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RESEARCH PAPER

Effect of diazotization and magnetic assembly on CNT dispersion observed with hardness and modulus measurement of their epoxy composite of low CNT volume fraction

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Abstract Polymer composites with small amount of CNTs (< 5 wt%) have been studied as a light-weight wear-resistant material with low friction, among other applications, but their modulus improvement often plateaus or diminishes with increasing CNT fraction due to agglomeration. Here, polymer nanocomposites were fabricated with randomly oriented or aligned CNTs across their volume (up to 5 mm length) by CNT surface diazotization and by static magnetic field application (400 G for 40 min). With the improved CNT dispersion and thus less agglomeration, the reduced moduli of PNCs stayed improved with addition of up to 1 vol% (or 1.3 wt%) of CNTs. In this work, the PNCs with randomly oriented CNTs exhibited higher stiffness than the PNCs with magnetically aligned and assembled CNTs, indicating again the negative effect of CNT agglomeration on stiffness. In future, other CNT structuring methods with controlled inter-CNT contacts will be conducted to dissociate alignment from local agglomeration of CNTs and thus to simultaneously improve hardness and modulus of PNCs with small CNT addition.

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Introduction

Integration of carbon nanotubes (CNTs) into polymer matrices, e.g., CNT-polymer nanocomposite (PNC), has been investigated over the past two decades for multi-functional property reinforcement (mechanical, thermal, electrical, and smart functions) (Breuer and Sundararaj 2004). Among many applications, CNT-PNCs are sought after as a potential light-weight material with low friction and/or high wear resistance (Lau et al. 2003); CNTs have the high crystalline structure with a high aspect ratio, low density (~1.4 g/cm^3), and exceptional mechanical properties (~1 TPa stiffness and ~45 GPa tensile strength) (Dresselhaus et al. 2001). The properties of epoxies related to wear resistance, including Yong's modulus and hardness, exhibited significant improvement, even with small addition of CNTs, but were also observed to plateau or even degrade with increasing CNT addition (> 0.1–1 wt%) (Bal et al. 2013; Bisht et al. 2018; Domun et al. 2015; Hong et al. 2015; Khan et al. 2013; Koumoulos et al. 2015; Lau et al. 2003; Lu et al. 2013; Martone et al. 2010, 2011a; Ogasawara et al. 2011; Wladyka-Przybylak et al. 2011), which was attributed to micro-voids, CNT agglomeration, and more. Modulus improvement with CNT addition was modeled based on micro-mechanics

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and molecular dynamics but still exhibits discrepancy from the experimental data. The Halpin-Tsai model (Affdl and Kardos 1976) and its modified versions have been rigorously studied to accommodate complex CNT morphologies (aspect ratio, waviness (Stein and Wardle 2015), multi-wall structures (Thostenson and Chou 2003), dispersion (De Villoria and Miravete 2007), and inter-CNT contacts (Yeh et al. 2006)) but did not simulate the decreasing trend. The shear lag model based on stress transfer (Cox 1952; Tucker and Liang 1999) is one of a few models that predicts property degradation due to agglomeration, but modeling of complex and often inhomogeneous CNT structures within PNCs in experiments is still a challenge.

In this work, an updated method to fabricate PNCs of small CNT volume fraction was demonstrated to improve CNT dispersion by surface diazotization and to improve homogeneity of aligned CNTs by magnetic field application. Among many surface treatment, aryldiazonium salts were selected to functionalize CNT surfaces, as the resulting covalent bonding is effective to improve dispersion and suspension and to promote effective stress transfer at CNT-polymer interfaces simultaneously(Mohamed et al. 2015). Magnetic assembly was selected as a scalable method to precisely organize CNTs suspended within an epoxy matrix. In the past, to disperse and organize CNTs in moderately viscous matrices, CNT-polymer mixtures were applied with either mechanical loading (stretching or shear loading (Hong et al. 2015; Khan et al. 2013)) and/or with external fields (electric (Hashemi et al. 2018; Oliva-Avilés et al. 2011; Oliva-Avilés et al. 2012; Park et al. 2006), acoustic (Strobl et al. 2004), and magnetic (Abdalla et al. 2019; Choi et al. 2003; Fujiwara et al. 2001; Garmestani et al. 2003; Hone et al. 2000; Kimura et al. 2002; Lu 1995; Piao et al. 2007; Shen et al. 2010; Smith et al. 2000; Walters et al. 2001; Wu et al. 2015)). The latter method has been effective to achieve homogeneous, complex, and potentially tailorable CNT structuring (Haibat et al. 2017; Spencer et al. 2018) of low volume fraction, and magnetic assembly is effective with insulating polymers, without the problems of acoustic damping or dielectric breakdown observed with electric/acoustic assembly. PNCs with homogeneously dispersed or aligned CNTs of low volume fractions (< 1 vol%) were fabricated. Modulus and hardness data of these CNT-PNCs measured by indentation confirmed that (1) improved CNT dispersion helps to delay the stiffness degradation onset with increasing CNT addition and that (2) randomly oriented CNTs can contribute to stiffness more than aligned, and thus bundled, CNTs when CNT volume fraction is low.

