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Review

Carbon nanotubes agglomeration in reinforced composites: A review

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Abstract: Carbon nano tubes (CNTs), comprising one dimensional (1D) carbon tubes that significantly strengthen the base matrix when added as a reinforcement element. It is light in weight and very low weight fractions (vol% or wt%) of well-dispersed CNTs enhance mechanical properties effectively. Due to its poor wettability during liquid mixing, CNTs reinforced composites are mostly prepared by solid-state processing, extrusion, hot pressing, etc. after premixing of the matrix and CNTs powders in nano size. Irrespective of the production routes, matrices, and chemical treatments, CNTs agglomerate within the matrix structure. That leads to dispersion problem of CNTs in matrix materials and weaken the properties of the composites. CNTs produce small clusters/agglomerates due to their high affinity and affect the texture of grain boundaries. This review discusses the effect of CNTs agglomerations in composites formation for various CNTs reinforced composites. The study covers the effect of vol%, wt%, and dispersion medium for reinforcement.

Keywords: carbon nanotube; dispersion; agglomeration; clustering; CNTs properties

1. Introduction

CNTs have regarded as nano-scale reinforcements elements led to promising results in improving a wide spectrum of properties for an engineering problem. Since the discovery of CNTs by Iijima [1] in 1991, it is considered ideal reinforcements of various range of composites due to their exceptional strength, high Young's modulus (YS) and low density [2–7]. It is viewed as a 1D substance and may arrange in one direction or randomly distributed. Randomly disperse CNTs decreases with higher weight/volume fractions owing to the formation of CNT agglomerates [8,9].

This agglomeration is sometimes referring as clustering or bundling effect in many researches. Figure 1a shows the CNT pillar regarding the direction of the CNT axis and Figure 1b shows the alignment of the 1D CNTs. Randomly orientated, agglomeration/aggregation and in homogeneous distributions are influenced by the presence of a chemical substance (chemical treatment), surface coatings, post-treatment strongly influences physical properties of CNTs reinforced due to the high surface-to-volume ratios of CNTs in the matrix [7,10,11].

The matrixes are pertaining to metallic matrices, ceramics matrices, polymer matrices, fiber matrices, etc. Researchers are using continuous and discontinuous reinforcements with CNTs to enhance the properties of different matrices approximately from the last two decades. Even hybrid composites containing CNTs have tried by many research groups for few sophistical purposes.

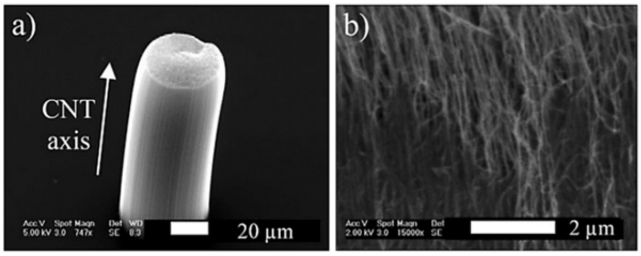


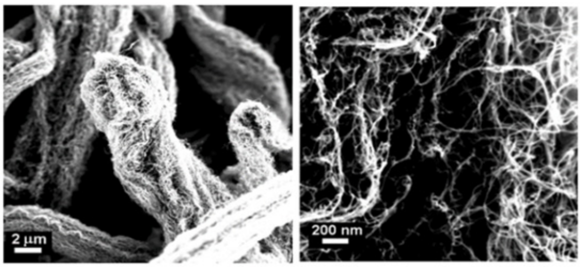
Figure 1. SEM images of (a) a CNT pillar, showing the direction of the CNT axis, and (b) the alignment of the CNTs possible for single dimensional behaviour [8].

CNTs/polymer matrix composites, CNTs/metal matrix composites, CNTs/fiber matrix composites, CNTs/graphene matrix composites and CNTs/ceramics matrix composites have been praised for having extraordinary features like strength, electrical and thermal properties, light weight, stiffness, chemical inertness, damping properties, etc. than any other standard composites [12–15]. Since the overall electrical performance of CNT reinforced composites dominated by the inter-molecular conductive network, the influence of the CNTs entanglement is a critical issue [16,17]. The use of CNTs are now not limited with absolute engineering concept, rather has been expanded for energy, environmental, and medical branches [18]. CNTs regarded as quasi 1D nanomaterials that have a tendency to aggregate in bundles when forming composites [19]. Dispersion of CNTs has few health effects and seems that agglomeration likely inspires this. CNTs have a more possibility to be aerosolized. CNTs reinforced composites during abrasion released protruding CNTs, agglomerates of CNTs, and freestanding CNTs [20–22]. In spite of having marvelous properties, CNTs is sometimes avoided due to its agglomeration effect. Another form of carbon is becoming popular such as graphene. Graphene is being used to form metal, polymer matrix composites [23].

The CNTs has now classified as single wall carbon nanotubes (SWCNTs), double wall carbon nanotubes (DWCNTs), multiwall carbon nano tubes (MWCNTs) and so forth depending on their constructions/microstructure. However, for CNTs reinforced composites microstructure variation, damage and agglomeration behavior of CNTs pre-consideration for property improvement [24–26]. Any metallic matrix, alloy show cluster of reinforced particles among the grain boundary area depending on their vol% or wt%, the porosity of based metals, and grain size [27,28]. CNTs have a strong intermolecular attraction called van der Waals force [29,30]. CNTs tube to tube interactions also reduced physical properties compared to those in a dispersed state [31].

This force entangles the triangular lattice structure of CNTs and produces bundling effect called clustering or agglomeration [32,33]. Even agglomeration exists irrespective of SWCNTs, DWCNTs, Amino-modified double wall carbon nanotubes (DWCNTs–NH_2), MWCNTs and COOH-modified thin multi-wall nanotubes (MWCNTs–COOH) [33]. Agglomeration of CNTs affects the size (diameter/length) and distributions of filer materials/particles and overall is likely to decrease the aspect ratio, while significant insights have been achieved on various processing techniques, post-processing, strengthening, treatment, etc [34]. Many unresolved issues still need to be addressed theoretically as well as experimentally to harness the maximum benefit of CNTs reinforced composites. Thus, the choice of the matrix for reinforcement, processing route, and the processing parameters are very important.

