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Re-agglomeration of Carbon nanotubes in two-part epoxy system; Influence of the concentration

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Abstract- Carbon nanotubes, because of their exceptional mechanical properties, are one of the potential reinforcements for polymers in near future. Before substituting these nanocomposites in commercial applications, there are many problems, like dispersion, agglomeration, cost effectiveness etc., which need to be sorted. Processing such nanocomposites for longer durations is quite frequently observed these days. Apart from the other major obstacles, re-agglomeration, because of strong van der Waals forces between carbon nanotubes, is one of the latest problems that has been always underestimated and ignored. In this study, different carbon nanotubes (Single-wall nanotubes (SWNT), Double wall nanotubes (DWNT), Amino-modified double wall nanotubes (DWNT-NH₂), Thin Multi wall nanotubes (MWNT) and COOH-modified thin multi wall nanotubes (MWNT-COOH)) at different concentrations (0.025, 0.05 and 0.1 %wt) in two-part epoxy system (Liquid Epoxy, Liquid hardener and Liquid epoxy-hardener mixture) were studied involving nano-particle size analyzer. After a study of 3 hours, it was observed that there is a strong dependence of re-aggregation profile on the employed homogenizing technique, i.e. high-power bath ultrasonication in this study. Apart from nanotubes/epoxy mixture, higher concentrations yielded higher aggregates profile and vice versa. Re-agglomeration, with the passage of time, in liquid epoxy was found to be least as compared to liquid hardener and liquid epoxy-hardener mixture. Hardener in liquid-epoxy mixture was the main culprit responsible for re-aggregation. Results were further verified by scanning electron microscopy, which revealed significant differences in the microstructures of the cured and fractured samples. Suggestions for altering processing parameters in order to avoid this major obstacle are discussed.

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) by a renowned Japanese scientist, Iijima in 1991 [1], many researchers studied various aspects of this outstanding reinforcement for advanced composite materials. CNTs “Fig. 1”, having sp² bonding, consisting of tiny concentric graphene cylinders, are the novel forms of crystalline carbon possess, an outstanding combination of electrical, thermal and mechanical properties [2-3]. Together, CNTs/ polymer composites have been praised for having extraordinary features like strength, stiffness, chemical inertness, damping properties, electrical/thermal properties, light weight etc. than standard composites [3-5]. These are some of the main reasons, that this material is being extremely researched across the world these days. The effective reinforcement by carbon nanotubes of thermosetting polymers, such as the epoxy resins favored in aerospace and other industries, still present great challenges [6-7]. Some of the major problems before the practical substitution of these

materials are dispersion [5-6,8-11], alignment [5,12-15], agglomeration [5-6,8,14,16-18], interfacial adhesion [5-6,10-11,14,19], effective stress transfer [11,15,17,20-21], compatibility of carbon nanotubes with the polymer matrix [14,22], control of nanotube structure [14,21, 23-25], avoiding intratube sliding between concentric tubes within multi walled carbon nanotubes [11,20,26-27] and intrabundle sliding within single walled carbon nanotubes ropes [11,20,26,28], processing difficulties [5,17,23,26,29-31], material availability [21, 23, 25] and cost effectiveness [26,30-33] need to be sorted [34]. This paper is the continuation of our latest work [34], in which we pointed another major issue, re-aggregation with the passage of time, during the processing of these composites. In this study, we reported the influence of concentration of different CNTs on the re-agglomeration behavior in epoxy, hardener and their mixtures.

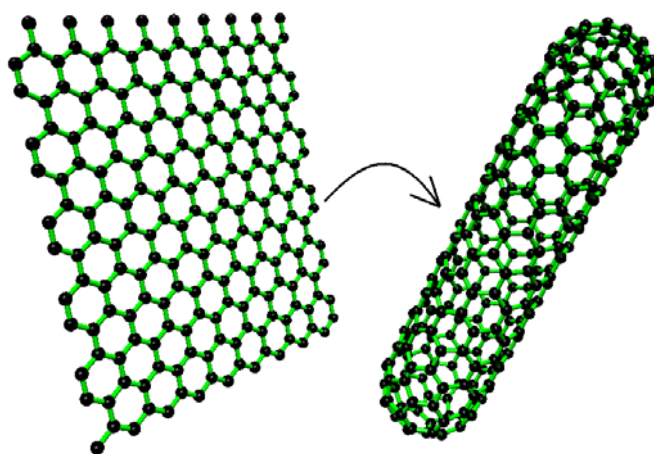


Figure 1. Graphene sheet rolled to make capped single wall carbon nanotube. Modeled in Nanotube Modeler, JcrystalSoft and MS Paint