Material and methods

Multi-walled carbon nanotubes (MWCNTs) were synthesized by chemical vapor deposition to have ~35–40 nm diameter, ~120 μm length, ~10–20 walls, and 1.55 g/cm^3 (Haibat et al. 2017). The as-grown MWCNTs are diamagnetic (Haibat et al. 2017; Kimura et al. 2002; Lu 1995; Piao et al. 2007) and were magnetized by coating their tips with thin ferromagnetic nickel films (~80 nm) with electron-beam evaporation; coercivity of ~326 Oe was measured along the CNT (Haibat et al. 2017). The Ni-coated CNTs are grafted with aryl diazonium salt as illustrated in Fig. 1 (Wang et al. 2006). The curing agent (~5.5 g) was diazotized by mixing with isoamyl nitrite (0.215 ml) with a PTFE stirrer (~200 rpm) in a heated ultrasonication bath (~65 °C) for 3 h; diazonium salt was formed by reacting primary amine from the curing agent with nitrous acid of isoamyl nitride. Such diazonium salt is unstable; when mixed with the Ni-coated MWCNTs (~5 mg before Ni coating, ultrasonicated in 5 ml of dimethylformamide, DMF), the salt rapidly loses its nitrogen and converts to carbocations and covalently bonds its aromatic ring with carbon surfaces by extracting electrons. After mixing, excess diazonium salt and DMF solvent were removed by washing with acetone using centrifuge (~3500 rpm for 10 min, repeated). The functionalized, Ni-coated CNTs were then dried in an oven (~140 °C for 30 min) to evaporate acetone. FTIR measurement was conducted (Vertex V70, Bruker, spectrum range of 6000–50 cm^{-1}) to confirm diazonium salt grafting on CNT surfaces. Three samples were prepared and compared: potassium bromide (KBr) pellets as a reference, pristine Ni-coated CNTs, and diazotized Ni-coated CNTs. As shown in Fig. 2a, two peaks at 2959 cm^{-1} and below 1500 cm^{-1}, which are associated with N-H bending and stretching within aryl diazonium salts (Lambert 1972), were observed only with the functionalized Ni-coated CNTs. Other observed peaks can be associated with water (3400 cm^{-1} and 1635 cm^{-1}) or to C-H bond (2913 cm^{-1} and 2845 cm^{-1}) (Lambert 1972). To note, this FTIR result only confirms existence of diazonium salt within the samples and does not necessarily confirm diazotization of the CNT surfaces.

The effectiveness of diazotization on dispersion and suspension of the Ni-coated CNTs was evaluated using

