**Synthesis and Characterization of Polystyrene Carbon Nanotube Nanocomposite for Utilization in the
Displaced Foam Dispersion Methodology**

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Abstract

Incorporating nanostructured functional constituents within polymers has become extensive in processes and products for manufacturing composites. The conception of carbon nanotubes (CNTs) and their heralded attributes that yield property enhancements to the carrier system is leading many industries and research endeavors. Reported Displaced Foam Dispersion (DFD) methodology is a novel and effective approach to facilitating the incorporation of CNTs within fiber reinforced polymer composites (FRPC). The methodology consists of six separate solubility phases that lead to the manufacture of CNT-FRPCs. This study was primarily initiated to characterize the interaction parameters of nanomaterials (multiwalled carbon nanotubes), polymers (polystyrene), and solvents (dimethyl formamide (DMF) and acetone) in the current paradigm of the DFD materials manufacture. Secondly we sought to illustrate the theoretical potential for the methodology to be used in conjunction with other nanomaterial-polymer-solvent systems. Herein, the theory of Hansen's solubility parameters (HSP) is employed to explain the effectiveness of the DFD materials manufacture ratios and aid in the explanation of the experimental results. The results illustrate quantitative values for the relative energy differences between each polymer-solvent system. Transmission electron microscopy (TEM) was used to characterize the multiwalled carbon nanotubes (MWCNTs) in each of the solubility stages and culminates with an indication of good dispersion. Additionally, the rate of acetone evaporation over 25 minutes is reported for the sorbed CNTaffy nanocomposites from 0 to approximately 60 weight percent loadings.

Keywords: A. Nanostructures, D. Optical microscopy Physical methods of analysis, D. Electron Microscopy, E. Forming

1. Introduction

The FRPC have been is used in applications ranging from sports equipment to aerospace [1-5]. Most FRPC systems consist of fiber layers (glass, carbon, orthotropic fibers, etc) encapsulated by a thermoplastic/thermoset resin matrix. Upon curing the composite is imbued with rigidity, strength, toughness and/or ductility. Driving the next frontier of FRPC is the inclusion of nanostructured materials with high surface area, specifically carbon nanotubes, which have been shown to add multifunctionality (outstanding tenacity, high electrical conductivity and excellent thermal resistivity) to the overall system. The new FRPC system make up with the incorporation of nanoparticles has been termed a multi-scale or hybrid composite [2].

Since Ijima first discovered the outstanding properties and potential of CNTs, they have been investigated and successfully implemented in various material systems including polymer composites. An issue of the most notable concern is the safe use of CNTs. Safety fears about carbon nanotubes are due to their structural similarity to asbestos. This can be alleviated by reducing their length, which makes the materials safe for application[6, 7]. Safety concerns can also be quelled by encapsulating the CNTs within a polymer substrate for handling as proposed the displaced foam dispersion (DFD) methodology [2, 8, 9]. Several methodologies have been investigated for the manufacture of CNT based multiscale composites (MSCs) [10-19]. Electrophoresis deposition (EPD), carbon vapor deposition (CVD), doped resin systems (DRS) are a few approaches that have yielded property enhancements to MSCs. Researchers using carbon nanofibers (CNFs) and CNTs to manufacture polymer nanocomposites (PNCs) have reported mechanical, electrical and thermal property improvements as a result of the nanoparticle additives to the matrix. Studies have shown that chemically modifying the surfaces of nanoparticles helps disperse the CNTs better in polymer matrices and results in improved physical properties [20]. Although these methods have proved beneficial and effective in small scale applications, limitations and inefficiencies arise due to manufacturability, scalability and selective placement for macro scale applications.