II. EXPERIMENTAL DETAILS

A. EPOXY MATRIX SYSTEM

The epoxy matrix used in this study consists of a CYCOM 823[®] RTM liquid epoxy resin with an aromatic anhydride hardener, supplied by Cytec engineering materials, UK. This epoxy system is a standard resin for aerospace industry and infusion processes. Important properties, for aggregation studies, of this epoxy system are given in “Table I”. The viscosity of epoxy, hardener and their mixture remains

constant upto 24 hours at room temperature [35], so there were no significant changes observed in the optical properties of these dispersants.

TABLE I
PROPERTIES OF TWO-PART EPOXY SYSTEM

Properties	Measured by	Epoxy (EP)	Hardener (HD)	Epoxy + Hardener (EPHD)
Viscosity (cps)	Brookfield viscometer (Brookfield engineering laboratories, Inc., USA)	250	58	234
Refractive index	Rudolph research analytical J257 automatic refractometer (Spectronic analytical instruments, UK)	1.58	1.48	1.56

B. CARBON NANOTUBES

SWNTs were supplied by Carbolex, Inc., USA. DWNT, DWNT-NH₂, MWNT and MWNT-COOH were supplied by Nanocyl, S.A., Belgium. As per manufacturers, the properties of the mentioned nanotubes are given in “Table II”.

TABLE II
PROPERTIES OF EMPLOYED CARBON NANOTUBES

Nanofillers	Commercial name	Average diameter (nm)	Length (microns)	Functionalization (%)
SWNT	Carbolex® AP-grade	1.4	2-5	NA
DWNT	Nanocyl® 2150	4.7	Several	NA
DWNT-NH ₂ “Figure 2”	Nanocyl® 2152	4.7	Several	<0.5
MWNT	Nanocyl® 3100	10	<1	NA
MWNT-COOH	Nanocyl® 3101	10	<1	<4

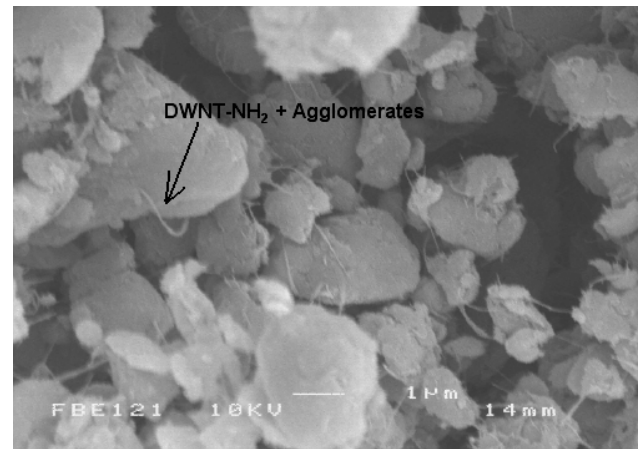


Figure 2. Amino-modified double wall CNTs in "as received form"

C. AGGREGATION ANALYSIS

Zetasizer nano-particle analyzer (series Malvern nano ZS) was used to determine the re-aggregation of different nanotubes in two-part epoxy system. The results were analyzed using standard software “Dispersion technology software, version 4.00”. The instrument performs size measurements using a process called “Dynamic Light Scattering (DLS)”, also known as PCS - Photon Correlation Spectroscopy, measures brownian motion and relates this to the size of the particles [36]. It does this by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light “Figure 3”. As DLS is sensitive to the intensity of light scattered by particles, and larger particles scatter more light than small particles, then the DLS is very sensitive to the presence of aggregates, and hence this technique is an excellent basis for studying the stability of nano particle dispersions. Both, Zetasizer nano-particle analyzer and software were supplied by Malvern instruments ltd., UK.

