Functionalization of carbon nanotubes for fabrication of CNT/epoxy nanocomposites

Jaemin Cha a, Sungghan Jin d, Jae Hun Shim c, Chong Soo Park c, Ho Jin Ryu b,⁎, Soon Hyung Hong a,⁎

a Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
b Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea
c Kukdo Chemical Co. Ltd. 61 Gasandigital 2-ro, Geumcheon-gu, Seoul 153-802, Republic of Korea
d Research Fellow IBS Center for Multidimensional Carbon Materials (CMCM), 50 UNIST-gil, Eonyang-eup, Ulsan 689-798, Republic of Korea

A R T I C L E   I N F O

Article history:
Received 19 November 2015
Received in revised form 15 January 2016
Accepted 18 January 2016
Available online 20 January 2016

Keywords:
Carbon nanotubes
Polymer-matrix nanocomposites
Mechanical properties

A B S T R A C T

To improve the dispersion of carbon nanotubes (CNTs) in epoxy matrix composites, polystyrene sulfonate (PSS) and poly(4-amino styrene) (PAS) were attached on the surface of CNTs by noncovalent functionalization. In the case of PAS, amino groups can also generate chemical bonding with the epoxide groups in the epoxy matrix. CNTs noncovalently functionalized with PSS and PAS were then fabricated to obtain CNT/Epoxy nanocomposites with enhanced mechanical properties. The incorporation of noncovalently functionalized CNTs into the modified bisphenol-A type epoxy matrix yielded Young’s modulus of 3.89 GPa and tensile strength of 82.59 MPa with the addition of 1 wt.% PAS-CNTs. The noncovalent functionalization of CNTs was effective in improving the composite’s mechanical properties due to their enhanced dispersion and strong affinity with the epoxy matrix.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Engineering polymers are used for a wide number of applications due to their high flexibility, processability and relatively low cost. However, many polymers have low absolute strength and poor fracture toughness, limiting their applications in structural components [1]. To improve the mechanical properties of engineering polymers, numerous fillers, such as carbon black, carbon nanotubes, nanoclay, silica, and polymeric particles have been compounded with the polymers [2]. Among them, carbon nanotubes (CNTs) have attracted lots of attention for the reinforcement of polymer-matrix nanocomposites, polymeric partic- lers, such as CNT/Polypropylene [8], CNT/Poly carbonate [9], CNT/Poly(vinyl alcohol) [10], CNT/Nylon 6 [11], CNT/Epoxy [12].

However, the poor dispersibility and low interfacial strength of CNTs in polymers have limited their applications. Because CNTs usually agglomerate with each other due to strong Van der Waals force, it is highly difficult to disperse CNTs in a polymer matrix [13]. In order to achieve better dispersion and strong interfacial interactions, the functionalization of CNTs has been considered an effective method to prevent the agglomeration of CNTs and to improve the load transfer across the interface of the CNTs and polymer [14].

There are two approaches for functionalization of CNTs; covalent functionalization and noncovalent functionalization [15]. The covalent functionalization is usually realized by oxidizing CNTs in an acid in order to attach carboxylic or hydroxyl groups to the end-caps or defect sites of CNTs [16]. This can form direct chemical bonding between the nanotubes and polymer [17]. Noncovalent functionalization is an alternative method for modifying the wall of CNTs [18]. Functional molecules such as various inorganic and organic molecules involved adsorption onto the side wall of CNTs via π–π stacking, van der Waals or charge transfer interactions. Among them, π–π stacking was the strongest interaction of delocalized π-bonds between CNT wall and functional molecules [16]. The advantage of noncovalent functionalization is that it does not destroy the CNT side-walls. Therefore, it is more attractive than the covalent method for maintaining the pristine structure and properties of CNTs [19].

However, in the case of noncovalent functionalization via π–π interaction, the efficiency of load transfer is limited when using functional molecules that have weak bonding to the polymer matrix. The functionalized CNTs can be pulled out from the matrix if the CNTs did not combine with the matrix [20]. When the bonds between the CNTs and matrix are formed simultaneously, the external tensile load can be effectively transferred from the matrix to the nanotubes.