The preparation of effective dispersions of carbon nanotubes exhibits a major impediment to the extension and utilization of CNTs [21]. CNTs intrinsically tend to bundle and/or aggregate [22] making their solubility (dispersion) pivotal. Main challenges for integration of this unique nano-material include: (1) uniform dispersion; (2) preferential interalignment in liquid and polymer melt phases; and (3) mass-production of high-purity material at low costs [23]. The use of a glassy carbon substrate as a model for unsized carbon fiber has been demonstrated as

appropriate for the study of interactions [24] between the materials in composite carbon fiber–epoxy polymer systems. CNT dispersion alone is essentially intercalated and can be characterized through solubility parameters respective to the relative energy differences of the solvent/dispersant system. Similarly, polymer-solvent systems can also be characterized. A strong physical compatibility is distinguished if their respective Hansen solubility parameters (HSPs) are close. Additionally, the prediction of how much an elastomer swells in contact with a given solvent is important in many industrial processes. This makes it possible to predict the swelling of the elastomers studied in contact with many untested solvents [25, 26]. The HSPs of glassy carbon are similar to those of carbon fiber and epoxy matrix [26] indicating the potential for good solubility of a composite system. The displaced foam dispersion methodology employs the principles of solubility between the CNTs, polystyrene polymer, and fiber and resin system phases to fabricate MSCs. The dispersed CNTs are mixed in stages to form a porous nanocomposite substrate (foam) capable of dissolution under flow of liquid composite molding (LCM) techniques [2, 8, 9]. The HSP theories are utilized to understand and characterize the dissolution of the substrate encapsulating CNTs. The goal of the DFD is to selectively place CNTs within FRPC for localized property enhancements.

1.1 Solubility Models

The solubility model of nonelectrolytes indicates the solvency behavior of a specific solvent which yields values associated with this primary solubility parameter (δ) [27]

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \quad (1)$$

Where, H is the change in enthalpy, R is the gas constant, T is the absolute temperature, and V_m is the molar volume.

Dispersion, polar, and hydrogen collectively account for other forces involved in the solubility of a system. The

most widely accepted three component system to date is the three parameter system developed by Charles M.

Hansen [28]. Hansen parameters divide the total Hildebrand [29] value into three parts: dispersion force component

(δ_d), polar bonding component (δ_p), and hydrogen bonding component (δ_h). Solubility parameters are sometimes

called cohesion energy parameters as they are derived from the energy required to convert a liquid to a gas. All types

of physical bonds holding the liquid together are broken by evaporation. The total cohesive energy, E , can be

measured by evaporating the liquid i.e. breaking the cohesive bonds. There are three major types of interactions in

common organic materials. The most general are the nonpolar interactions. These are derived from atomic forces

and have also been called dispersion interactions in the literature. The dipole-dipole interactions cause a second type of cohesion energy, the polar cohesive energy, E_p . The third major cohesive energy source is hydrogen bonding. This can be called more generally an electron exchange parameter. The basic equation governing the assignment of Hansen parameters is that the total cohesion energy which must be the sum of individual energies that make it up.

$$E = E_d + E_p + E_h \quad (2)$$

The total solubility parameter is the sum of the squares of the Hansen **d**, **p** and **h** components,

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (3)$$

where V is molar volume. The term cohesion energy parameter is more properly used when referring to surface phenomena by using a dispersion force component instead of the Hildebrand value as the third parameter, and by relating the values of all three components to the total Hildebrand value. This means that Hansen parameters are additive:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

where δ_t^2 =Total Hildebrand parameter, δ_d^2 = dispersion component, δ_p^2 =polar component, and δ_h^2 = hydrogen bonding component

Hansen [30, 31] found that, by doubling the dispersion parameter axis, an approximately spherical volume of solubility would be formed for each polymer. This volume, being spherical, can be described in a simple way. The coordinates at the center of the solubility sphere are located by means of three component parameters (δ_d , δ_p , δ_h), and the radius of the sphere is called the interaction radius (Ra). To aid the solubility parameter criterion of Hansen's methodology for the selection of "good" versus "bad" solvents, the use of relative energy difference (RED) was proposed. In this approach, values of RED < 1 imply that the solvent is "good" or the solvent is "bad" when RED > 1. The relative energy difference can be approximated from the interaction radius (Ra) divided by the radius of solubility (Ro).