On the other hand, those are mandatory criteria to provide a uniform distribution of CNTs in the base matrix and good matrix-reinforcement interface. The surface of CNTs clusters are highly tortuous and considerably influence by processing techniques and chemical treatment solution. A good chemical agent can potentially reduce agglomeration tendency even after post processing [35]. To proclaim the uniform dispersion of CNTs in the matrix, several methods have been reported based on the processing route. They are ball milling, sonication, stirring (mechanical/magnetic), etc. followed by post-treatment [36–39]. The post-treatment also contribute for untangling of CNTs clusters and must not damage its structure. This clustering or agglomeration behavior is also real for any other composites that produce binary phase. The grain boundary becomes the agglomeration zone in two-phase CNTs-matrix interface [40,41]. A cluster of catalytic chemical vapor deposition-grown multi-wall carbon nanotubes is shown in Figure 2.



(a) (b)

Figure 2. SEM images of a cluster of catalytic chemical vapor deposition-grown multi-wall carbon nanotubes in (a) 2 µm, and (b) 200 nm. Typical lengths/diameters/aspect ratios of the CNT are ~15 µm/15 nm/~1000 [42].

CNTs not only form clusters during reinforcement, but it also remains in cluster form when it is even pure. Most of the researchers worked with clustered CNTs when received from any company irrespective the way they produced [43]. In most of the composites, after a certain amount of CNTs, there is no significant additional reinforcing effect due to agglomeration [44]. Even after acidic, alcoholic, milling, functionalizing is done to reduce the agglomeration tendency, CNTs agglomerated at high contain rate. In this review, we have studied the effect of agglomeration on metal matrix, polymer, epoxy resin, ceramic matrix composites. In this work, we have presented some graphical and statistical evidence after reviewing numerous research papers.

2. Effect on metal matrix composites

The agglomeration or clustering is a more acute problem for metal matrix composites. It is hard to disperse CNTs inside the metal matrix to prevent the formation of large CNTs clusters or aggregates due to their electrostatic and van der Waals forces as well as the density difference between CNTs and metal matrix composites [45,46]. The agglomeration and poor distribution of CNTs as reinforcement particles within a metal matrix depend on many factors such as homogeneity, the orientation of CNTs, nanotube matrix adhesion, nanotube aspect ratio, and the volume/weight fraction of nanotubes in the matrix [47]. The most common ever tried is Aluminum (Al) matrix. Simões et al. [48] worked on the 1.00 vol% of CNTs reinforced in the Al matrix and found enhance properties by Powder Metallurgy (PM) route with Sonication techniques for dispersion. However, the SEM image in Figure 3 shows the darks spotted region around the grain boundaries and depicted as clustering or agglomeration of CNTs. Better dispersion method produces less clustering effect up to 1.0 vol% of CNTs in Al. The size and cluster increase with vol% of CNTs increase in reinforcement. In the same work, the researcher has summarized the clustering effect in an Al/CNTs and Ni/CNT composites depending on the grain size presented in Table 1. In their work, the introduction of more than 1 vol% CNTs reduce the mechanical properties while enhancing the clustering effect and soften the formed composite. This introduction also creates non-uniformed dispersion of CNTs with poor texture effect.

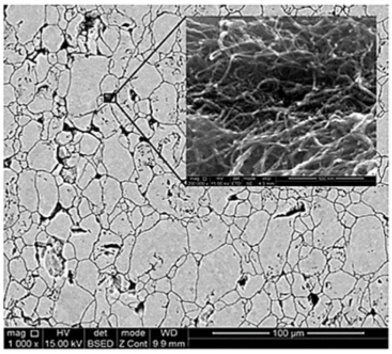


Figure 3. SEM image of the Al/CNTs (1.0 vol%) nanocomposite [48].

Table 1. Maximum size of CNTs cluster, percentage of porosity, CNT clusters and average grain size as a function of CNTs content [48].

Composites	CNT content (vol%)	Porosity and CNT clusters (vol%)	Maximum size of CNT clusters (μm)	Average grain size (μm)
Al/CNT	0	1.00	-	17
	0.50	4.88	89	16
	0.75	6.53	102	15
	1.00	5.95	78	16
	1.50	7.38	177	16
Ni/CNT	0	1.05	-	15
	0.50	3.22	83	14
	0.75	3.96	155	13
	1.00	6.67	137	14
	1.50	12.47	310	16

Agglomeration not only effects on the mechanical properties but also on the machining characteristics. Woo et al. [49] tried an exceptional method of producing Al/CNTs powder by cryogenic milling. Al particles have ductility compared to 5 wt% and 10 wt% Al/CNTs composites. When sintered, Al particle welding may be more pronounced leading to the large particle agglomerates. The change of agglomeration is presented in Raman analysis publicized in Figure 4 showing the growth of clusters spotted on the surface. These clusters adversely affect the machining process and subsequent micro/nano finishing operations.

In Al/CNTs, CNTs exist in the form of bigger agglomerates and are co-embedded in the matrix. Figure 4 shows the comparison of optical microscopy and Raman images of Al powder and Al/CNT powder particles milled for different duration of time. The Raman image shows the distribution of the integrated intensity (area under the curve) of the CNT Raman signal in the wave number range of 1320–1420 cm^{-1} [49].

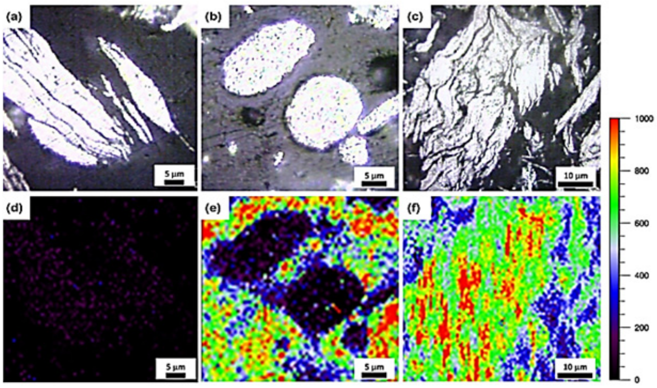
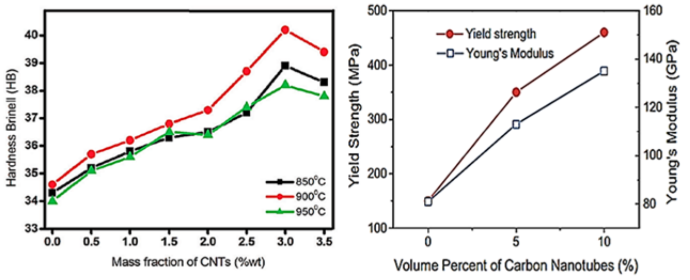


Figure 4. Optical microscopy (upper row) and Raman images (bottom row) of (a,d) cross-sectioned Al powder particles milled for 9 × 10 min in comparison to (b,e) Al/CNT powder particles containing 10 wt% Al/CNT after milling for 3 × 2 min and (c,f) 9 × 10 min [49].