Poly(4-aminostyrene) (PAS), used in this work, adopts a conjugated structure with CNT walls and also has amine groups that can form strong chemical bonds with the epoxy matrix. J. Zhu et al. [21] fabricated CNT/Epoxy nanocomposites functionalized by amine groups using chemical reactions. The addition of the amino-terminated amide derivative of the CNT increased the ultimate strength and modulus of the CNT/Epoxy nanocomposites by 30–70%. Chemical reactions, however,
change the intrinsic properties of CNTs by producing many defects. Therefore, PAS is one of the most suitable molecules for maintaining the intrinsic properties of CNTs while forming strong interfacial bonds with epoxy.

In this study, we provide a method to obtain noncovalently functionalized CNTs by using two functional molecules, polystyrene sulfonate (PSS) and poly(4-aminostyrene) (PAS). PSS has a molecular structure similar to PAS and is used to form nanocomposites with CNTs. The functionalized CNTs were produced by a nondestructive method such as the ball milling process. The morphology of the functionalized CNT/Epoxynanocomposites was characterized to evaluate the dispersibility of the functionalized CNTs. The tensile properties of the CNT/Epoxynanocomposites and their dependence on the contents of the CNTs were investigated to determine the effects of functionalization on the tensile properties.

2. Experimental section

2.1. Functionalization of carbon nanotubes

Multiwall carbon nanotubes (MWCNTs) synthesized by chemical vapor deposition method (JEIO Co. Ltd., Korea) were used. Polystyrene (PSS, Sigma Aldrich) and poly(4-aminostyrene) (PAS, Polysciences) were used as functional molecules. Both have benzene rings suitable for π–π interactions with CNTs. 300 mg of each of the functional molecules was dissolved in N,N-dimethylforamide (DMF, Junsei) by stirring for 20 mins, and then the DMF solution was sonicated for 1 h with 700 mg of CNTs. The solution was ball milled in a PP bottle at a ball-to-product weight ratio of 1000:1 and a rotation speed of 200 rpm for 24 h for noncovalent functionalization. After the functionalization of the CNTs via π–π interactions, the solution was filtered under a vacuum for 30 mins. After filtration, the resulting black solid was dried at room temperature in a vacuum.

2.2. Fabrication of CNT/epoxy nanocomposites

Epoxy resin (modified bisphenol A type, KFR-120, Kukdo Chemical) was dissolved in CNTs suspended in acetone and DMF co-solvent and a curing agent (amine type, KFH-163, Kukdo Chemical) was added under sonication (30 wt.% to epoxy). After sonication, the mixed solution was stirred at 135 °C for about 3 h to evaporate solvent. The homogeneous mixture of epoxy with PSS-CNTs or PAS-CNTs was cast into a dog bone-shaped stainless steel mold, and then dried and degassed at 65 °C for 1 h under a vacuum. Finally, a curing process was conducted at 110 °C for 7 h. For the epoxy nanocomposites with PAS–CNTs, different loading ratios ranging from 0.5 to 3 wt.% were prepared. The content of pristine CNT and PSS-CNTs in the nanocomposites was 1 wt.% for comparison studies.

2.3. Characterizations of functionalized CNTs and CNT/epoxy nanocomposites

Microstructural observation of the functionalized CNTs and CNT/Epoxynanocomposites was carried out using scanning electron microscopy (Hitachi S-480). When making functionalized CNTs samples, a spin coating of CNT solution on silicon substrates was used. In the case of CNT/Epoxynanocomposites, their fracture surfaces were observed after mechanical tests to observe the degree of dispersion of CNTs. The FT-IR (Fourier transform infrared spectroscopy) and XPS (X-ray photoemission spectroscopy) used in this work were performed using a FT-IR spectrometer from Jasco (FT/IR-4100) and a XPS spectrometer from Thermo VG Scientific (Sigma Probe). The Raman spectra were measured using a laser with an excitation wavelength of 514.5 nm at room temperature on ARAMIS (Horiba Jobin Yvon). For the thermogravimetric analysis (TGA) measurements, a TGA 92–18 device (Setaram) was utilized at temperatures from 50 to 1000 °C at a heating rate of 10 °C/min in air. Tensile properties were measured using a universal testing machine (INSTRON 8848 Microtester) according to ASTM D 638 with a crosshead speed of 0.75 mm/min at room temperature. The dog bone-shaped specimens with a length of 41.25 mm, and a width of 4.75 mm were used after the surfaces of the specimens were polished.