$$RED = \frac{R_a}{R_o} \quad (5)$$

where R_a is the distance between center of the polymer solubility sphere for the solvent-solvent system and R_o is the radius of the sphere. R_a is calculated according to Equation

$$R = (R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \quad (6)$$

Liquids whose parameters lie within the spherical volume are active solvents for that polymer. A polymer is probably soluble in a solvent (or solvent blend) if the Hansen parameters for the solvent or the solvent blend lie within the solubility sphere for the polymer. In order to determine this (without building a model) it must be calculated whether the distance of the solvent from the center of the polymer solubility sphere is less than the radius of interaction for the polymer:

$$D_{s-p} = \sqrt{4(\delta_d s - \delta_d p)^2 + (\delta_p s - \delta_p p)^2 + (\delta_h s - \delta_h p)^2} \quad (7)$$

Where, equivalent to R_a , $D_{(s-p)}$ = Distance between solvent and center of polymer solubility sphere, $\delta_s s$ = Hansen component parameter for **solvent**, and $\delta_s p$ = Hansen component parameter for **polymer**. The value "4" in the first term of the equation, which doubles the dispersion component scale, is intended to create a spherical volume of solubility. If the distance ($D_{(s-p)}$) is less than the radius of interaction for the polymer, the-solvent would be expected to dissolve the polymer.

This method avoids the reliance on graphic plots of solubility behavior and can be used effectively in solely numerical form. In order to plot all three parameters on a single planar graph, a certain departure must be made from established solubility theory. Understanding the solubility parameters associated with each phase of the DFD methodology is one of the most critical to quality notions through which all dispersions, distributions, micromechanics and resulting properties affected. The construction of the Teas graph (a two-dimensional triangular Ternary plot) is based on the hypothetical assumption that all materials have the same Hildebrand value. According to this assumption, solubility behavior is determined, not by differences in total Hildebrand value, but by the relative *amounts* of the three component forces (dispersion force, polar force, and hydrogen bonding force) that contribute to the total Hildebrand value. Hansen parameters are additive components of the total Hildebrand value.

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \quad f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \quad f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \quad (8)$$

In other words, if all three Hansen values (squared) are added together, the sum will be equal to the Hildebrand value for that liquid (squared). Teas parameters, called fractional parameters, are mathematically derived from Hansen values and indicate the fraction contribution that each Hansen parameter contributes to the whole Hildebrand value.

This report seeks to incorporate solubility parameter to help explain how relative energy differences impact the inclusive stages of nanocomposite synthesis to be used as substrate for the DFD methodology.

2. Materials and Experimental Method

Porous polymer nanocomposites (aptly called foams) were fabricated for this study by calendaring plasticized polystyrene-carbon nanotubes (PS-CNT) nanocomposite (CNTaffy) into films and expanding them into PS-CNT foams aided by chemical foaming agent azobisisobutyronitrile (AIBN). The plasticization transforms the solid material into a malleable/formable nanocomposite (see [Figure 7](#)~~Figure 7~~[Figure 7](#)), which is herein referred to because its processing resembled that of Taffy candy. *Taffy is made by stretching or pulling a sticky mass until it becomes aerated (meaning that tiny air bubbles are produced, resulting in a light, fluffy and chewy candy)* [32]. (Note: CNTaffy can also be processed sans AIBN). Multi-walled carbon nanotubes (MWCNT) (0.5-700µm in length) (SMW-200) was purchased from Southwest Nanotechnologies Inc. and used without further purification. The outer diameter, inner diameter, number of median walls and median aspect ratio of the MWCNT were 20-30nm, 5-10nm, 7 walls, and 350:1 respectively. These specifications were confirmed through transmission electron microscopy (TEM). Specific surface area (350m²/g) were measured using Micromeritics ASAP 2020. The bulk density of the MWCNT is 0.10g/mL with 99% purity. These MWCNTs were utilized in the dispersion solution processing. The polystyrene used was originally received in the form of clear plastic pellets. The pellets were purchased from Entec Polymers, Orlando, FL, USA having an approximate 47% crystallinity that was estimated using the method reported elsewhere [33, 34].