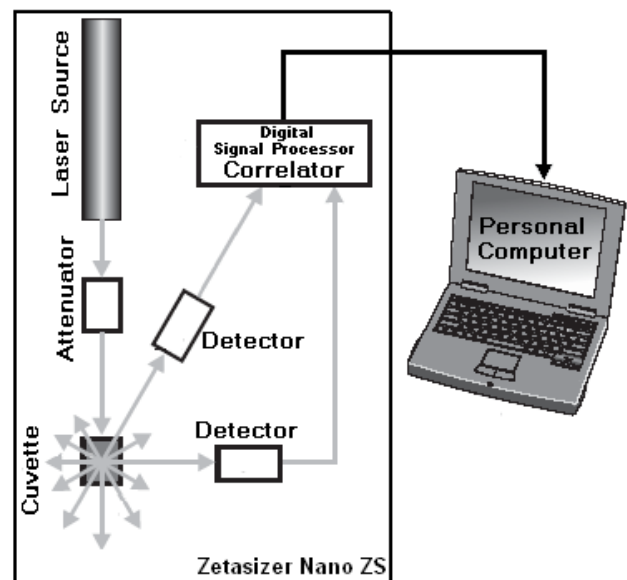


Figure 3. Schematics of Zetasizer nano-particle analyzer [34]

SWNTs (0.025 %wt) were sonicated (Bath sonicator, Model: FS minor, 75 Watts, supplied by Decon ultrasonics ltd, UK.) for 60 and 30 minutes in *EP* and *HD* respectively. A batch of homogenized solution was taken from “SWNT-*EP*” mixture and mixed with *HD* (*EP:HD* = 4:1 by weight) to make SWNT-*EPHD* colloidal solution. The solutions were then transferred to standard polystyrene cuvettes (10x10x45mm) separately. The cuvettes were filled upto 10-15 mm, as per standard instructions [36]. The same procedure was employed for other types of carbon nanotubes and other compositions as well. The cuvettes were then placed in nano-particles size analyzer (at a time) for ~185 minutes of analysis. The machine (nano-particle size analyzer) was programmed to display an average of 30 readings with respect to time. The readings were taken after almost regular intervals. It took ~140 hours to conduct this study for all 5 different kinds of carbon nanotubes with 3 different weight concentrations. More time was given for homogenizing nanotubes in *EP* and *EPHD*, as 30 minutes were not sufficient to make a macroscopic dispersed mixture. This was because of the viscosities of *EP* and *EPHD*, which were ~5 times greater than that of *HD*.

D. SCANNING ELECTRON MICROSCOPY

DWNT-NH₂ (0.025 %wt) were sonicated for 60 minutes in *EP* and mixed with *HD* (*EP:HD* = 4:1 by weight) to make DWNT-NH₂-*EPHD* colloidal solution. The same procedure was employed for other compositions as well. These three mixed solutions were poured in a Teflon open mold having cavities (50x12.7x3 mm). The mold was then placed in a vacuum oven. After degassing the solutions at 25” Hg for 30 minutes, they were cured at 125 °C for 65 minutes. The composite samples were removed easily by bending the mold. A batch of fractured samples was also prepared by same way. All samples were gold coated for 5 minutes and then transferred to SEM (Jeol JSM-6300 at 10 kV, working distance 13-23 mm) for examination.

III. RESULTS AND DISCUSSION

The aggregation of nanotubes is unavoidable in the fabrication of their composites [37]. In preparing novel composite materials, successful fabrication depends crucially on maintaining stable colloidal mixtures (homogenous dispersion) of nanotubes and polymer [37]. The authors studied three weight percentages (i.e. 0.025, 0.5 and 0.1) of different CNTs in epoxy “Figure 4” (on next page). For comparison reasons, the scale (for x and y axis) in all graphs is same. Once placed in the nano-particle size analyzer, the cuvettes were not removed for the whole duration (~185 minutes), in order to avoid shaking of mixture and scratches on the surface of the transparent cuvettes. The z-average diameter is the mean diameter of the agglomerates based on the intensity of scattered light [34]. Using spreadsheet software, linear trend lines were drawn from size analysis “Figure 4” and slopes were obtained “Table III”.

