PREDICTION OF MECHANICAL PROPERTIES OF CARBON NANOTUBE/POLYVINYLIDENE FLUORIDE COMPOSITES BY HANSEN SOLUBILITY PARAMETERS METHOD

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1 Introduction

In this work, Hansen solubility parameters [1] (HSP) are introduced to predict the physical properties of filler-matrix composite system. This highly efficient and economical method could be potentially applied in both control and guiding of composites processing. Excellent mechanical properties of carbon nanotubes (CNTs) enable them an excellent choice of reinforcement material for polymeric composites [2, 3]. However, due to the high aspect ratio, CNTs tend to form agglomerates, which cause the dispersion of carbon nanotubes in polymer matrix a big challenge. In order to obtain good nanotube dispersion, many methods have been tried, among which modification of the CNTs and ultrasonic dispersion are widely used [4-6]. Normally the dispersion state of the nanotubes in the polymer is evaluated after the whole composite fabrication process is completed. However, using Hansen solubility parameters (HSP) could help predicting the dispersion state of the CNTs in polymer before fabricating the composites.
In this study, the mechanical properties of carbon nanotube / Polyvinylidene Flouride (PVDF) are investigated. Equal amount of purified single walled carbon nanotubes (SWNTs), nitric acid treated SWNTs, octadecylamine (ODA) modified SWNTs and multi-walled carbon nanotubes (MWNTs) blends with piezoelectric polymer PVDF have been prepared by using dimethylformamide (DMF) solution blending and injection molding method. The HSP of the various carbon nanotubes have been determined in order to predict the physical affinities between the PVDF and the various CNTs. The dispersion state of nanotubes in PVDF matrix was observed by light optical microscopy (LOM) and compared with the HSP. The prediction of the physical compatibility of CNT / PVDF composite materials by the HSP method will be discussed in this paper.

The mechanical properties of neat PVDF and PVDF composites were measured by tensile tests. The Young's modules, ultimate tensile strength, and toughness of the PVDF composites are enhanced or affected in different extents by adding carbon nanotubes.

2 Prediction of dispersion state of CNTs in PVDF

2.1 Hansen solubility parameters method

In three dimensions, the Hansen solubility parameters (δ_D, δ_P, δ_H representing the dispersion forces, dipolar interactions and hydrogen bondings respectively) of a solute represents the center of the sphere and the radius of this sphere R_o indicates the maximum tolerance of the solution. With the best data fit, good solvents are included within the sphere and bad solvents are excluded. For a specified solvent in the HSP sphere, R_a is the distance between

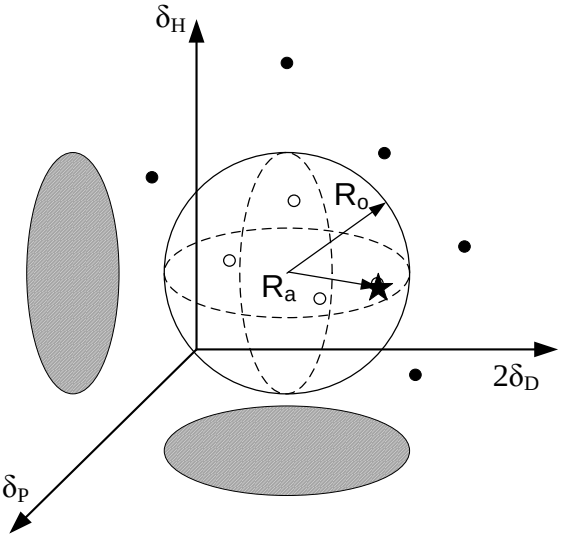

Fig.1. Schematic drawing of HSP sphere (solid dots: bad solvents outside the HSP sphere; hollow dots: good solvents; star: specified solvent)