Dimethylformamide (DMF) was used as a dispersant for the CNTs and a solvent for the PS. In the sonication-dispersion process the nanotubes (50mg or 5.0 volume percent concentration) were mixed with 100mL DMF. The mixture was placed in an ice bath to keep the exothermic processing temperature of the solution under

control. The contents were sonicated to disperse the CNTs into the PS chain or molecules. A Misonix Sonicator 3000 was used with the processing intensity ranging between 100-120 watts and set to a 10 second pulse and a 2 second rest to achieve good dispersion. 5 gm of PS pellets were dissolved in a separate 100 mL DMF or 5% (w/v). Prior to mixing the two solutions with the common DMF solvent, both solutions were set aside and allowed to reach a common equilibrium temperature. The PS-DMF suspension was then added to the CNT-DMF solution and stirred for an additional 30 minutes.

Upon completion of the sonication cycle under processing conditions, the CNT-DMF solution was immediately introduced into the PS-DMF polymer processing stage. Note that the DMF is a good solvent and studies have shown that PS can be dissolved in DMF up to 23% (w/v) [35]. The PS-DMF suspension is then added to the CNT-DMF solution, magnetically stirred, and followed by a strong sonication. The mixture is added drop-wise to de-ionized (DI) water (volume ratio 1:5, DMF: DI-Water) under high shear mixing using a homogenizer with 5000 rpm. By introducing the dispersed/dissolved PS with CNTs into the de-ionized water, the material coagulates upon contact and is precipitated. The coagulating droplets coupled with shear mixing in high ratio DI water allows *creaming* to occur with increased particle separation and thus greater dispersion.

The additional mixing allows the individual polymer coils to encapsulate the CNTs and the sonication processing helps to facilitate further dispersion of the combined PS-CNT particles into a stable system ([Figure \[36\]](#)). The precipitates are collected by filtration using micro-filter press and dried in a low vacuum condition at about 50°C [9]. Through sonication, PS dissolution, magnetic stirring, shear mixing, and filtration the carbon nanotubes and polystyrene were able to be combined to form the PS-CNT raw material ready for manufacturing of CNT based hybrid composites. Once the PS-CNT material was dissolved, the predesigned amount of chemical foaming (AIBN) agent was then added. Foaming additives and/or solvents are those which either initiate a chemical reaction or cause a physical reaction that results in bubble nucleation and growth.

Figure 1 Schematic view of the synthesis process of DFD material using batch process.

Separation of Solvents:

Once the dissolved PS-CNT nanomaterial with sorbed AIBN begins to re-agglomerate, a distinct separation of the liquid DMF and the homogeneous polymer is evident. The excess DMF is poured off and allowed to evaporate at RT until the polymer is firmly solidified with minimal residual DMF. The semi-dried material is then placed into an oven until completely dry and brittle. The dried material is soaked in acetone until ready for calendaring and foam processing. The plasticizing acetone evaporates once exposed and aids in the foam nucleation. A study of mass loss was conducted over 25 minutes to show the variation and impact of the CNT loadings.

3. Results and Discussion

The PS showed excellent solubility in DMF and accommodation of the AIBN (a chemical foaming agent). Note that AIBN is an organic compound, which is often used as a foaming agent in plastics and rubber. It is soluble in alcohols and common organic solvents but insoluble in water [37]. The solubility force constants of solvents, polymer, particles and aqueous surfactant emulsions are shown in [Appendix](#)

[Table 1Appendix](#)

Graphical 3D and 2D plots were simulated using HSP model in conjunction with MatLab software to calculate and create the spherical representations (see [Figure 2Figure-2Figure-2](#), [Figure 4Figure-4Figure-4](#) and [Figure 9Figure-9Figure-9](#) approximate radius of solubility for each two-part system [38]. The Hansen volume of solubility for a polymer is located within a three dimensional model by giving the coordinates of the center of a solubility sphere (δ_d , δ_p , δ_h). It was found that the nanotubes were homogeneously dispersed into the solvents with certain dispersive component (δ_d) values. They were precipitated in the solvents with high polar component (δ_p) values or hydrogen-bonding component (δ_h) values. The solvents in the dispersed group occupied a certain region in a 3-dimensional space of three components (δ_d , δ_p , and δ_h). RED values of CNT-DMF and PS-DMF remain in the range of 0.25~0.28 ([Figure 2Figure-2Figure-2](#)), which is indicative of suitable solvent-solute system.

