	1.0	3.1	18.0

RESULTS AND DISCUSSION

As is seen in table 2 and 3 the different SWCNT materials behaved very different in the various solvent and the method seems to be a valuable additions to the traditionel methods as for instance FTIR when analysing the modification of SWCNT. HNO_3 modified SWCNT are well dispersed in all the solvents with a combination of strong hydrogen bondings and strong polar bondings i.e. solvents with high δ_H and δ_P. The carboxylic groups added on the nanotubes explains the great affinity for hydrogen bondings. Because for the strong affinity for all solvents with high δ_H and δ_P it is not possible to estimate a very reliable value of the HSP and especially the value for R_0 is also somewhat uncertain. ODA modified SWCNT on the other hand is only dispersed well in a few solvents and determination of the HSP is better and also R_0 becomes very small. For purified CNT HSP values are not very good. Cyclohexanone is a bad solvents but have a RED values of 1. Chloroform which is an excellent solvent has a RED slightly higher than 1. H.T.Ham et al. also measured the HSP of purified SWCNT in a similar way [11]. However, they got some different results. They got very bad dispersion in ethanol and methanol. Their SWCNT was from Carbon Nanotechnologies produces by the HiPco process which is a CVD process. The SWCNT in this study is produced by electric arc discharge. Normally much more than 17 solvent with well defined HSP are required to determine the HSP for a unknown material and more solvents would give much better results. However for HNO_3 and ODA modified CNT

the agreement is very good and it is also to be noted that solvents resulting in bad dispersion also are associated with a high RED value which is in good agreement with the theory.

Table 2. Dispersion state and RED value for the tested materials.
Marks for the dispersion state: 1: completely dispersion, 2: dispersed but inhomogeneous 3: very inhomogeneous, 4: Swollen, but sedimented, 5: sedimented
Only solvent with mark 1 was considered as a good solvent.

	Purified		**HNO3**		**ODA**	
	Dispersion	RED	Dispersion	RED	Dispersion	RED
Methanol	2	1.34	1	0.95	5	4.52
Ethanol	2	1.06	1	0.79	4	3.50
2-propanol	1	0.86	1	0.79	4	2.61
Acetone	1	0.46	1	0.72	4	1.67
Tetrahydrofuran	1	0.75	2	1.02	1	0.78
Cyclohexanone	4	1.00	2	1.26	2	1.11
Ethyl acetate	1	0.64	2	1.02	1	0.50
Acetonitrile	1	1.00	1	0.95	5	3.50
N.N-dimethylformamide	1	0.87	1	0.60	4	2.84
Triethylamine.	2	1.01	3	1.52	3	1.21
Dicloromethan	2	1.02	3	1.24	3	1.25
Chloroform	1	1.12	3	1.43	1	0.89
Tetrachloromethane	4	1.57	4	1.99	2	1.82
Hexane	4	1.40	5	1.93	3	1.80
Decahydronaphthalene	4	1.72	4	2.10	2	2.20
Benzene	4	1.56	4	1.94	2	1.77
Xylol. o-xylene	4	1.37	4	1.74	3	1.31

Table 3 HSP from the materials involved in this study. HSP for the epoxy is from H.Launay et al.[3] HSP for PC is from C.M.Hansen [8]

	CNT			**Polymer**	
	Purified	HNO3	ODA	Epoxy	PC
δ_D	13.8	14.8	15.8	20.0	18.6
δ_P	9.4	12.6	3.7	10.0	8.4
δ_H	9.8	13.3	6.0	8.0	6.0
R_0	9.8	9.1	4.1	9.0	

As seen in fig.2 and table 4 the strain transfer is generally more effective for the epoxy composites. 5M HNO_3 dispersed very well in ethanol and 5M HNO_3 is known to exfoliate/debundle CNT bundles which must be the reason for the much better strain

transfer in the 5M HNO$_3$ modified CNT/epoxy composite [12]. The better dispersion of HNO$_3$ modified compared to purified SWCNT can be seen in the SEM images in figure 3 showing the CNT after filtrating the CNT/solvent mixtures through a membrane filter. The bundles for HNO$_3$ modified CNT is clearly smaller. Octadecylamine-modified (ODA) CNT dispersed very well in THF but the dispersion in epoxy according to the HSP is bad and the strain transfer is inferior. None of the CNT materials dispersed very well in cyclohexanone which could be an explanation for the poorer strain transfer in the PC composites compared to the epoxy. The choice of chloroform or tetrahydrofuran as a solvent for the ODA modified CNT and also the purified CNT could be a better choice as these solvent also dissolves PC.