Table 1. Solubility and RED values of CNT in various solvents

Solvents	δ_D [a]	δ_P [a]	δ_H [a]	δ_T	Purified SWNTs		HNO_3 SWNTs		ODA SWNTs		MWNT	
					S [b]	*RED*	S [b]	*RED*	S [b]	*RED*	S [b]	*RED*
Methanol	15.1	12.3	22.3	29.6	1	1.01	1	0.93	0	5.99	0	1.92
Ethanol	15.8	8.8	19.4	26.5	1	0.68	1	0.84	0	4.53	0	1.37
2-propanol	15.8	6.1	16.4	23.5	0	0.62	1	0.93	0	3.34	0	1.00
Acetone	15.5	10.4	7	19.9	0	1.06	1	0.89	0	2.20	0	1.40
Tetrahydrofuran	16.8	5.6	8	19.4	1	0.84	0	1.21	1	0.46	1	0.81
Cyclohexanone	17.8	6.3	5.1	19.6	0	1.00	0	1.44	0	1.04	0	1.00
Ethyl acetate	15.8	5.3	7.2	18.2	1	1.01	0	1.24	1	0.83	0	1.01
Acetonitrile	15.3	18	6.1	24.4	0	1.44	1	1.00	0	4.72	0	1.99
N,N-dimethylformamide	**17.4**	**13.7**	**11.3**	**24.8**	**1**	**0.74**	**1**	**0.58**	**0**	**3.42**	**1**	**1.40**
N,N-Diethylethenamine	14.6	3.7	1.9	15.2	0	1.53	0	1.78	0	2.43	1	1.39
Dicloromethan, methylenchlorid	18.2	6.3	6.1	20.3	0	0.90	0	1.40	0	1.06	0	0.88
Chloroform	17.8	3.1	5.7	19	1	1.03	0	1.64	1	0.92	1	0.83
Tetrachloromethane	17.8	0	0.6	17.8	0	1.54	0	2.24	0	2.81	0	1.44
Hexane	14.9	0	0	14.9	0	1.75	0	2.22	0	3.25	0	1.77
Decahydronaphthalene	18.8	0	0	18.8	0	1.57	0	2.35	0	3.18	0	1.49
Benzene	18.4	0	2	18.6	0	1.42	0	2.18	0	2.57	0	1.26
Xylol, 1,2-dimethylbenzene	17.8	1	3.1	18	0	1.31	0	1.98	0	1.95	0	1.13

The HSP are in units of $MPa^{1/2}$

[a] Refs.[7, 8]

[b] S represent the solubility. "1" and "0" stand for the good and bad solvent, respectively.