Powder can rolling technique was successfully implemented in order to get carbon nanotubes reinforced aluminum strips and better dispersion of the nanotubes was made possible [50]. Good uniform distribution of CNTs without agglomeration of Al matrix reported being found in ultrasonic and ball mill attrition [51,52]. Pham et al. [44] observed that CNTs percentage could be increased up to 3 wt% for Copper (Cu)/CNTs composite with an effective increase of Brinell hardness as presented in Figure 5. An increasing trend of CNTs drops the hardness due to clustering or agglomeration of CNTs in a large group. Some research her is suggesting chemical treatment of CNTs before composite formation to prevent the clustering effect. However, the dispersion of Cu particles can be enhanced by molecular level mixing of Cu particles in functionalized CNTs in a solvent. Presence of CNTs clusters in processed composites especially when CNTs are more than 1 wt%, has often led to a reduction in the properties instead of improvement. For example, the effect of CNTs agglomeration on the conductivity of Magnesium (Mg) matrix has been studied by Nai et al. [54]. Liu et al. [55] suggested Ultrasonic dispersion to disperse CNTs in Mg alloy (AZ91D) and using a dispersion agent due to the strong interface bond between CNTs and Mg alloy matrix.



(a) (b)

Figure 5. (a) Dependence of the Brinell Hardness (HB) of the Cu/CNT nanocomposite on the mass fraction of the CNTs, and (b) Yield strength and Young modulus of Cu/CNT nanocomposites with an increasing volume percentage of CNTs [53].

During a review of metal matrix nanocomposites, Malaki et al. [56] emphasized the use of dispersing techniques (e.g., melt ultra-sonication) to avoid agglomeration of nanoparticles. However, in their work the de-agglomeration of nanoparticle clusters in the matrix is possible but need special in-situ observation to develop a dynamic principle. Park et al. [57] attributed the difficulty of dispersing the 1–5 wt% CNTs in Mg matrix due to the stickiness of CNTs. This group coated CNTs with Silicon (Si) to reduce the agglomeration behavior and sintered the composite. However, the results are not as imperative as expected. Thus, they further smash the sintered product using zirconia ball (10 mm dia) in a tri-axial vibrating-type ball miller with a rolling rate of 1200 rpm for 12 h in presence of argon gas. The resulting uniformed dispersion of MWCNTs is shown in Figure 6.

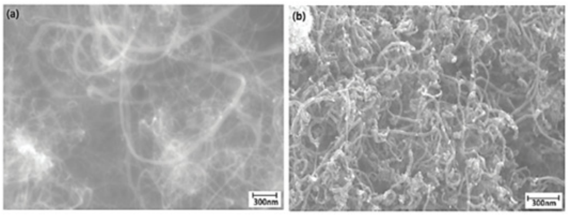
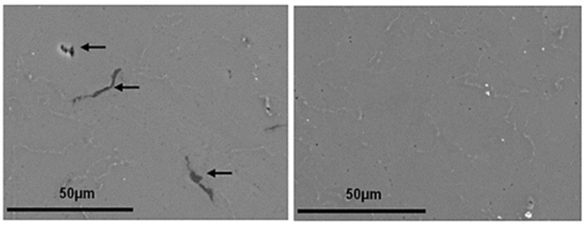


Figure 6. SEM micrographs of (a) the pristine MWCNTs, and (b) MWCNTs with Si coating [57].

However, sintering and hot extrusion as the post-treatment process damage CNT structure. Even for the successful sintering CNTs agglomerates around the grain boundaries [58]. Researchers are continuously working to enhance the interfacial characteristics of CNT in the matrix as reinforcement elements. Reinforced Mg–CNTs composites are more adversely affected by the clustering effect of CNTs compare to Nickel (Ni) coated Ni/CNTs in Mg matrix. The consequence has discussed by Nai et al. [54]. They observed simultaneous enhancements of the micro-hardness, ultimate tensile strength and yield strength (0.2%) by 41%, 39%, and 64% respectively for the Mg/CNTs (0.3 wt%) composites with Ni coating on CNTs.

From Figure 7a [54] it is depicted that small clusters of CNTs are formed in some areas of the monolithic Mg/CNTs reinforced composites. In these cluster zones, CNTs come into contact directly among themselves other rather than with the Mg particles. Thus, effective bonding is hindered between the CNTs and the Mg particles resulting in the associated porosity and low fracture toughness. In contrast, the addition of Ni coating on CNTs prevents the clustering of Ni–CNTs (Figure 7b) [59]. Yamanaka et al. [60] used laser near-net shape melting processing of Ni/MWCNT composites. Physical properties such as thermal conductivity reduce up to half of the original conductivity of pure Ni. The reasons are reported to be the presence of a large amount of porosity and CNTs degradation into carbides, a large amount of porosity and CNT degradation into carbides and agglomerations also mention by other few authors [60–62]. The sintered direction has also the influence of thermal conductivity up to 3 vol% and 4 vol% [60]. Beyond this percentage, conductivity has reported being decreasing constantly due to large agglomeration phenomenon. The large number of CNTs in the Ni matrix caused restriction of CNTs movement and form cluster. For Ni/MWCNTs, the 5 vol% MWCNTs SEM image is shown below. The presence of cluster CNTs, as in Figure 8, is confirmed in the CNTs concentrated parts of the sample.



(a) (b)

Figure 7. Representative SEM micrographs of (a) Mg/0.3 wt% CNT [54], and (b) Mg/0.3 wt% Ni–CNT composites, showing the difference in porosity levels and clustering [59].