3. Results and discussion

3.1. Characterizations of functionalized CNTs

Fig. 1 shows a schematic illustration of the epoxy nanocomposite with PSS or PAS functionalized CNTs. Fig. 1(a) shows the mixture of PSS-CNT and the epoxy matrix. After a curing process, the PSS functionalized CNTs are homogenously mixed with epoxy monomers. The CNTs were conjugated with benzene rings in part of the polystyrene [22,23], but it was not possible to form bonds between the epoxy and the sulfonic groups (−SO3−). Then the PAS functionalized CNTs cannot have strong interactions with the epoxy matrix. In the case of PAS functionalization in Fig. 1(b), the CNTs and the benzene rings in the PAS also have π–π interactions, and strong chemical bonds formed between amine groups (−NH2) in the PAS and epoxide groups (−C−O−C−, ring shape) in the epoxy as ring-opening of epoxides by amine [24]. CNTs adhere heavily to themselves due to the strong van der Waals force between the CNTs caused by their large aspect ratio and their nanoscale size [25]. Thus, functionalization of the CNTs is important when CNTs are added to an epoxy matrix. The functionalization of CNTs can be identified by FT-IR analysis and XPS spectroscopy, as shown in Figs. 2 and 3.

The FT-IR spectra for the raw PSS and PAS, pristine CNTs, and CNTs functionalized by PSS and PAS are shown in Fig. 2. The FT-IR spectra of PSS show the presence of three major signals: 1007 cm−1, 1036 cm−1, and 1638 cm−1. The signals of 1007 cm−1 and 1036 cm−1 indicates the SO bond in PAS. The peak at 1036 cm−1 is assigned to the SO symmetrical stretching vibrations, and the peak at 1007 cm−1 is attributed to aromatic in-plane vibrations [26]. The signal of 1638 cm−1 indicates the CC bond in benzene rings. The spectra of PAS also showed the peak of the CC bond, as 1621 cm−1. The peaks at 1511 cm−1 and 3343 cm−1 indicate the N−H bond in PAS [27]. The pristine CNTs do not show any peaks corresponding to functional groups on the surface of the CNTs. However, after functionalization, peaks of the PSS-CNT at 1661 cm−1 (CC in benzene rings), 1008 cm−1, and 1056 cm−1 (SO in sulfonic groups) similar to PSS and of PAS-CNT at 1663 cm−1 (CC in benzene rings), 1507 cm−1, and 3418 cm−1 (N−H in amino groups) similar to PAS appear in the FT-IR results. These peaks come from benzene rings, sulfonic groups, and amino groups that are noncovalently functionalized on the CNTs by the ball milling process. These results prove the successful functionalization of PSS or PAS on CNTs.

The XPS narrow scan spectra of the PSS-CNT, PAS-CNT, and pristine CNT presented in Fig. 3 show that C and O elements appear in all CNTs, and only S on PSS-CNT and N on PAS-CNT samples. The C 1s peak region in the XPS spectra of the PSS-CNT, PAS-CNT, and pristine CNT (Fig. 3(a)) was deconvoluted to four peaks at around 284.0, 285.4, 286.6, 289.6–290.0 eV corresponding to CC, C−C, CO, and π−π* shake-up, respectively [28]. A main peak at 284.0 eV attributed to the sp2 graphitic structure [29] and a peak at 285.4 eV can be assigned to sp3-hybridized carbon atoms as in diamond-like carbon [30]. Moreover, a peak at 286.6 eV was attributed to defects on the all CNT structures [29]. Finally, the π−π* transition loss peak reveals interactions between each CNTs of pristine CNT or CNT and functional molecules in PSS-CNT and PAS-CNT [31].

In addition, chemical states of −SO3− groups were detected by S 2p spectrum of PSS-CNT in Fig. 3(b). The S 2p lines were fitted to a spin-split doublet, 2p3/2 and 2p1/2. Two peaks are located at 167.6 and 169.0 eV, respectively [32–34]. In PAS-CNT and pristine CNT, any peaks were not found. In contrast, the amine functionalization of PAS was further confirmed in the N 1s spectrum of PAS-CNT in Fig. 3(c),
where the binding energy peak at 399.0 eV is attributed to the formation of PAS linkage on the CNTs [35,36]. There are no peaks at PSS-CNT and pristine CNT, then they cannot be distinguished using the N 1s spectra.