The slopes indicated the trend of re-agglomeration of nanotubes in different liquid solutions with time. Higher the magnitude of slope, faster the re-agglomeration and vice versa. Re-agglomeration of CNTs is strongly dependant on the viscosity of the media and dispersing technique employed. During ultrasonication and because of heat, viscosity was further reduced to ~100, favouring quicker re-aggregation in all samples. “Table III” does not show any strict correlation between agglomeration trend and concentration of CNTs, but certain important results can be deduced. In *EP*, re-agglomeration with passage of time slowed significantly with increasing CNT content, due to the viscous and sticky nature of epoxy. It appears as the agglomerate size increased, it retarded further aggregation process. But in other two solutions (*HD* and *EPHD*), opposite effect was observed, i.e. higher concentrations yielded quicker aggregation and vice versa. This was due to the presence of hardener, inducing lower viscosity and ionic concentration, which decreases the repulsive barrier between particles and allow nanotube reagglomeration [23]. In *HD*, the viscosity was lowest, which resulted in fastest re-agglomeration trend of different CNTs, as compared to other two medias.

TABLE III
SLOPES OF LINEAR TREND LINES (OBTAINED FROM “FIGURE 4” INDICATING TREND OF RE-AGGREGATION WITH TIME

▼ Nanofillers Liquid Media ►	Epoxy			Hardener			Epoxy + Hardener		
Concentration (wt%)	0.025	0.05	0.1	0.025	0.05	0.1	0.025	0.05	0.1
SWNT	0.22	0.42	0.32	1.33	1.25	1.26	0.80	0.66	0.90
DWNT	0.35	0.35	0.33	3.02	2.81	4.59	0.60	0.87	0.59
DWNT-NH ₂	0.70	0.44	0.31	1.78	1.42	2.29	0.44	0.68	0.58
MWNT	0.30	0.32	0.27	2.31	4.28	5.31	0.96	1.42	2.06
MWNT-COOH	0.41	0.84	0.30	2.46	3.31	3.05	0.56	0.56	1.03

Non-uniform trend is observed from “Table III”. Re-agglomeration occurred faster in samples having 0.05 wt% CNTs and then it slowed in samples containing 0.1 wt% CNTs. More work need to be done to study this (0.05 wt%) concentration.