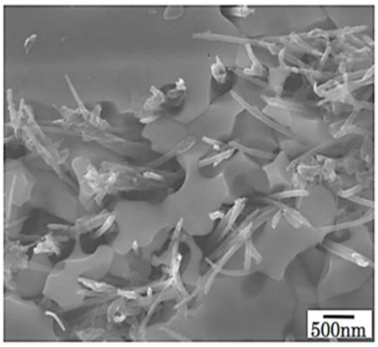
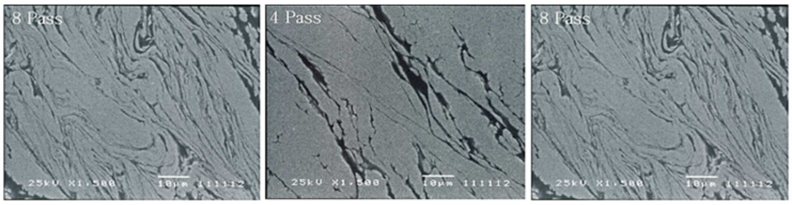


Figure 8. CNT bundles of Ni/5 vol% CNT composite [60].

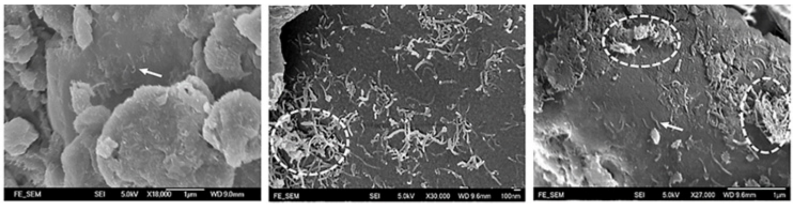
In 1 vol% Cu/CNT composite formation by Equal Channel Angular Pressing (ECAP), the researcher has primarily used ethanol and vibration treatment for an hour with an ultrasonic cleaner to isolate agglomerated CNTs powder. Afterward, severe plastic deformation by ECAP techniques appears effective in de-agglomerated the CNTs in the Cu matrix for multiple numbers of treatment [63]. An increasing number of ECAP passes can effectively break the cluster CNT agglomerates to form better dispersion of CNTs in the Cu matrix as shown in Figure 9 [64].



(a) (b) (c)

Figure 9. Scanning electron micrographs of powder ECAP processed CNT–Cu samples by (a) 1 pass, (b) 4 passes, and (c) 8 passes [64].

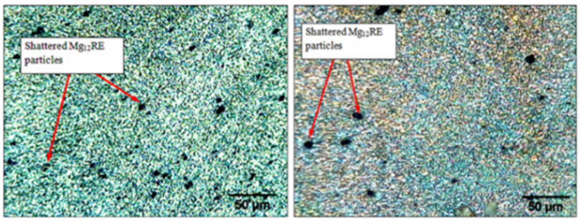
In a similar type of work, ball milled Al/CNTs powders have used for bonding Mg sheet. In this case, Al/CNTs function as an intermetallic compound containing and occurring CNTs inter-diffusion into the Mg sheet. Due to shear flow, CNTs become separated from Al/CNTs bond and eventually distributed uniformly in Mg matrix [54,65]. Researcher working on the CNTs agglomeration undoubtedly concluded that wt/vol% increase of CNTs as reinforced particles accelerated the clustering effect [66]. Akinwekomi et al. [67] attempted to develop Mg/CNTs composite by rapid sintering method. The properties improvement remains acceptable up to 3 vol% of CNTs. Increase the volume fraction of CNTs to 5 vol% in the composite mixture is not successful, as agglomerates of CNTs remain on the alloy powder (dashed circle) in Figure 10b,c.



(a) (b) (c)

Figure 10. (a) CNTs embedded on AZ61 surface after milling for 30 min (AZ61/3 vol% CNT), (b) agglomerates of CNTs in AZ61/5 vol% CNT, and (c) persistent agglomerates of CNTs after milling (a) for 60 min [67].

To reduce the agglomeration and clustering, in AZ61/5 vol% CNT is milled for 60 min. The milling of the composite mixture for 60 min does not significantly improve the dispersion of the CNTs and some agglomerates can still be seen in Figure 10c. Therefore, further Mg-based AZ61 matrix is restricted to reinforced with a maximum of 3 vol% of CNTs processing. CNTs agglomerations exist irrespective of the processing techniques and found for Mg-based alloy process through stir friction process. Magnesium alloy (RZ 5) with Boron Carbide, MWCNTs particles reinforcement are founded with no agglomeration effect [68]. Figure 11 shows that Mg particles become shattered with no agglomeration effect. However, this research is based on the grain size difference of the matrix and reinforcement materials and low contaminations. The density of the CNT reinforced composites possibly comparable up to 8 wt% CNTs. Addition of CNTs beyond this amount causes a decrease of composite density drastically due to agglomeration and clustering [69,70]. Electroless deposition and spark plasma sintering are capable to remove the agglomeration problem of the MWCNTs and the grain growth problem of the nanocrystalline Cu matrix [71]. In a similar manner, a lot of researches have done on such a study. A statistical analysis is shown in Table 2.



(a) (b)

Figure 11. Microstructure achieved at the stir zone after single pass FSP (a) without the use of particle reinforcement, and (b) using MWCNT particles [68].

Table 2. CNTs/metal matrix composite agglomeration.