Figure 2 a) and b) RED value estimated as 0.2520 exhibits, c) and d) RED value estimated as 0.2850 exhibits

The additional mixing allows the individual polymer coils to encapsulate the CNTs and the sonication processing helps to facilitate further dispersion of the combined PS-CNT particles [36]. [Figure 3](#) shows distribution with possible inter-molecular interactive features of the individual CNTs and bulk polymer structures.

[Figure 3](#) (a - c) show the dispersion and distribution of the PS-CNT mixture and is scaled down

encapsulating of a single CNT by the PS in [Figure 3](#) [Figure 3](#) [Figure 3](#) (d) can be seen. The intermediary images (b) linkages formed by the interconnecting CNT strands and PS nodules. The nanostructured CNT-PS agglomerated particles are clearly indicative of the inter-molecular interaction of extended surface structures of carbon and the PS polymer chain. Furthermore, the white arrows in [Figure 3](#) [Figure 3](#) [Figure 3](#) (d) suggest that the individual MWCTs with nanostructured polymer structure that is certainly capable in extending the crosslinking of the entire bulk structures. Interestingly, the entire structures show network-like interconnectivity with well oriented nanostructured capsules which is potentially providing foam like behavior to this synthesized PS-CNT hybrid structures.

Figure 3 Micrograph images of 2.0 wt. % PS-CNT a) and b) after sonication and stir mixing, c) and d) SEM imaging showing PS encapsulating CNT

[Figure 4](#)[Figure 4](#)[Figure 4](#) (a-b) shows an estimate of the RED value of CNT in PS bulk system at 0.0741, of high intermolecular affinity between polystyrene chain and the external surface of CNTs. The CNT sphere is located well within the PS sphere and their center points are relatively located close and is confirmation of its low RED value. It may be inferred that the small RED value is remarkably indicative of less intermolecular critical strain in between PS and CNTs.

Figure 4 HSP spheres illustrating the CNT-Bulk PS mixture solubility with RED values estimated at 0.0741

Figure 5 illustrates the effects that sonication time has on the dispersion and distribution of encapsulating CNTs. After 15 minutes of sonication, the clusters of CNTs are still present indicating poor dispersion throughout the polystyrene bulk structures. At the 60 minute mark the cluster aggregates have been disentangled and separated but relatively large agglomerate is still shown to be present. At the 90 minute mark the disentangled clusters appear more evenly distributed. However, the darker particles may be indicative of higher CNT compaction within the dispersed regions. The amount of dispersed CNTs was positively correlated with the nano inclusions concentrations, and the length of the CNTs. It has been reported that the promotion of oxygen-containing functional groups on dispersed CNTs can occur at relatively low sonication energies or duration [39, 40]. The remaining parts of the CNTs need larger sonication energy or time, which is evidenced in Figure 5c. The minimum

using sonication to achieve maximum and homogeneous dispersion of CNTs with the DMF solution is CNTs size and diameter-dependent, because the larger van der Waals forces work between tubes of smaller diameter. [40]

Figure 5 Microscopy images of PS-CNT (2 wt%) system with different sonication time in DMF.

It is well known that carbon nanotubes (CNTs) have excellent electrical properties and can be used as the nanofiller in natural polymers to produce conductive CNT/polymer nanocomposites [41]. TEM analysis with this hybrid composites was made to illustrate the CNT specifications (i.e diameters, median walls,... etc) previously mentioned (see section 2) and to explain the dispersion states of CNTs in the polymers. The interfacial surface fraction of CNT and PS chain/bulk structures provides a well defined homogeneous hybrid composite, which is evidenced in TEM analysis ([Figure 6](#)[Figure 6](#)[Figure 6](#)). The TEM results showed an excellent dispersion ([Figure](#) bulk PS and formation of connected three-dimensional network structures between the CNTs and PS, which may result in the good conductive property of CNT/PS nanocomposites. FTIR spectroscopy, reported elsewhere, has indicate good intermolecular interactions between PS and CNTs [42]. However, it must be noted that only partial dissolution/integration was observed during completion of the resin curing process in this study.

Figure 6 High resolution Transmission Electron Microscopic (TEM) image of MWCNT illustrated in a) Pristine MWCNT b) PS-CNTaffy, c) individual CNT from PS-CNT foam/resin infusion and d) dispersion of CNTs in PS-CNT system.