Hansen solubility parameters are a valuable tool when trying to predict and understand the dispersion of carbon nanotubes in polymers. However it seems that other effects also influence the strain transfer which is important as we try to evaluate the dispersion by measuring the strain transfer. HNO$_3$ as mentioned is capable of debundling the SWCNTs. Compressive stresses from the polymer, which are formed during cooling have a great influence on the strain transfer and could also be the reason for the differences between the PC and the epoxy [1,10] .
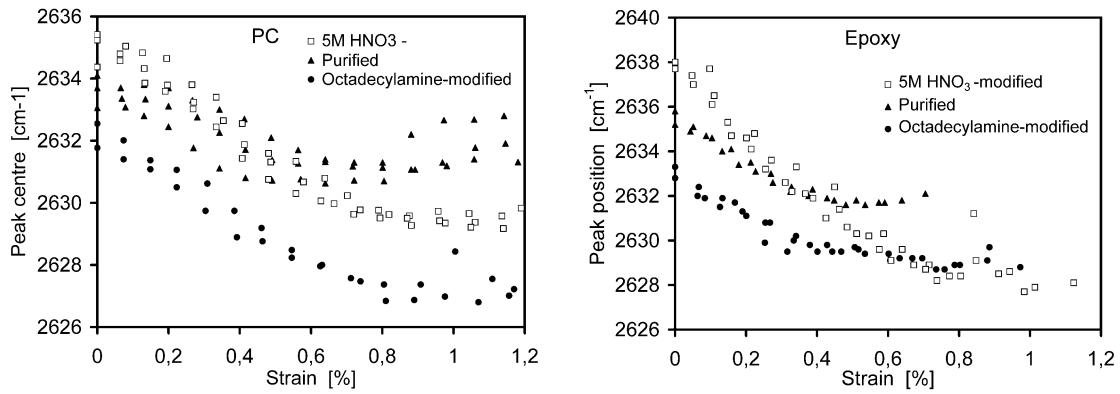

Figure 2. G' Raman band shift as a function of the applied strain to the composite.

Table 4. The Raman shift rate and the max. shift providing information on the interfacial shear strength is shown together with the compatibility parameters RED for CNT in the solvent and the polymer.
[1] The parameter is calculated but purified CNT did not disperse well in cyclohexanone.

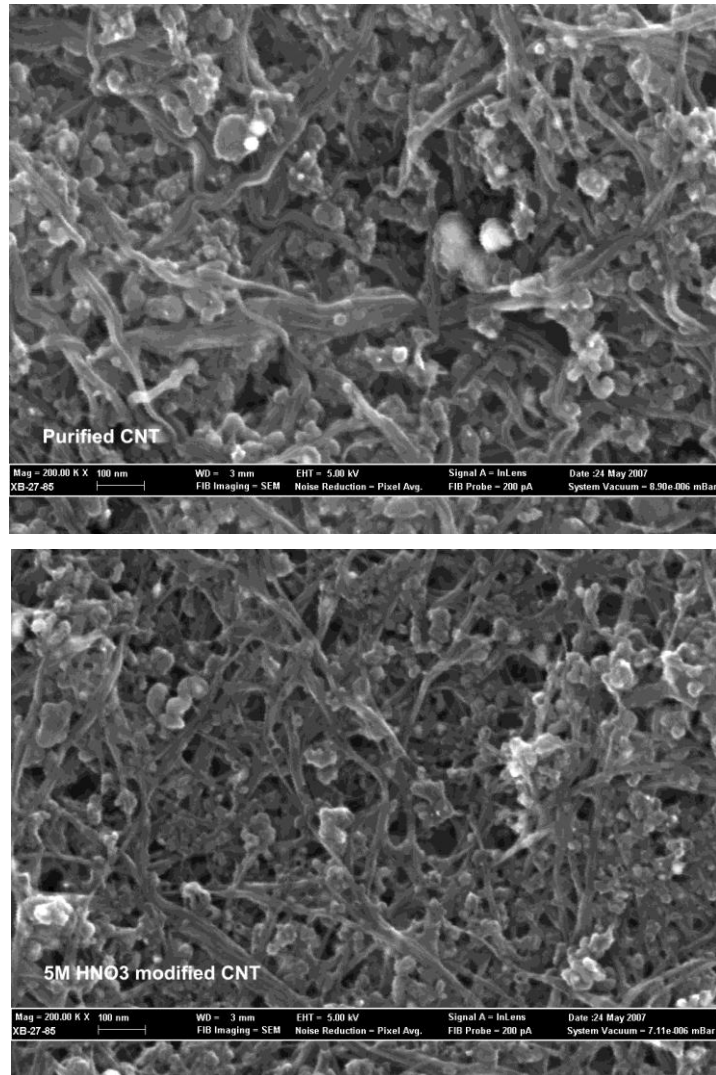| Polymer/solvent	CNT material	Raman shift rate [cm^{-1}/%]	Max shift [cm^{-1}]	RED solvent	RED polymer
Epoxy/EtOH	Purified CNT	10.1	~4	1.06	1.28
Epoxy/EtOH	5M HNO3	14.2	~9	0.79	1.31
Epoxy/THF	ODA CNT	8.9	~4	0.78	2.61
PC/Cyclohexanone	Purified CNT	4.2	~3.5	1.00[1]	1.05
PC/Cyclohexanone	5M HNO3	8.0	~5.5	1.26	1.25
PC/Cyclohexanone	ODA CNT	7.1	~5	1.11	1.78

Figure 3 SEM images of the purified and HNO3 modified SWCNT after ultrasonically dispersion in ethanol and filtrated through a gold-coated membrane filter

CONCLUSION

Determining Hansen Solubility Parameters is experimentally a simple task and gives information on the chemical affinity of the materials and can be used to predict if additives will disperse in a solvent or polymer. It can thus be a tool to choose solvents and modifications of the SWCNT for a given polymeric matrix.

The HNO_3 modified CNT generally gives a good strain transfer between the polymer matrix and the nanotubes, this can be explained by the Hansen solubility parameters but is probably also caused by the debundling caused by the HNO_3 treatment. Thermal stresses from the manufacturing of the composites also play a role in the measured strain transfer.

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