Matrix	Reinforcement & strengthening method	CNTs (vol/wt%)	Presence of agglomerates & remarks	Ref.
Cu	Ultrasonic cleaning + particles composite system + spark plasma sintering	5, 10 wt%	Yes. CNTs are aggregated into ropes or knotted lumps due to strong inter-tube van der Waals attraction.	[6]
Cuprous oxide	Vacuum hot pressing at H_2 atmosphere	0, 1, 3, 5 wt%	Yes, at 5 wt%. Thermal conductivity decreases with the increase of the CNTs concentration.	[72]
Al	Ball milling + Sonication	2 wt%	Yes. Adverse effects on the properties of final composite products due to the increased porosity.	[73]
2024Al matrix	Cold isostatic pressing + Hot pressing	1 wt%	Yes, but low. Elastic modulus and the tensile strength were enhanced markedly.	[74]
Aluminum–silicon alloy powders	Spray drying	5, 10 wt%	Yes, 10 wt%. Partial CNT surface damage in case of the 10 wt% CNT coating due to CNT mesh formation and smaller size of spray dried agglomerate.	[75]
Al	Ball milling	2 wt%	Yes. Presence of clusters at the early stage of milling which acts as the precipitates results in the lower Young’s modulus.	[76]
Al	Ball milling + Nanodispersion	0.8, 1.6 vol%	Yes. Poor dispersion of CNTs in the matrix exhibited a non-uniform fracture surface. No aggregations in secondary steps are claimed.	[77]
Magnesium oxychloride + epoxy	Magnesium oxychloride cement pastes were prepared by ratios of $MgO:MgCl_2 = 2.2:1$. Then coated with epoxy/CNTs	0, 0.02 wt%	Yes. Water consistency value increases by the addition of CNTs due to that the additional high specific surface area acts as an interface for an efficient stress transfer and causes the strong tendency of the CNTs to form agglomerates.	[78]
AZ91 + Mg	Melt stirring + high-pressure die casting	0.1, 0.5, 1 wt%	Yes, at 1 wt%. Agglomerates of entangled MWCNTs with a size of up to 2 µm can be observed.	[79]
Al	Induction melting	0, 0.1, 0.2 vol%	No. No cluster or segregation of the nanotubes was seen.	[80]
Mg	Hot isostatic pressing under high pressure.	1, 2 wt%	Yes. Homogeneous dispersion of MWCNTs in Mg matrix is obtained.	[81]
Ag	Modified molecular level mixing method	0, 6, 12 vol%	Yes, at 12 vol%. Electrical conductivity reduces.	[82]
Cu	Melt stirring	0.1 wt%	Yes. The micrograph shows that the raw MWCNTs are agglomerated in big bundles. This act as defects instead of reinforcements.	[83]
Al (AA5XXX)	Ball milling + hot isostatic pressed + extrusion	2 wt%	Yes. CNTs clusters were dispersed and claimed as uniform distribution.	[84]

3. Effect on polymer/epoxy resin/ceramic matrix composites

Polymer and ceramics have shown well dispersion characteristics than metal matrix composites and are being considered since the innovation of CNTs in 1991 [53]. If CNTs disperse in the matrix, they can be hardly identified due to their small size, the only agglomerated portion could be visualized. This agglomeration can further be promoted by a temperature increase in pre- or post-processing of the composites is shown in Figure 12. Thus, before composite formation, the cured CNTs is better to keep into the refrigerator to prevent agglomeration growth [42]. The CNTs network in epoxy resin is affected by the shear force rates. This shearing force with low shear rates (0.001–0.1 s^{-1}) produce CNTs agglomeration while shearing with high shear rates (1–100 s^{-1}) destroyed the clusters. The electrical percolation threshold for this type of composites depends on the calendered and non-calendered CNT/epoxy suspensions.

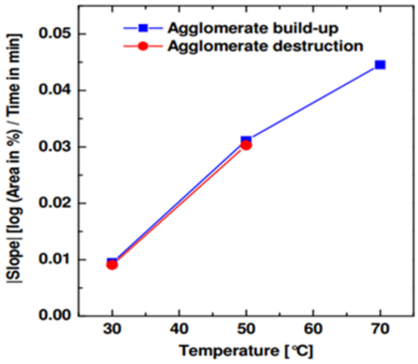
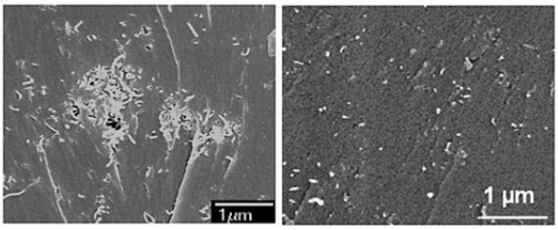


Figure 12. Absolute values of the agglomerate build-up and destruction velocity-measured in log(agglomerate area%) per time (min)—for various suspension temperatures. The suspension consists of 0.05 wt% nanocyl CNT in LY556 epoxy resin [42].

In a similar type of work, Bisphenol F-based epoxy resin/CNTs were investigated. Beforehand, the processed mixture was cured with diethyl toluene diamine. The optical micrographs and Raman analysis show reduced agglomeration and a homogeneous distribution of MWCNTs in the epoxy matrix. The solvent-free method is the reasons behind this reduced tendency [85]. The better the dispersion of CNTs in epoxy resin, the better the electrical conductivity is achievable [85–87]. Shi et al. [88] and Alian et al. [89] develop an elastic model to analysis the agglomeration behavior mathematically. The model was also followed by RAE model which is an analytical micromechanics method. Rafiee et al. [90] used RAE method to study the young modulus of CNTs/polymer composites. They studied agglomeration, non-uniformed dispersion and wavy pattern of CNTs as random parameters by Equivalent fiber theory [91], N3M method [92]. The results concluded are the change of Young modulus with single/multilayer CNTs construction, clustering size, etc. in the two-phase sphere model.

Peng et al. [93] develop modeling to create a 2D finite element modeling of nanocomposite with polymer nanoparticles. They showed that the degree of clustering has a strong influence on the elastic modulus of the nanocomposite. The agglomeration effect can be reduced by using treated CNTs in reinforcement.

Ma et al. [94] has worked on the amino-functionalization to reduce the clustering effects. The clustering effect further forms CNTs ropes and tangle larger. This amino-functionalization has proven effective up to 1 wt% of CNTs in epoxy–polymer composites. This can be justified by the SEM image is shown in Figure 13. Javadinejad et al. [95] applied numerical FEM to demonstrate the clustering effect of CNTs in the composite as shown in Figure 14. Figure 14 shows a 3D view of four colonies in different volume fractions of CNTs. The colonization/agglomeration effect increases with the increase of vol% of CNTs in epoxy resin is shown in Figure 15.



(a) (b)

Figure 13. SEM images of the fracture surface of epoxy-containing 0.5 wt% (a) pristine CNTs, and (b) amino-CNTs [94].

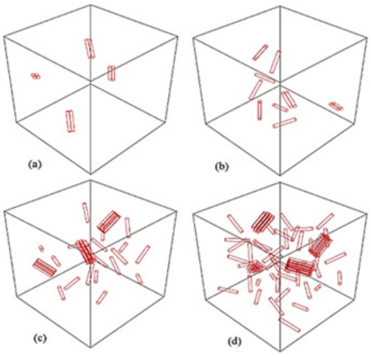
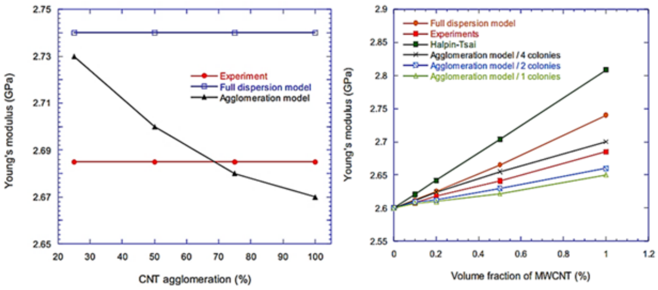


Figure 14. 3D view of the RVE with clustering of CNTs in four colonies in epoxy resin: (a) 0.18 wt%, (b) 0.36 wt%, (c) 0.9 wt%, and (d) 1.8 wt% [95].