DMF as compared to DI water (HSP sphere figure not shown for the sake of brevity but calculation dictated) represents the “*creaming*” solubility phase of the system as shown in [Figure 1](#)~~Figure 1~~[Figure 1](#). The RED around 0.4 indicating a mid-level potential of solubility. Having such a large spherical ratio further illustrates the need for such high-volume of water when diluting the DMF encompassing solution. Additionally, the deionized water serves to allow better separation in the high-volume fluid for the precipitated PS-CNT encapsulated particulates thought to further increase disentanglement and separation. The HSP interactions of polystyrene as

compared to water show spheres that have center points relatively far from one another. There are overlapping regions between the two and the center of maximum solubility spheroid (R_M) lies within that of the PS and on the border of the water HSP. The RED value is estimated to be 0.73 which puts it in the higher range where solubility becomes less likely thus making this evident as a precipitating liquid for PS and its encapsulates.

Following the processing of the raw material manufacture, the resulting PS-CNT nano composite material must undergo a final plasticization phase that will soften the material into a malleable state. The material is submerged in acetone and allowed 12 - 24 hours to absorb. As shown in [Figure 7](#) [Figure 7](#) [Figure 7](#) (a), upon removal nano composite material behaves similar to a low viscosity colloid. As time out of the soaking increases, the material begins to coagulate as the acetone evaporates and is shown in [Figure 7](#) [Figure 7](#) [Figure 7](#) (b) after 60 the material loses its acetone content first and fastest while the interior loses its acetone content more slowly which can be seen graphically in [Figure 8](#) [Figure 8](#) [Figure 8](#) (a-h).

Figure 7 Malleable/formable PS-CNT-AIBN hybrid composite CNTaffy – (a) straight from acetone soak ($t = 0s$), and (b) after setting for $t = 60s$

A detailed kinetic study was conducted at room temperature and approximate 40% humidity in order to determine the effect CNT loading within the PS carrier system has on acetone evaporation. As shown in [Figure](#) the increasing PS-CNTaffy samples at lower CNT concentrations exhibited less average mass loss per second within the first 25 minutes compared to the higher concentrations and neat acetone.

Molecular sieves are, typically zeolite, etc., compounds that strongly adsorb solvent and have predesigned controlled pore sizes [42, 43]. While the solvent molecules are adsorbed strongly to the molecular sieve surfaces, the large surface area within the pores is only accessible to the smaller solvent molecules, so they are effectively removed from a mixture of solvent. The internal diameter of MWCNTs is 1-2 nm while its wall thickness is about ~0.3-0.5nm [44]. The pore size of acetone molecule is 3.08Å with 0.308 nm average molecular diameter [45]. The acetone molecules were easily penetrated to occupy the extremely large internal tubular surface area or vacant space of CNT and thus difficult to remove due to various active intermolecular interaction. If the acetone could not enter the tubular pores, it would compete or be physisorbed at the external surface area of the CNTs or PS. Those molecules are comparatively evaporated faster than those of internally adsorbed ([Figure 8Figure 8Figure 8](#)). The internally adsorbed solvent molecules are not suitable for drying under normal evaporation condition that is illustrated in [Figure 8Figure 8Figure 8](#). Additionally this shows that the malleability span of the material is highly acetone content and presence within the polymer.

Figure 8 Acetone evaporation kinetics of the plasticized PS and PS-CNTaffy over a-b) 10 seconds, c-d) 1 minute, e-f) 5 minutes, and g-h) 25 minutes.

Figure 9 shows the rigid HSP spheres for PS and smoother HSP sphere for acetone. In this uniformly overlap one another placing the center points respectively within the domain of the opposite. The maximum solubility spheroid entirely encompasses the shared region and the estimated RED of 0.31 indicates a soluble system. However, due to the nature-dispersion, polar and hydrogen of the forces involved between the solvent at the boundary of the R_m , the material remains in accordance state (colloidal) versus a dispersed suspension. It can also be noted, as shown in Figure 8, CNT loading plays a critical part in not only acetone evaporation but conversely the capacity for acetone absorption. This means that higher loadings of CNTs will decrease the malleability of the nanocomposite material.