The resolution O 1s spectra of PAS-CNT and pristine CNT can be fitted to two peaks in Fig. 3(d). The binding energies at 531.0 and 532.2 eV can be assigned to the O in the CO and alcoholic C–O groups, respectively [37]. Moreover, in PSS-CNT, a peak at 533.1 eV was additionally appeared that it can be assigned for the oxygen present in the –SO3− groups [33]. Consistent with FT-IR results, these XPS results confirm the conversion of functionalization of PSS and PAS on CNTs.

The resonance Raman spectra from 1000 to 2000 cm−1 are shown in Fig. 4 to investigate the amount of defects produced by noncovalent functionalization using the ball milling process. It can clearly be seen that the band around 1580 cm−1 in the spectra can be assigned to the tangential mode (G-band) and associated with the ordered sp2 hybridized carbon network. A disorder-induced D-band was observed at 1321 cm−1, which was related to local defects that originated from structural imperfections and is associated with the disordered sp3 hybridized carbon network [38]. The intensity ratio of the D-band (sp3)
to G-band (sp²) is related to the structure of the CNTs. If both bands have similar intensities, it indicates that a high quantity of structural defects exist on each of the CNTs. In this study, the D/G intensity ratios (I_D/I_G) of PAS-CNT (0.939) and PSS-CNT (0.920) were closer to pristine CNT (0.896) than acid treated CNT (0.981). That means that the amount of defects in PAS-CNT and PSS-CNT are less than for acid treated CNT. During the ball milling process, a small amount of defects occurred, but the PAS-CNT and PSS-CNT maintained a sp² carbon network better than the acid treated CNT did. Besides, the intensified D’-band appears as a shoulder peak of G-band on CNTs, implying the defects in the structure of CNTs [39].

TGA curves provide the evidence of successful noncovalent functionalization of CNTs. Fig. 5 presents a comparison of TGA curves of pristine CNTs, PSS, PSS-CNTs, PAS, and PAS-CNTs in air. Pristine CNTs showed high thermal stability and do not decompose up to 1000 °C. The PSS remained only 40 wt.% after TGA test (60 wt.% vanished), and PSS-CNT degraded about 31 wt.% (Fig. 5(a)). Then PSS remained ~50 wt.% in PSS-CNTs. In case of PAS, The PAS did not show any decomposition after 400 °C. On the other hand, the thermal degradation behavior of the PAS-CNTs was found to be qualitatively similar to the sum of melamine curve and CNT curve. The quantity of functionalized melamine is estimated to be ~33 wt.% (Fig. 5(b)). PSS and PAS were well attached at the wall of CNTs after functionalization [40,41].

The stable homogeneous dispersion of PSS-CNTs and PAS-CNTs in acetone and DMF co-solvent remained intact without any precipitation after 2 days (Fig. 6(b) and (c) inset), whereas pristine CNTs appeared to precipitate obviously in solution because of the low solubility of pristine CNTs in organic solvent (Fig. 6(a) inset). SEM images of spin-coated pristine CNTs, PSS-CNTs, and PAS-CNTs, dried on a Si wafer, are shown in Fig. 6(a), (b), and (c) respectively. The pristine CNTs remain highly bundled and agglomerated, while PSS-CNTs and PAS-CNTs showed quite uniform dispersion. These results demonstrate that the noncovalent functionalization of CNTs is an effective method for preventing agglomeration of CNTs. The PSS-CNTs and PAS-CNTs could be mixed uniformly with an epoxy matrix.

3.2. Mechanical properties of CNT/epoxy nanocomposites

Representative stress–strain curves for pure epoxy and pristine CNTs, PSS-CNTs, and PAS-CNTs nanocomposites are plotted in Fig. 7(a). Fig. 7(b) presents the values of the Young’s moduli (red bar) and ultimate tensile strengths (blue bar) of pure epoxy, pristine CNT/Epox, PSS-CNT/Epox, and PAS-CNT/Epox nanocomposites. For the
pure epoxy, the Young’s modulus, and ultimate tensile strength are 2.76 GPa and 61.51 MPa, respectively. The addition of PAS-CNTs enhanced the modulus and strength most effectively. At 1 wt.% PAS-CNTs, the Young’s modulus and ultimate tensile strength of the nanocomposites are 3.89 GPa and 82.57 MPa, corresponding to increases of 41% and 34%, respectively.

However, measurements of the mechanical properties of the pristine CNT/Epoxy nanocomposite show a very slight increase in Young’s modulus but a decrease in tensile strength. The modulus and tensile strength of PSS-CNTs/Epoxy nanocomposite were increased very little. The modulus increased from 2.76 GPa to 3.45 GPa (25%) and tensile strength was lightly enhanced from 61.51 MPa to 62.63 MPa (13%).