(a) (b)

Figure 15. (a) Variation of YS of CNT/epoxy nanocomposite with respect to MWCNT volume fraction, and (b) Effect of CNTs agglomeration on YS of CNT/epoxy nanocomposite for four colonies model and 1 vol% CNT loading [95].

Polymer/CNT composites, ultrasound and high-speed shearing is a powerful dispersion method. They are the simplest and suitable to increase the dispersion of CNTs in a polymer matrix [96]. If the dispersion is not worked effectively, it may be leading to many defect sites (agglomerate, bundle together and entangle) in the composites and limit the efficiency of CNTs on polymer matrices. Nguyen-Tran et al. [97] have found agglomeration for carbon fiber-reinforced polyamide-6/polypropylene composites. CNTs of 1.5 wt% significantly introduce agglomeration defects and reduce mechanical properties.

Figure 16 shows the image of a fracture surface also contains agglomerated CNTs that are claimed as low fracture toughness. Villoria et al. [98] compute the properties of CNT clusters by their developed model as in Eqs 1 and 2. The model could be applied to any type of fiber reinforcement where agglomeration of CNTs is present.

$$k_{dsc} = k_m + \frac{(k_{cluster} - k_m)C_c}{1 + \frac{k_{cluster} - k_m}{k_m + \frac{4\mu_m}{3}}} \tag{1}$$

$$\mu_{dsc} = \mu_m[1 - \frac{15(1 - v_m)(1 - \frac{\mu_{cluster}}{\mu_m})C_c}{7 - 5v_m + 2(4 - 5v_m)\frac{\mu_{cluster}}{\mu_m}}] \tag{2}$$

Where C_c refers to the volume fraction of agglomerations zone which is related to the overall CNTs fraction by $V_f = C_f C_c$, C_f being the CNT concentration in of a cluster.

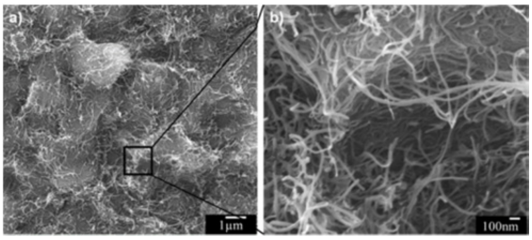
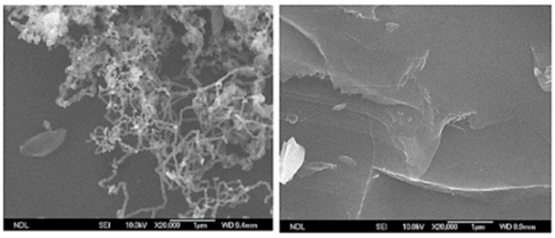


Figure 16. FE-SEM images of (a) CNT agglomeration in the fracture surface of CF-reinforced PA6/PP composites (30 wt % PP) with 1.5 wt % CNTs, and (b) its enlarged image [97].

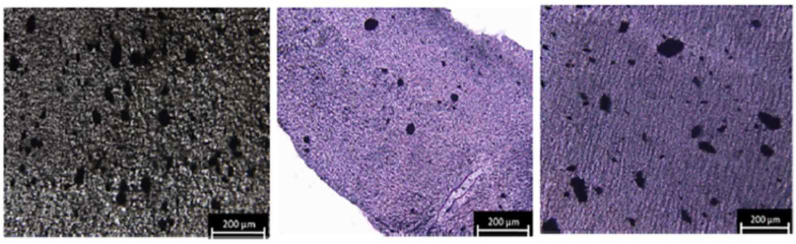
Li et al. [99] obtained the same effect for CNT-reinforced carbon/carbon composites. As CNTs content increases up to 1.2 wt%, inter-laminar shearing strength increases by 30%. But, like the other CNTs shearing strength starts to decrease as CNTs content increases up to 1.5 wt%. Agglomeration attributed to a lot of CNTs content ends up in the decrease of contacted space between CNTs and matrix and reduces the result of resistance to delamination. Hence, inter-laminar shearing strength decreases. The SEM image of the failure surface of nanocomposites is given below in the Figure 17.

Agglomeration of CNTs leads to non-homogenous dispersion with small assemblies of CNT reinforcements in certain points throughout the composite. That causes a decrease in the mechanical properties [100,101]. Some researchers have proposed degassing the CNTs powder to remove moisture from the powders. The moisture content of only 0.1 wt% shows considerable agglomeration [102]. Moisture added weight of the composites and act as an interfacial agent of intermolecular attraction. The dispersion defect and agglomeration are clearly visible for Casini et al. [103] experiments. Inadequately scattered CNTs in the polymer matrix appeared by the biggest size of agglomerates. Figure 18 displays the representative microscopy images of polypropylene compounds containing 0.5 vol% for each kind of CNTs considered are non-functionalized, functionalized with amino groups (–NH_2), functionalized with carboxyl groups (–COOH) [103]. Long CNTs have a diameter of 8 nm, and length of 10–30 µm. Therefore, aspect ratio becomes 2500 for long CNTs than the short CNTs. Entangling and agglomeration of CNTs are accelerated by this high aspect ratio [104]. Krause et al. [105] worked to gain better electrical properties of polycarbonate/CNT composites. These composites required a high degree of CNT dispersion within the thermoplastic matrix.



(a) (b)

Figure 17. Fracture surface of inter-laminar shearing strength of (a) 1.5 wt%, and (b) 1.2 wt% CNTs C/C composite [99].



(a) (b) (c)

Figure 18. Optical micrographs illustrating the state of agglomerate dispersion of nanocomposites with a different type of 0.5 vol% MWCNTs: non-functionalized (a) functionalized with amino groups, (b) and (c) functionalized with carboxyl groups [103].