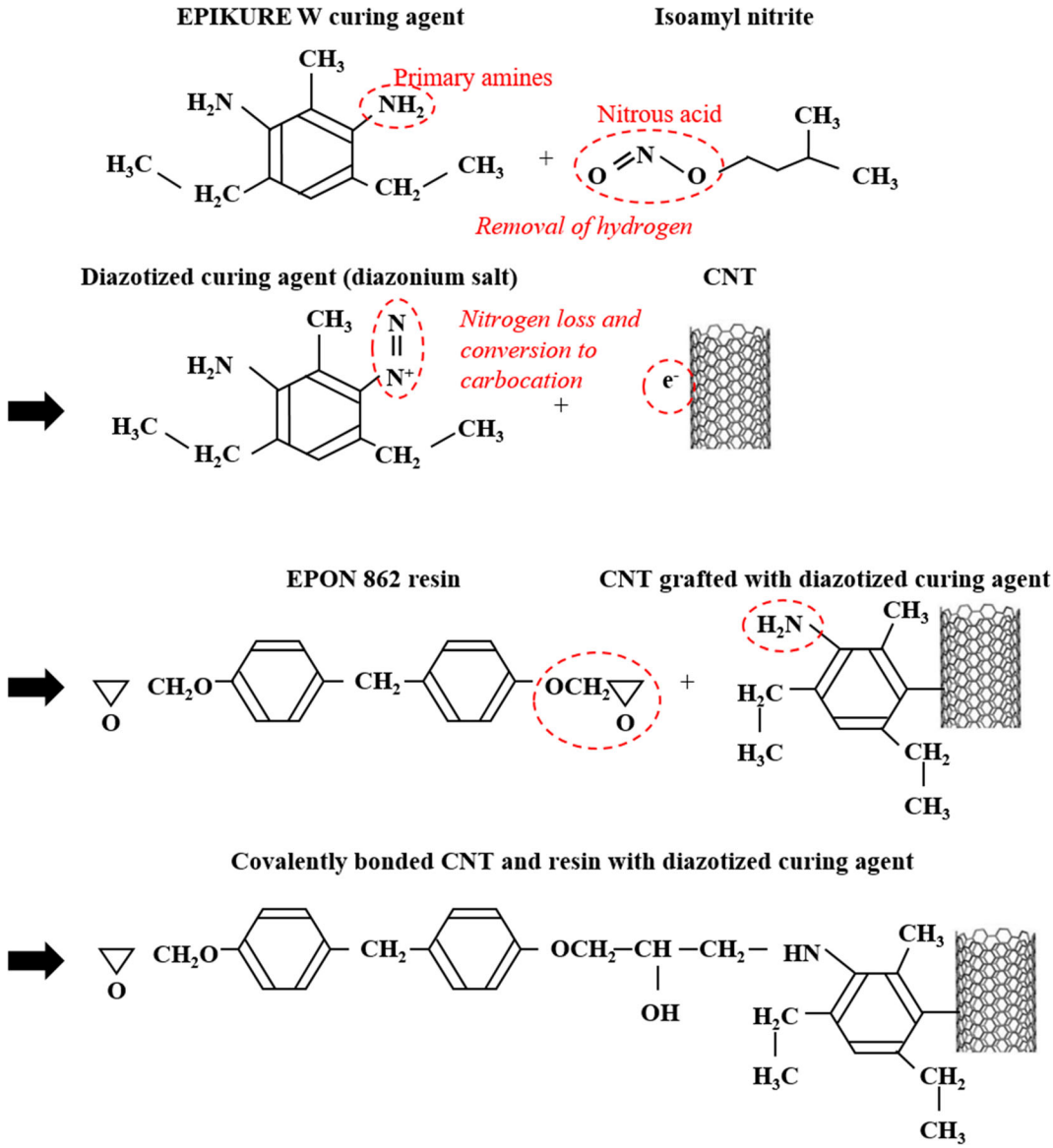

Fig. 1 Schematics of covalent bonding formation between CNTs and the epoxy system

two techniques. First, zeta potentials of the diazotized Ni-coated CNTs (0.2 vol% in DI water) were measured using dynamic light scattering (Zetasizer NanoZS, Malvern, particle size range of 0.3 nm–10 μm). Electric fields (~0.0008 V) was applied to electrophretically move the electrically charged particles in the solvent (water, 0.88 P); the Zeta potentials were calculated from the particle velocity measured by dynamic light scattering. As shown in Fig. 2b, the zeta potential magnitude increased from −15.3 ± 0.5 mV to −18.3 ± 1.0 mV after diazotization, indicating improved electrostatic repulsion and more stable suspension. Second, agglomeration sizes of the Ni-coated CNTs, diluted in DI water (0.0005 vol% to allow ~85–95 % light transmission), were measured using laser diffraction (Mastersizer 3000, Malvern, particle size range of 10 nm–3500 μm). As shown in Fig. 5c, the peak CNT agglomeration size decreased from ~104 μm to ~30 μm after diazotization, smaller than the as-grown CNT length of ~120 μm, indicating CNT length shortening and improved dispersion. In summary, the diazotization process decreased the bundle size of the Ni-coated CNTs, through both loosening and shortening, and improved their suspension. Separately, Raman spectroscopy of pristine CNTs and diazotized CNTs was measured