Figure 9 Estimation of RED (0.3057) value for PS-Acetone system.

The teas plot illustrated in [Figure 10](#) yields a two-dimensional representation of the three-
the inclusive entities dictating their centers and respective relative radius of solubility. In this graphical
representation the distance between the center points can be better observed and the affinities (common forces) for
each of the components' system interactions determined. Particularly, it can coherently be seen from the teas plot
that both PS and CNT have relatively low hydrogen bonding and polar force factors. Additionally, DMF has a large
radius encompassing the two primary entities and the plasticizing acetone borders the PS which yields evidence to
why the material does not completely dissolve into a uniform mixture.

Figure 10 Teas plot of DFD constituents and their respective HSP values with solubility radius overlay.

Furthermore, the CNT/PS hybrid structures show conductivity that can be applied for advanced application [41]. The DFD methodology concludes with the ability to integrate the PS foam substrate into the resin matrix system. An individual test was done to establish the solubility of a neat PS (foam and pellets) in uncatalyzed unsaturated polyester resin. The observation yielded three different phase states. Within the first week the PS in both cases congealed to form a mass visually distinct from the surrounding resin. This mixture remained viscous until finally curing around the third week in which case the PS still exhibited a separate region from that of the resin. This necessitates further investigation in order to create a more compatible dissolution system between polystyrene (or polymer) and resin.

4. Conclusion

This study explains the differences between polymer and solvent in the description of various mixing systems of the DFD methodology. Hansen's Solubility Parameters (HSP) were employed to model, illustrate and understand the interactions' relative energy differences (RED) and to facilitate the three-dimensional spherical representations

of each polymer and solvent (or solvent-solvent) sphere. For each of the six phases of polymer and solvent (or solvent-solvent) integration within the DFD, a plot and subsequent relative energy difference (RED) was calculated. RED shows the relative distance to sphere center divided by its radius of solubility which confirms the visual states illustrated through images. From the evidence shown within, the DFD has viable working solubility parameters for each of its phases of material synthesis. Culminating the DFD in its most beneficial implementation phase, the PS (polymer -foam) integration within the resin (solvent) matrix is shown to be soluble along the boundary region which yields vinyl ester resin as a *good* solvent for the low molecular weight PS. As illustrated in the transmission electron microscopy (TEM), the aforementioned processing capabilities and parameters show the multi walled facets of the CNTs used during the DFD phases and the resulting dispersion within the final infused nanocomposite. These results indicate the effectiveness of producing dispersed CNTs within the matrix region of a composite. This work demonstrates the ability to manufacture thin films and P-PNC (foams) encapsulated with relatively dispersed and distributed CNTs utilizing a simplistic low temperature plasticizing, calendaring, and foaming process. The nanocomposite product has cell voids in the micron range with cell wall thickness in the submicron regime. The high aspect ratio and large surface area of CNTs offer the potential for high reinforcing efficiency in both nanocomposite and multi-scale hybrid composite systems. DSC gave supporting evidence that the acetone plasticization lowered the decomposition temperature of the AIBN and the glass transition temperature of the polystyrene. The acetone evaporation kinetics study showed the effects of CNT loading on the PS encapsulate and yielded applicable “workable” time periods for the CNTaffy. Validation of the CNTs integration within the nanocomposite has been observed and analyzed via TGA to report up to 60 wt. % achieved loading. It is therefore concluded that the manufacturing process detailed herein gives way to this methodology as a potential tool for incorporating CNTs into multi-scale hybrid composites.

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Appendix

Table 1 – Hansen Solubility Parameters for DFD Polymers/Solvents

Polymer/ Solvent	δ_d	δ_p	δ_h	R_o	Ref.
CNTs	19.7	6.2	4.2	1.0	Kim
PS	21.3	5.8	4.3	12.7	HSP
DMF	17.4	13.7	11.3	24.3	HSP
DI-Water	8.1	17.1	16.9	13.0	HSP
AIBN	-	-	-	-	
Acetone	15.5	10.4	7.0	12.7	HSP
Vinyl Ester	19.7	6.2	4.2	1.0	HSP