They observed clustering of CNTs in polycarbonate due to strong interactions between neighbored CNTs caused by high van der Waals forces and physical entanglements. The research group suggested shortening of CNTs length by ball milling. This suggestion is better to explain by Ahn et al. [106] who described that MWCNTs tend to be compacted by the impact of the milling balls. Afterward, SEM image shows CNTs form agglomerates with increased size during the ball milling process. On the same time, these agglomerated CNTs adversely affect the dispersibility. The researcher has simulated the effect of CNTs agglomeration in computer-generated samples. For example, Tarlton et al. [107] developed an algorithm called Monte Carlo hopping algorithm showing that uniformly disperses decrease conductivity of chae with the sacrifice of mobility and vice versa. They found that when the CNTs focus was near the permeation edge, a progressively uniform CNTs dissemination could be accomplished and lead to an improved conductivity.

Recently it has been shown how bundling or agglomeration of DWCNTs affects the behavior of the composite. Dispersion of the CNTs within the polymer matrix plays a key role in the preparation of the conducting nanocomposites. TEM and Raman spectroscopy have been used by Tishkova et al. [108] to characterize the distribution of the DWCNTs in the polymer matrix. Figure 19 represents examples of the TEM images of 0.8 wt% DWCNTs/poly (ether-ether-ketone) composite (PEEK). Figure 19a shows a DWCNTs agglomerated surrounding by PEEK matrix particles. From the images of Figure 19b, it is revealed an inhomogeneous dispersion of CNTs in the polymer matrix and most of the nanotubes form large agglomerates.

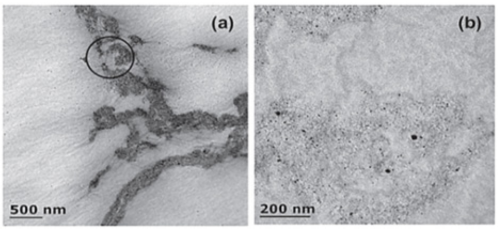
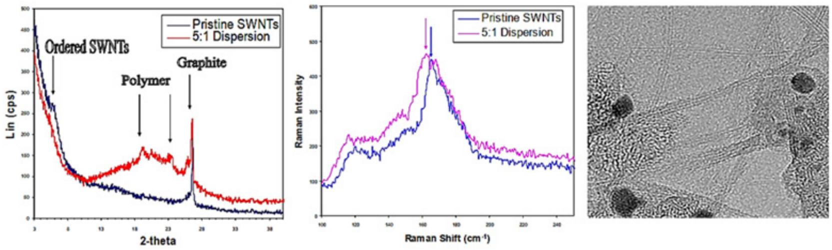


Figure 19. (a) TEM image of 0.8 wt% DWNTs/PEEK composites, and (b) higher magnification view of (a) in the selected area [108].

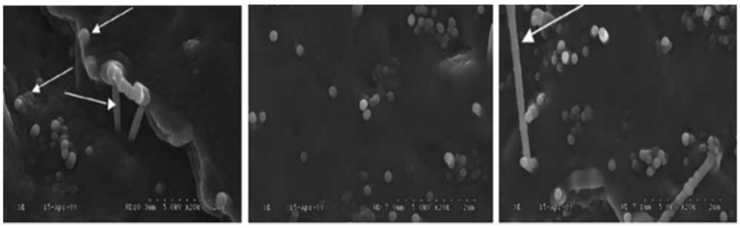
Domínguez et al. [32] show the bundling effect SWCNTs in a polymer matrix by Raman analysis as shown in Figure 20. They characterized the dispersion of SWCNTs by X-ray diffraction, Raman Spectroscopy, and TEM is shown in Figure 20a,b,c, respectively. Figure 20a indicated desegregation because of the bundle's lattice peaks disappearance [109]. Figure 20b supported the de-bundling of SWCNTs due to the radial breathing mode shift displacement [110]. From TEM micrographics of Figure 20c, it is clear that individual polymer warps the CNTs and produce bundles of 3–4 tubes at a different spot.



(a) (b) (c)

Figure 20. (a) XRD diffractogram, (b) Radial Breathing Mode part of Raman Specter, and (c) TEM micrography [32].

Again, MWCNTs filled polypropylene (PP) nanocomposites prepared through PP/MWNT master-batch dilution process was found with insignificant agglomeration tendency. The master-batch dilution assisted with a high shear extruder eliminates significant agglomeration of MWCNTs [111]. However, this happens for only 1 wt% of CNTs. Increase in wt% aggregates CNTs as clusters clearly visible by SEM images is shown in Figure 21. Kumar et al. [112] describe an express method called Representative Volume Element (RVE) model to incorporate the effects of CNTs agglomeration on the elastic behavior of CNTs reinforcement in polymer composites. The vertically aligned CNTs–polymer architecture presented by García et al. [8] and Bello et al. [113] has described reducing the agglomeration effect. CNTs potentially modify glass–fiber reinforced polymer (GFRP) composite laminates. Researches tried to form such composite laminates using ultrasonication and the hand lay-up method [114]. CNTs content of 0.75% resin (phr) improves interlaminar shear strength and flexural strength 15.7% and 9.2%, respectively. Though agglomeration reduces the interlaminar shear strength.



(a) (b) (c)

Figure 21. SEM images of MWCNTs filled polypropylene nanocomposites at (a) 1 wt% MWCNTs, (b) 2 wt% MWCNTs, and (c) 3 wt% MWCNTs [111].

With further increase of the content of CNTs become easily, induce an agglomeration of CNTs is shown in Figure 22. When MWCNTs is epoxidized with polysulfide resin to form CNTs/epoxy polysulfide nanocomposites, agglomeration in the nanocomposites with a higher content of MWCNTs act as large particles. The clusters then create space/void to contain higher apparent filler loading. These agglomerates confine polymer particles in the void space between MWCNTs and effectively reduce the volume fraction of the epoxy polysulfide matrix [115,116]. CNTs/polysulfone composites with 0.068 wt% CNTs also agglomerate similarly, but CNTs-to-CNTs contact after the percolating network increases conductivity for this case [117].