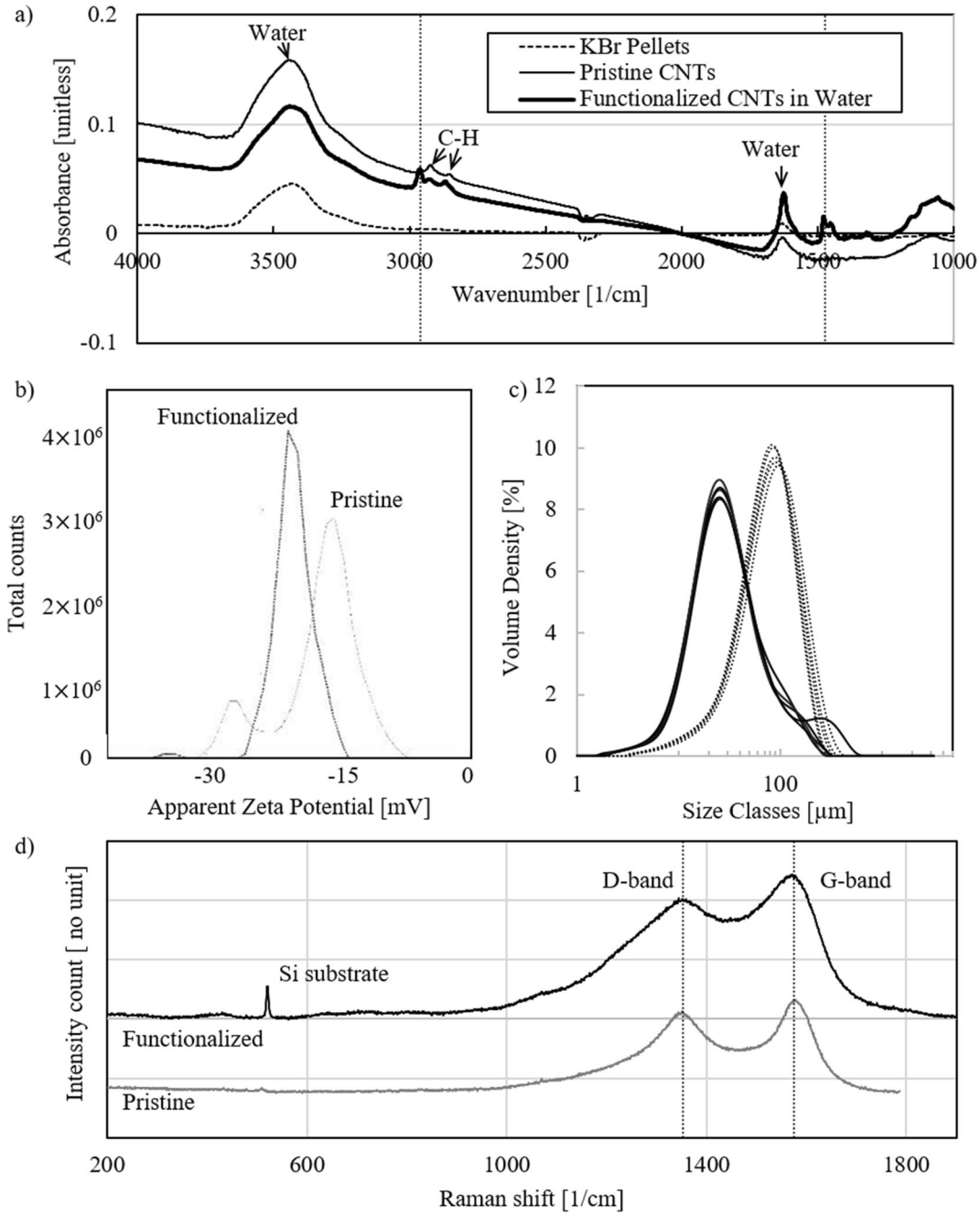

Fig. 2 Evaluation of the functionalization effects with diazonium salts: (a) FTIR measurements, (b) zeta potential, (c) particle size, and (d) Raman spectroscopy plots

(over > 100 points) to evaluate the effect of diazotization on CNTs' crystallinity. Both CNT samples were prepared by dispersing in acetone and by drying the CNT-acetone solution droplets on a silicon substrate. With the diazotization, the D/G ratio of the CNTs slightly decreased from 0.87 to 0.85, and the D and G peaks became wider, indicating the small but negative effect of diazotization on the CNT crystallinity (see Fig. 2d).

To form CNT-PNCs, the functionalized Ni-coated MWCNTs (~5 mg before Ni coating and functionalization, to form ~0.06 vol% and ~84 mg for ~1 vol%) were dispersed in the resin (EPON^{TM}862, 0.89