These results demonstrate that noncovalent functionalization of CNTs can enhance the reinforcement of CNT/Epoxy nanocomposites by improving the dispersion of CNTs. PSS and PAS molecules interact with CNTs via π–π interactions and inhibit the agglomeration of CNTs. In addition, when comparing the PSS-CNTs and PAS-CNTs nanocomposites, the reinforcing effect is very different depending on the types of functional molecules. The sulfonic groups (−SO₃) of the PSS molecule have no strong affinity to epoxy resin, as seen in Fig. 1(a), while the amino groups (−NH₂) within the PAS molecule provide strong interactions with the epoxy system through a chemical reaction (Fig. 1(b)). As a result, more effective load transfer in the epoxy matrix could be achieved with the PAS-CNT/Epoxy nanocomposites.

Fig. 7(c) and (d) shows strain–stress curves and the values of Young’s moduli and ultimate tensile strengths for various contents of PAS-CNT/Epoxy nanocomposites. When compared to pure epoxy, the moduli and strengths of all PAS-CNTs nanocomposites increased more than pristine CNT and PSS-CNTs. In Fig. 7(c), the curve of 1 wt.% PAS-CNT/Epoxy nanocomposite has the best steep slope within the range of 1% strain and the highest values of stress. It means that the modulus and ultimate tensile strength of 1 wt.% PAS-CNT/Epoxy nanocomposite was the greatest. When the CNTs contents were reduced to 0.5 wt.%, the reinforcing effect was less remarkable than with 1 wt.% PAS-CNTs nanocomposites. The Young’s modulus of 0.5 wt.% only increased 19% to 3.26 GPa and the tensile strength at that content was enhanced just 23% to 76.27 MPa. In addition, when greater than 1 wt.% PAS-CNTs were added to the epoxy, modulus and strength were reduced. When the contents of CNTs in the epoxy were highly increased, the resulting non-uniform dispersion of CNTs restricted the mobility of epoxy chains producing poor tensile properties. Although the CNTs were functionalized, at higher loading the CNTs could be agglomerated.
3.3. Microstructures of CNT/epoxy nanocomposites

The SEM images of fracture surfaces of the pure epoxy and epoxy nanocomposites after tensile tests are shown in Figs. 8 and 9. Fig. 8(b) shows that pristine CNTs are agglomerated in the epoxy matrix, which could be divided into two regions; a CNT-rich region and a CNT-poor region. The PSS-CNTs and PAS-CNTs seemed to be more homogeneously dispersed in the epoxy matrix (Fig. 8(c) and (d)). The functional groups prevented CNTs from agglomerating through π-π interactions.

In addition, PAS-CNTs embedded in the epoxy matrix were likely to have covalent bonds with epoxide groups in the epoxy matrix via the amino groups of the PAS, which provided strong interfacial interactions between the PAS-CNTs and the epoxy matrix. However, as the loading of the PAS-CNTs increased, PAS-CNTs agglomeration occurred due to degradation in their dispersion (Fig. 9(b), (c), and (d)). The frequency
of aggregated CNTs increased with higher CNTs content. Then, mechanical properties were reduced as the CNTs loading increased. The agglomeration of CNTs degraded the load transfer between CNTs reinforcements and the epoxy matrix and acted like defects in the CNT/Epoxy nanocomposites.

4. Conclusion

In summary, this study has demonstrated an approach to improve the mechanical properties of epoxy nanocomposites filled with noncovalently functionalized CNTs. The surfaces of CNTs were chemically modified by PSS or PAS to inhibit agglomeration, and the amino groups within the PAS provided strong interactions with the epoxide groups of the epoxy resin. The Young’s modulus and ultimate tensile strength of the epoxy nanocomposites using 1 wt.% PAS-CNTs were effectively increased to 3.89 GPa and 82.57 MPa (an increase of 41% and 34%), respectively, compared with the pure epoxy. The significantly improved mechanical properties are attributed to effective CNTs dispersion in the epoxy matrix, as well as enhancement of the interfacial interaction between PAS and the epoxy.

Acknowledgements

This work was supported by a grant (Code no. 2013M3A6A5073173) from the Center for Advanced Soft Electronics under the Global Frontier Research Program of the Ministry of Science, ICT & Future Planning, Korea.

References