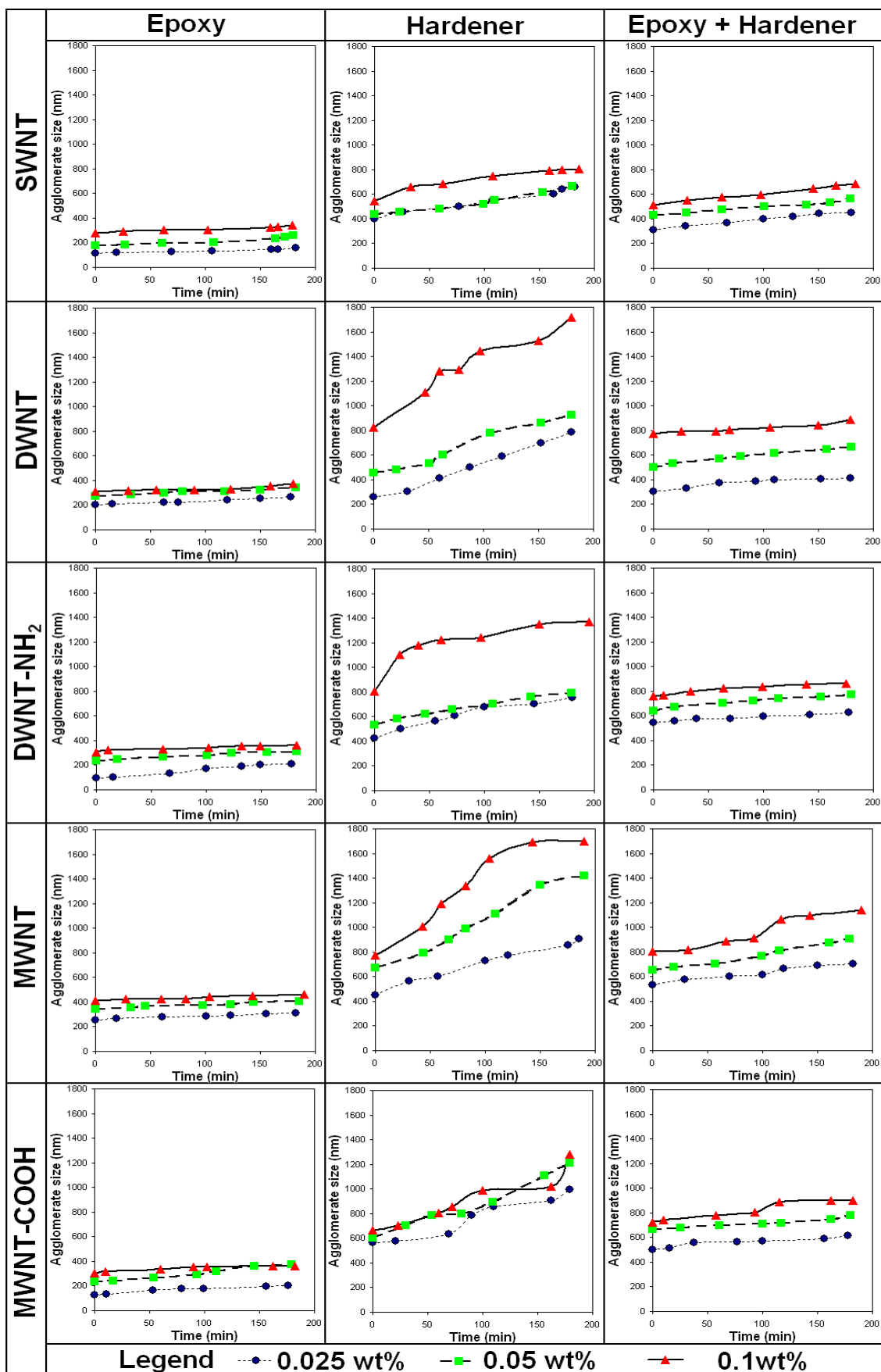


Figure 4. Re-agglomeration of different CNTs in different liquid solutions

Microscopy can be biased [38]. We selected representative areas on the fractured surface to study dispersion of CNTs. SEM images (“Figure 5”) reveal that good dispersion was not achieved. Light/ white spots (agglomerates of CNTs) are visible in samples containing 0.025 and 0.05 wt% CNTs. No agglomerates or very few are observed in last sample (containing 0.1 wt% CNTs) indicating non-homogenous distribution of nanofillers. Bath sonication employed for shorter time was not sufficient to disperse CNTs homogenously.