g, ~70 cP at 65 °C) in the heated ultrasonication bath for 25 min and mixed for another 5 min after adding the curing agent (EPIKURE™ W, 0.23 g with 100:26 ratio of resin: curing agent). The mixed solution was then poured into a heated aluminum mold (20 mm× 20 mm × 5 mm) between a solenoid coil pair driven to align CNTs with the static magnetic field (~400 G for 40 min) (Haibat et al. 2017; Spencer et al. 2018) at 70 °C. After CNT alignment was complete, the mold was heated to 120 °C for 60 min to cure the mixture where the field was kept on. Post-curing, without the field, is followed in an oven (171 °C for 120 min). Assembly structures of CNTs within the polymer nanocomposites were inspected using an optical microscope (Nikon L200ND) as shown in Fig. 3; microscope images were focused at three different planes (top, middle, and bottom) along the sample thickness (~5 mm). Without diazotization, pristine CNT structures exhibit a large gradient along the sample thickness direction (see Fig. 3a). The CNT bundles are large (~70 μm) comparable with the measured particle size of ~104 μm (see Fig. 2c); this large size caused particle settlement and ineffective magnetic assembly, especially at the bottom plane. With diazonium salt functionalization, CNT bundle size decreases to the degree where their size cannot be effectively measured using the optical microscopy of 0.15 μm resolution (see Fig. 3b). Most CNT bundles are smaller than 20 μm, comparable with the measured particle size of ~30 μm (see Fig. 2c); with this decreased size, CNTs did not settle and were magnetically aligned (see Fig. 3c).

Nanoindentation (Hysitron TI980, Berkovich tip, 9 mN) was conducted on the fabricated CNT-PNCs to evaluate the effect of CNT structures on their mechanical properties (reduced Young's modulus and hardness). The CNT-PNCs were polished using silicon carbide polishing papers, diamond colloidal suspensions (~1 μm size), and colloidal silica suspension (~0.04 μm size). The PNCs were prepared so that indentation can occur in the directions that are parallel to or perpendicular to the CNT alignment to measure their anisotropic properties and also on the top, middle, and bottom planes along the thickness direction to evaluate sample inhomogeneity due to CNT settling. Indentations were repeated nine locations that are 50 μm apart for each sample location. The reduced Young's modulus and hardness of the CNT-PNCs were calculated from the load-displacement curves using the standard Oliver and Pharr's method (Oliver and Pharr 1992). The nanoindentation imprint size is smaller (~3–5 μm length) than the feature size of the CNT assembly (~20–30 μm). Thus, CNT-PNCs of 0.06 vol%, with the smaller CNT volume fraction, were also tested with microindentation (Leco M-400H, Vickers tip, 0.98 N, 5 indentation per location, ~70 μm of imprint length) to compare their hardness data with those obtained by nanoindentation.

Results

The hardness data obtained using nanoindentation and microindentation are compared in Fig. 4. The values obtained from nanoindentation are larger than those obtained from microindentation, due to their smaller indenter size (Broitman 2017; Elmustafa and Stone 2003). Meanwhile, the relative differences among the samples and sample locations stay the same regardless of the indentation size scale, confirming the validity of nanoindentation data for comparative study. The PNCs with pristine CNTs, especially at the bottom locations where CNTs settled, exhibit high hardness data and large standard deviation. This trend can be associated with the larger CNT agglomerate size; with the low volume fraction, CNTs are not dense enough to contribute to hardness (Ji et al. 2004), unless the indenter hits CNT agglomerates. In contrast, the hardness of PNCs with functionalized CNTs stays comparable with that of a neat polymer, confirming that functionalized CNTs are well-dispersed without agglomeration, either randomly oriented or aligned, up to at least 1 vol%. It should be noted that, when the CNT volume fraction is low as 0.06 vol%, the PNCs with functionalized CNTs exhibit slightly smaller hardness than neat epoxy samples; the excessive diazonium salt left on CNT surfaces can potentially cause such softening.

The reduced modulus data obtained using nanoindentation are compared in Fig. 5. The reduced modulus of the polymer improves by adding 0.06 vol% of CNTs but then decreases by adding more CNTs (1 vol%); this trend has been observed in the past and attributed again to CNT agglomerates and associated stress concentration and poor load transfer at a small CNT fraction of 0.25–0.3 wt% (Bisht et al. 2018; Khan et al. 2013; Koumoulos et al. 2015; Lu et al. 2013). Meanwhile, with functionalization, this trend is mitigated, and the improved modulus values are maintained even with 1 vol% of CNTs due to their improved dispersion.