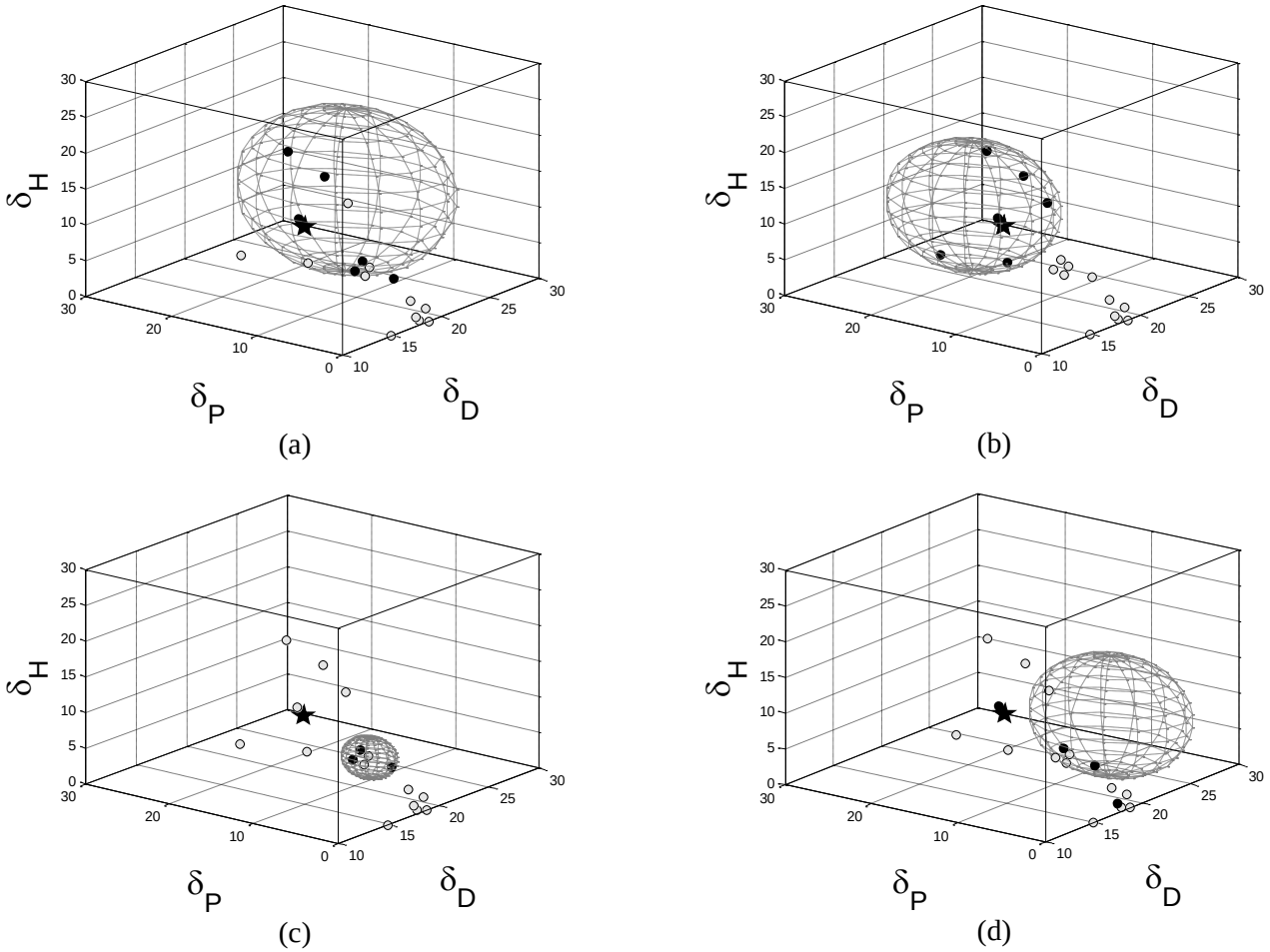

Fig 2. The HSP sphere of different CNT (solid dots: bad solvents; hollow dots: good solvents; star: PVDF) (a) Purified SWNTs; (b) HNO_3 modified SWNTs; (c) ODA modified SWNTs; (d) MWNT in solvents

the solvent and the center of the solute sphere. The schematic drawing of HSP sphere is shown in Fig.1. The ratio of R_a and R_o are described as relative energy difference (*RED*) value:

$$RED=R_a/R_o \quad (1)$$

A perfect solvent has a *RED* value of 0. The *RED* of good solvents are normally less than 1.0 and bad solvents larger than 1.0. From the *RED* values and the HSP spheres of the two materials, the physical affinities between a PVDF matrix and various CNTs could be predicted.

In this study, HSP of various CNTs and PVDF were determined based on a set of solubility experiments. Very small amount of CNT was added into different solvents with known HSP and sonicated for 24 hours, hereafter the determination was made on the observation of the solubility after sonication.

In Table 1, the solubility of each CNT in various solvents is displayed and *RED* values are calculated. DMF was chosen as the solvent in the composite process, as PVDF is soluble in it. At the same time, DMF is good solvent for purified SWNTs, HNO_3 modified SWNTs and MWNT, but not for ODA modified SWNTs.

Figure 2 and Table 2 illustrate the distance between the HSP sphere for the CNT and the PVDF; the *RED* values are calculated with respect to PVDF. The results indicate that the nitric acid treated SWNT have the best physical surface affinities with PVDF. The purified SWNT shows lower physical affinities, while MWNT and the ODA functionalized SWNT possess higher *RED* values and the further distance of CNT sphere and PVDF matrix, so they may have worse physical affinities with PVDF.

Table 2. HSP, and Ro of various CNTs and PVDF

Material	δ_D	δ_P	δ_H	*Ro*	*RED*[b]
Purified SWNTs	19.4	10.3	15.0	11.1	1.35
HNO_3-SWNTs	15.2	14.0	14.1	9.0	1.07
ODA-SWNTs	17.0	4.7	7.1	2.9	1.73
MWNT	18.9	2.4	12.2	8.4	2.19
PVDF[a]	17.1	12.6	10.6	5.0	

a Calculated using published data in [9]
b The RED of CNTs are calculated with respect to PVDF

Based on the above results, the HNO_3 modified SWNT and purified SWNT might disperse well in the composite due to the good solubility in DMF solvent and good physical affinity with PVDF. As opposed to this, due to its insolubility in DMF and poor compatibility with PVDF, the ODA modified SWNT might disperse badly in composite. MWNTs is dispersed well in DMF but have poor compatibility with PVDF, such that the dispersion in PVDF composites might be in between HNO_3 modified SWNTs and ODA modified SWNTs.

2.2 Dispersion state

The dispersion state of the CNTs in PVDF composites were characterized by LOM (light optical microscopy) and compared with the predicted results obtained by HSP method.

Figure 3 exhibits the LOM images of various CNT/PVDF composite films. The dispersion of purified SWNT, HNO_3 modified SWNT and MWNT were good in the PVDF, no obvious agglomerations of CNTs were observed in Fig.3 (a)(b)(d), while the ODA modified SWNTs were dispersed badly in the PVDF composites and lots of agglomerates were observed from the image Fig.3 (c). These observations agree very well with the prediction by using Hansen solubility parameters method.

The dispersion of CNTs in polymer matrix was largely influenced by the solubility of CNTs in solvent, secondly influenced by the surface physical affinities of the polymer matrix and the CNT fillers.