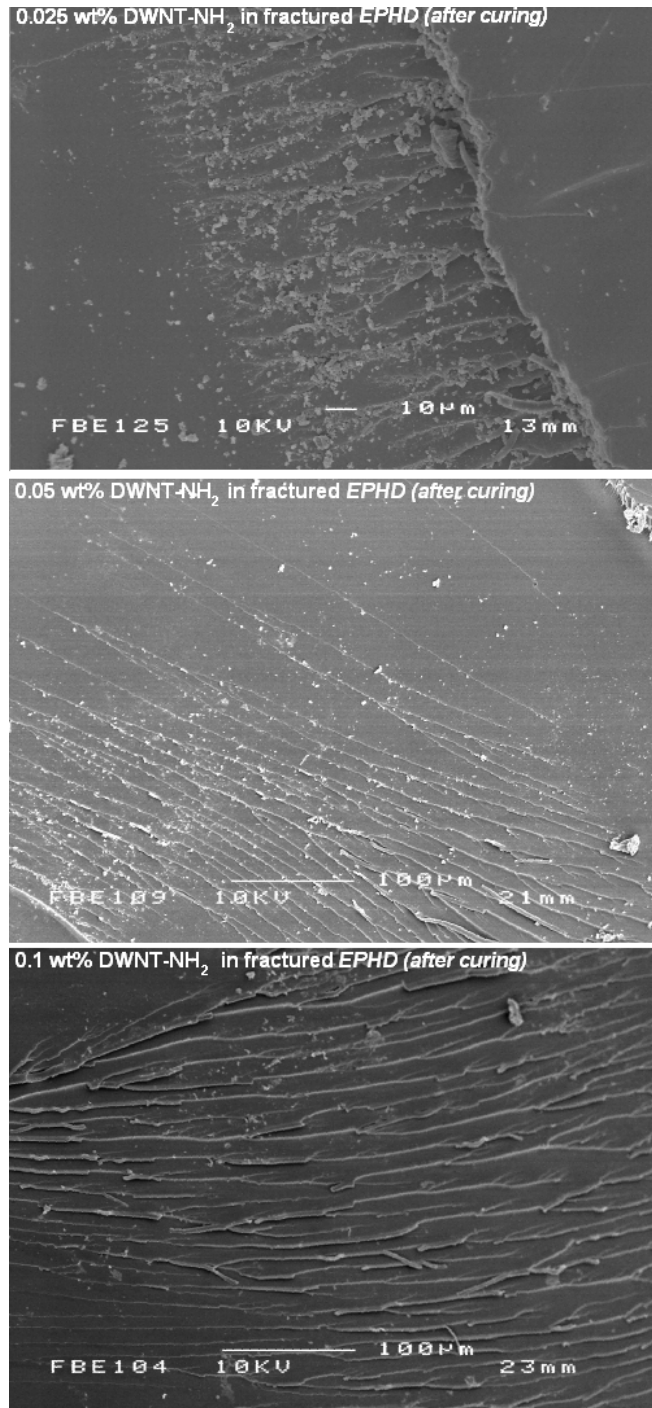


Figure 5. Representative fractured surfaces of cured nanocomposite

Presence of appropriate functional groups is expected to strongly improve the dispersibility of nanotubes on any matrix [39]. From our results, it also appeared that modified CNTs (DWNT-NH₂ and MWNT-COOH) slowed reagglomeration significantly in most of the solutions as compared to pristine CNTs (DWNT and MWNT) respectively. This was observed in all compositions. This is due to covalent functionalization, which provides “handles” for dispersion in host polymers and in exfoliation of the bundles [40].

A. OPINION FOR AVOIDING RE-AGGREGATION

Temperature is mainly responsible for agglomeration of nanotubes, as it activates the formation of bonds (van der Waals forces between carbon nanotubes). Epoxies, which can be cured at room temperature in very short time, seem to be an ideal solution of this issue. They will initially possess low values of glass-transition temperature (*T_g*), but it can be enhanced by suitable post curing cycles. While processing mixtures of carbon nanotubes and epoxy, hardener should be added quickly and the system should be cured immediately, giving less time for re-aggregation of carbon nanotubes [34].

Addition of chemicals (solvents, diluents, surfactants etc.) may be useful for homogenization of CNTs, but it may require another processing step, i.e. removal of these chemicals before curing, and the residual chemicals may also have detrimental effects on the final properties of the composite material [34].

Even with the use of other chemicals (surfactants), homogeneous dispersion of carbon nanotubes in polymer matrix was not achieved as shown by Gong et al. [41]. Dispersed carbon nanotubes also reaggregate under optimized processing conditions involving an increase in resin temperature and the application of low shear forces when adding the hardener [23]. Only the recommended minimum amount of hardener should be added in order to minimize re-aggregation of nanotubes [34].

SPARK PLASMA SINTERING® (SPS) is a comparatively new sintering process that allows compaction of ceramics and powdered metals at low temperature with short holding time, but the mechanisms for densification and grain growth behind this process have not yet been well-explored. The unique features of the process are the possibilities of using very fast heating rates and very short holding times (minutes) to obtain fully dense samples. [42]. This could be very beneficial for avoiding re-agglomeration of CNTs in epoxy due to shorter curing times. Omori [43] set thermosetting polymers using SPS. His results suggested that spark plasma energy should be weak so as not to damage the polymer structures, but sufficient to excite chemical bonding [43]. More work needs to be done in this area to realize the possible potential of SPS in polymer processing.

IV. CONCLUSION

Re-agglomeration has been underestimated and often ignored. Hardener is mainly responsible for re-aggregation of different CNTs in two-component epoxy system. Apart from nanotubes/epoxy mixture, higher concentrations yielded higher aggregates profile (size and trend) and vice versa. Re-agglomeration, with the passage of time, in liquid epoxy was found to be least as compared to liquid hardener and liquid epoxy-hardener mixture. Functionalised CNTs retard re-aggregation as compared to pristine CNTs. According to SEM results, CNTs were not homogeneously dispersed indicating the employed technique was inappropriate. Temperature, heating rate and viscosity are the critical parameters and should be adjusted for avoiding re-agglomeration. More work need to be done to avoid this major obstacle before the actual substitution of these nanocomposites in applications.

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