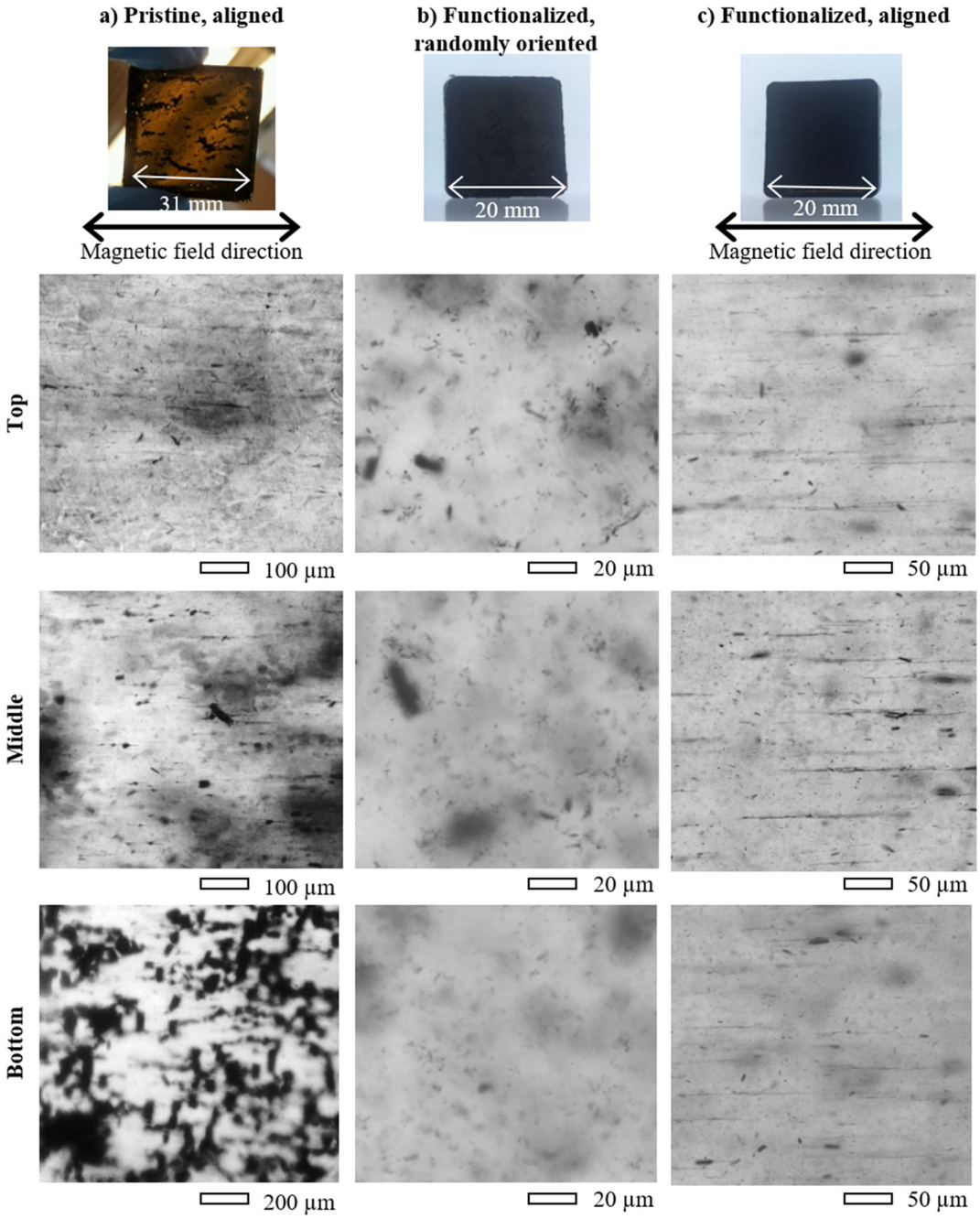

Fig. 3 Digital and microscope images of CNT-PNCs with and without functionalization and magnetic alignment

Another trend to note is that PNCs with randomly oriented CNTs exhibit higher modulus values than PNCs with aligned CNTs. In the past studies, modulus values increased with increasing CNT alignment degree enabled by shearing and/or electric/magnetic fields (Bal et al. 2013; Khan et al. 2013; Prolongo et al. 2013), but such modulus improvement plateaus or even diminishes at a small CNT fraction due to agglomeration as noted above. In this work, the modulus improvement was less with CNT alignment, because, with static magnetic field application, CNTs do not just reorient and align themselves but also connect with neighboring CNTs through head-to-tail assembly and zippering (Spencer et al. 2018), forming agglomerates even with small CNT