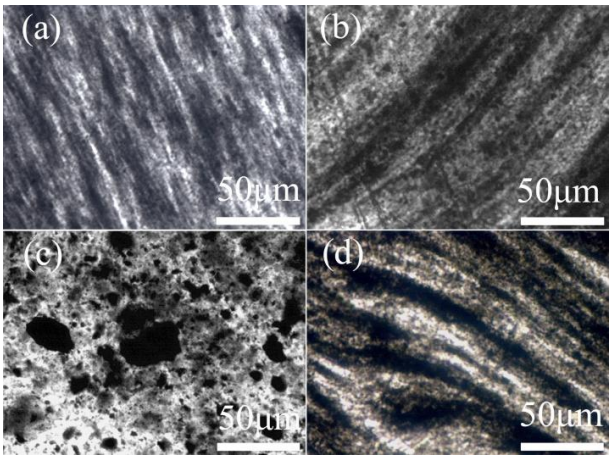

Fig. 3. The LOM images of CNTs in PVDF, (a) Purified SWNTs; (b) HNO_3 treated SWNTs; (c) ODA modified SWNTS; (d) MWNTs

3 Mechanical properties

Several researchers have observed that the mechanical properties of the nano-composites are affected by the dispersion of the CNTs in polymer [10, 11]. The achieved mechanical properties in terms of Young's modulus, ultimate tensile strength, toughness, failure strain and respective standard deviation of PVDF and the composites with 1wt% nanotubes are listed in Table 3.

The Young's modulus was calculated according to ISO527-1. The neat PVDF samples fabricated with the same procedure with DMF as the solvent and molded by injection molding and have a Young's modulus of 1.138 ± 0.101GPa and strength of 41.84 ± 0.85MPa. All the SWNTs filled PVDF composites lead to higher Young's modulus than the original PVDF. The Young's modulus improvement of the purified SWNTs and MWNT filled PVDF composites are the best. However, it seems that the measured Young's modulus does not come close to the Young's modulus predicted by the rule of mixture [12, 13] in any of the samples. Addition of MWNT improves the ultimate tensile strength despite the apparently poor physical affinity with the PVDF. However, addition of SWNT does not improve the ultimate tensile strength. Despite good dispersion of the purified SWNTs and HNO_3 modified SWNTs as well as MWNTs, the Young's modulus show little improvement and tensile strength is close to pure PVDF. The poor mechanical properties could be due to poor debundling of the carbon nanotubes.

Toughness and failure strain are deteriorated by adding CNTs in PVDF. The composites with ODA functionalized nanotubes have the lowest toughness and failure stain only at 10.37 ± 1.40 J/m^3 and 28.92 ± 3.98%. The ODA functionalized SWNTs are poorly wetted by PVDF, and form lots of agglomerates. The poor physical affinity also results in an interface with low strength, reducing the mechanical performance of the composite.

Many other researchers have found that the surface functionalization of SWNTs could improve the mechanical properties of composites [14-17]. In our study, it was found that the properties of the composites are affected by the modification mainly because the modification affects the dispersion of CNTs. And the above observations indicate that the dispersion state of the filler in matrix affect the mechanical properties of composites.

Despite the difficulties, the effort to increase the dispersion and thus the mechanical properties would be interesting. The application of HSP method to predict the dispersion of CNTs in polymers needs to be developed and discussed more in the future.

Table 3. Mechanical properties from Tensile Testing at room temperature for PVDF and SWNT/PVDF composites

Composite type	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Toughness (J/m^3)	Failure strain(%)
Neat PVDF	1.138 ±0.101	41.84 ±0.85	12.34 ±2.94	34.48 ±7.51
1 wt% purified SWNT/PVDF	1.264 ±0.028	41.28 ±0.97	11.73 ±1.05	32.34 ±2.79
1 wt% HNO_3-SWNT/PVDT	1.180 ±0.004	41.07 ±0.09	10.81 ±1.81	29.76 ±4.92
1 wt% ODA-SWNT/PVDF	1.167 ±0.003	40.70 ±0.17	10.37 ±1.40	28.92 ±3.98
1wt% MWNT/PVDF	1.242 ±0.009	43.15 ±0.14	11.38 ±0.29	30.56 ±0.64

4. Conclusion

Hansen solubility parameters could help selecting solvent for composites processing, and predict the dispersion state of SWNTs in PVDF polymer matrix. Purified and HNO_3 functionalized SWNTs dispersed well in PVDF, while ODA functionalized dispersed badly, which were in agreement with the compatibility predicted by Hansen solubility parameters.

The better mechanical properties are related to better dispersion. The Young's modulus of PVDF was improved by adding SWNTs, the purified SWNT/PVDF shows the largest Young's modulus, the MWNT/PVDF is the strongest, the toughness of the PVDF composites isn't improved by adding CNT, ODA functionalized SWNTs composites exhibit the poorest mechanical properties due to the agglomeration of the SWNTs in PVDF.

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