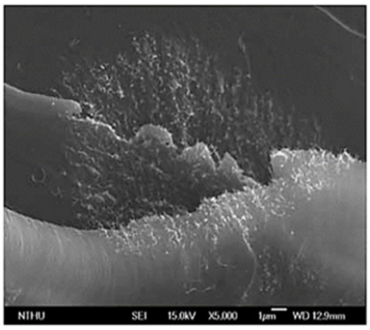
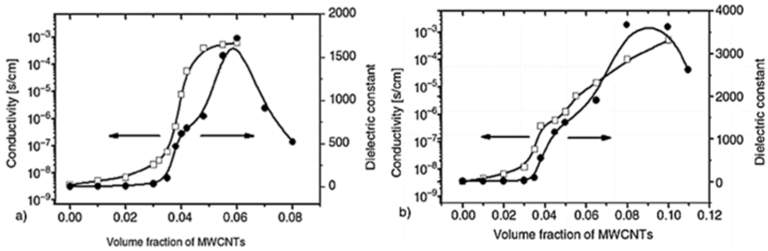


Figure 22. SEM micrograph of ILSS test showing an agglomeration particle in 0.75 phr CNTs/GFRP composite laminates fracture surface [114].

In the word of Yurdakul et al. [118] electric field effects on CNTs/vinyl ester has affected by the agglomeration of CNTs. Composite formed by vinyl ester matrix containing low content (0.05, 0.1 and 0.3 wt%) of DWCNTs and MWCNTS with and without amine functional groups brings synergetic effect to reorient the agglomerated CNTs clusters. This synergetic effect modifies the distribution of radicals in the resin. In bulk composite (large CNTs contents) due to the synergetic effect, field-induced agglomeration and cluster formation occurs. Li et al. [119] studied electrical conductivity about the CNTs/polymer composites. As the CNTs concentration increases within the composite, the number of the molecular interfaces increases. From Figure 23, we can see that dielectric constant increases with increasing MWCNT concentration. When pristine MWCNTS reaches 0.06 vol% and oxidized MWCNTs reaches 0.08 vol%, they are at percolation threshold energy. More concentration of CNTs beyond this value will agglomerate MWCNTs. CNTs produces cluster in cement pastes [120]. MWCNTs (up to 0.5 wt% of cement) with/without surfactant were characterized. Composites with surfactant has found with 0.25% increased tensile strength and better mechanical properties. In a similar manner, a lot of researches have done on such a study. A statistical (Table 3) is given below.



(a) (b)

Figure 23. Dependence of the electrical conductivity and dielectric constant of (a) pristine MWCNT/polyvinylidene fluoride composites, and (b) oxidized MWCNT/ polyvinylidene fluoride composites on the MWCNT concentration [119].

Table 3. CNTs/polymer/epoxy resin/ceramic composite agglomeration.

Matrix	Reinforcement & strengthening method	CNTs vol/wt%	Presence of agglomerates & remarks	Ref.
Epoxy system	Sonication	0.025, 0.05 wt%	Yes. Good dispersion was not achieved.	[33]
-	-	-	Yes. A review paper that has described a lot about agglomeration of CNTs in the polymer matrix.	[121]
Polypropylene	Melt mixing	0.5–7.5 wt%	Yes. Low agglomeration effect due to melt dispersion. Lower matrix viscosity promotes secondary agglomeration during the compression molding step.	[122]
Polyvinyl alcohol	Used prepared sample to study machining	1, 2, 4 wt%	Yes. CNTs loading beyond 4 wt%, the CNTs were observed to form clusters within the polymer matrix.	[123]
Polystyrene	Injection moulding process	20 wt%	Yes. Monte Carlo model was used for simulation to predict the electrical conductivity. The agglomeration has been neglected.	[124]
Polymer	Injection molding	1 wt%	Yes. Both partial alignment and MWCNTs agglomeration were observed.	[125]
Polyvinyl alcohol	Solvent method	Not mentioned	Yes. Substantial agglomerates of nanotubes are visible.	[126]
Vinyl alcohol	Melt mixing	0.1, 0.3, 0.5, 1 wt%	Yes. Entanglement of CNTs reduce conductivity.	[127]
Epoxy	Sonication	Varying ranges	Yes. Varying cluster/aggregate depending on the composites.	[128]
Vinyl alcohol	Gum arabic treatment	2 wt%	Yes. Interfere with the tensile properties.	[129]

Modelling the behavior of CNTs composites is therefore a long queue of scientific works, both theoretical and experimental approaches. Kundalwal et al. [130] worked on the micro-mechanics of CNTs/fiber composites and discussed about some theoretical model. Kundalwal also proposed SWCNTs/fiber analysis model called Fuzzy model [131]. Typical issue covered by the model is agglomeration of CNTs, the misalignment and the difficulty in manufacturing very long CNTs. The same model is quite effective for polymer also. Feng et al. [132] used micro and nano approaches to elucidates the key factors of CNTs agglomeration, that influence the mechanical properties of formed composites. Wernik et al. [133] analyzed agglomeration in embedded nano-reinforced adhesive for the case of 3.0 wt% CNT loading. Results shows that composite may begin to degrade for agglomeration. They suggested to investigate the effect of CNTs agglomeration. Thus research introduces additional parameters related to the size and density of the agglomerates with the conclusion of a micro model. Some research made on multiscale model of hybrid composites such as Eshelby–Mori–Tanaka model isotropic hybrid material [134,135]. This scheme takes into account the agglomeration of the nanoparticles in the CNTs/polymer/fiber laminated composites.

4. Discussion

This review on CNTs agglomeration comprises the overview of reinforcement structure, the bonding method, dispersion method, and consequences of clustering of CNTs along with their effects. The review has retrieved the following outcomes by a sharp understanding of the cited literature. They are:

(a) CNTs remained in aggregated form when prepared due to van der Walls forces. Dispersion method can considerably reduce this tendency. However, re-agglomeration is common when contamination increases.

(b) Metal matrix CNTs reinforced composites have more agglomeration than polymer, epoxy, ceramics, etc.

(c) Agglomeration/clustering of CNTs has a direct effect on the thermal, electrical, and mechanical properties of composites. They act as a barrier to load transfer among the grains. Thus all physical properties are reduced.

(d) Maximum volumetric/weight percentage addition is limited with a maximum of 20% for metal matrix, and 5 % for polymer, epoxy, ceramics etc. However, 2–5% CNTs/metallic matrix and 0–2% CNTs/polymer, epoxy, ceramics, etc. are recorded common. Agglomeration occurs around the grain boundaries.

(e) Few rare earth/CNTs are available materials, but their production method is the major concentrated rather than agglomeration.

Conflict of interests

The authors declare no conflict of interest.

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