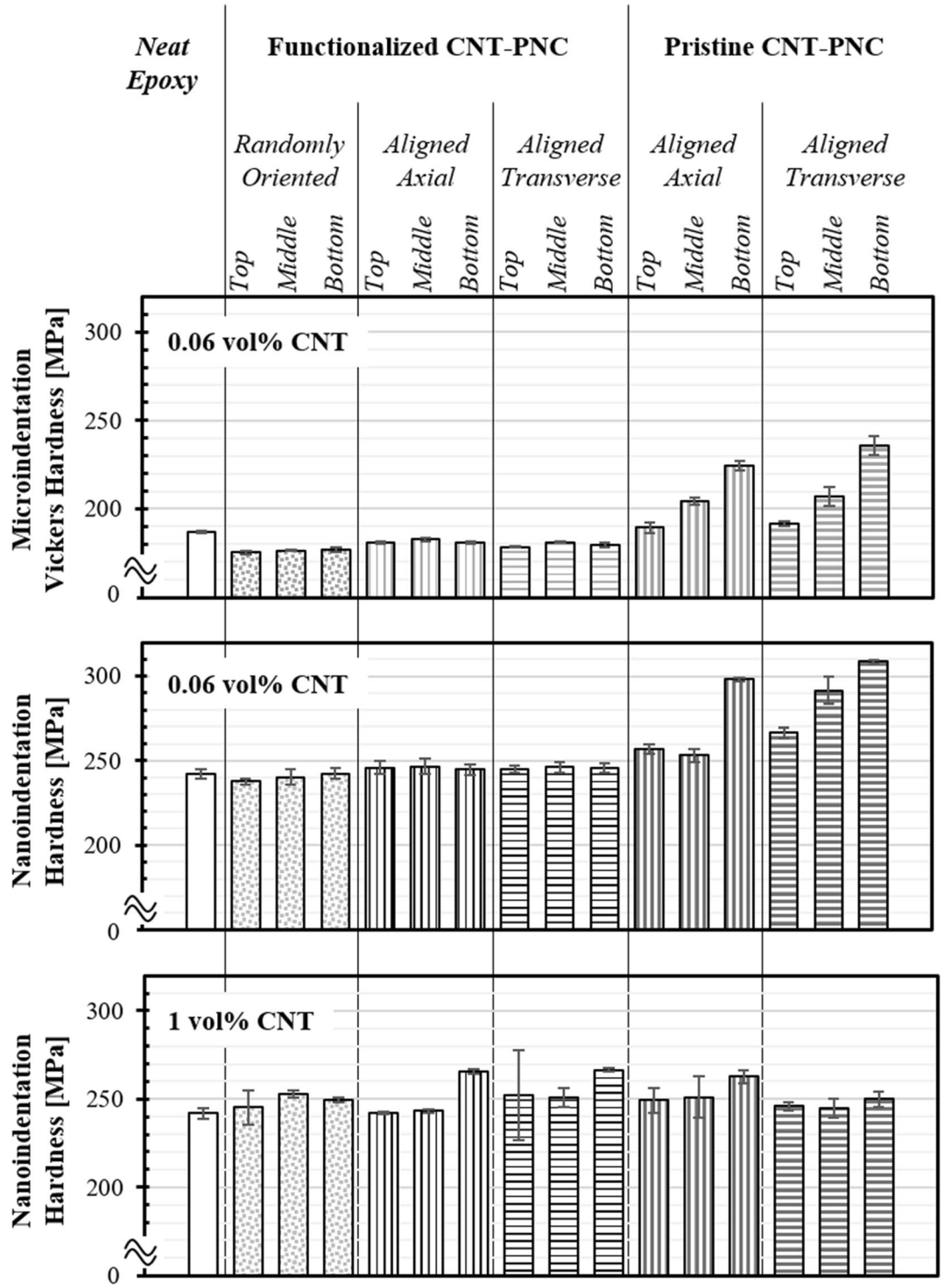

Fig. 4 Hardness data of CNT-PNCs compared by method (micro vs. nanoindentation) and by CNT volume fraction (0.06 vol% and 1 vol%)

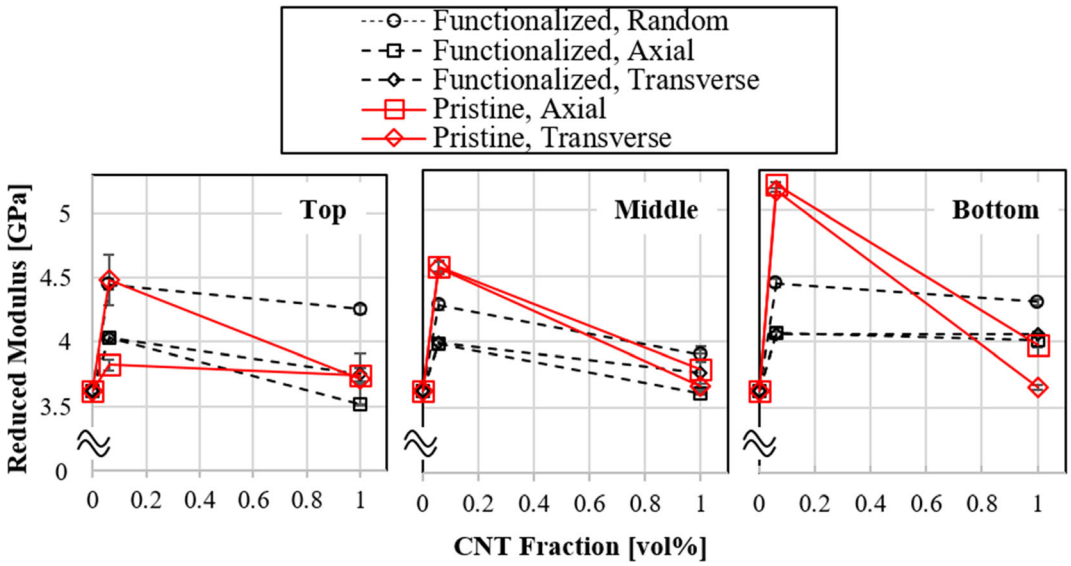

Fig. 5 Reduced modulus data of CNT-PNCs as a function of CNT volume fraction. Lines between the data points are only to guide the eyes

volume fraction. Without magnetic field application, CNTs stay dispersed without agglomeration, contributing to stiffening even with the randomly oriented structure.

Discussion

Potentially scalable fabrication of PNCs with well-dispersed CNTs of small volume fraction (<1 vol%) was demonstrated using diazotization and magnetic field assembly, as confirmed by their hardness data. Previous studies exist about strengthened CNT-thermoset interface with diazotization (Wang et al. 2006), but their study focus has been on the interface strength measurement and not on nanocomposite properties (Bahr and Tour 2001; Bahr et al. 2001; Dyke and Tour 2003; Wang et al. 2009). Sizable PNC samples (20 mm length× 20 mm width× 5 mm thickness) were successfully fabricated where CNTs of low volume fraction (0.06–1 vol%) are structured homogeneously using short application (40 mins vs. a few hours required for electric/acoustic field) of relatively small magnetic field (400 G vs. ~50 G of a typical refrigerator magnet). With diazotization, CNT agglomeration and thus decreasing trend of modulus with increasing volume fraction were deterred at least up to 1 vol% (or 1.3 wt%); previous studies exhibited the modulus decrease with CNT fraction of 0.25–0.3 wt% (Bal et al. 2013; Bisht et al. 2018) even with functionalization (Khan et al. 2013; Lu et al. 2013). When CNTs are aligned using static magnetic fields, CNT alignment cannot be dissociated from CNT bundling and thus agglomeration; such assembly behavior was observed as the higher modulus of PNCs with randomly oriented CNTs than that of PNCs with magnetically aligned CNTs. In future, instead of static magnetic fields, oscillating magnetic fields can be used to dissociate magnetic alignment and formation of local agglomeration of CNTs (Spencer et al. 2018).

Conclusions

In this work, PNCs of well-dispersed and structured CNTs were prepared by surface diazotization and magnetic assembly of CNTs. Improved CNT dispersion was confirmed by CNTs' negligible contribution to hardness of PNCs (0.06–1 vol% CNTs); dense CNTs, and thus higher volume fraction, is necessary to improve hardness. Improved CNT dispersion, and thus less agglomeration, was confirmed that the reduced moduli of PNCs stayed improved with CNT addition of up to 1 vol%; in the past, higher CNT volume fraction (> 0.3 wt%) resulted in less modulus improvement due to CNT agglomeration. The negative effect of CNT agglomeration was also observed by comparing the modulus data of CNT-PNCs with

aligned vs. randomly oriented CNTs. Magnetically aligned CNTs inevitably formed agglomeration by magnetically attracting neighboring CNTs, resulting that the PNCs with randomly oriented CNTs has higher modulus than the PNCs with magnetically aligned CNTs. In other words, this experimental study contributes to understanding the effects of CNT volume fraction, alignment, and agglomeration separately, which will potentially help achieving simultaneous improvement of hardness and modulus of PNCs with small CNT addition. Further statistical analysis of the work and comparison with modeling should be followed in future (De Villoria and Miravete 2007; Hamdia et al. 2017; Martone et al. 2011b; Msekh et al. 2018; Stein and Wardle 2015). Next, the authors plan to further control magnetic CNT assembly to provide structuring with less inter-CNT contacts using oscillating magnetic fields. Fabrication methods will be expanded to accommodate higher CNT volume fraction and to conduct 2D and 3D CNT structuring using the triaxial Helmholtz coil system recently obtained, for mechanical and multifunctional property improvement.

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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