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Robust, Conducting and Transparent Polymer Composites using Surface-modified and Individualized Double Walled Carbon Nanotubes **

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Single-walled carbon nanotubes (SWNTs) have been examined as multi-functional filler in polymer matrices due to their outstanding electronic, optical, thermal and mechanical properties [1]. Since SWNTs are intrinsically bundled due to the high van der Waals forces of attraction between adjacent tubes, various methods have been used to disperse the bundles into isolated tubes so that they could be used in the fabrication of polymer composites. These methods include: mechanical mixing [2], chemical functionalization of the tubes [3-5] and utilization of organic [6,7] and polymeric surfactants [8] via the noncovalent interactions. However, chemically modified SWNTs exhibited altered (depressed) electronic and optical properties caused by the introduction of chemical moieties on the sidewall [9], while tubes noncovalently dispersed in aromatic polymers are expected to experience low stress transfer between tubes and polymers. In order to fully exploit the intrinsic properties of carbon nanotubes in polymers, two critical issues (i.e., isolation and good bonding nature between the

filler and the matrix) should be targeted simultaneously. Here we demonstrate that double walled carbon nanotubes (DWNTs) [10,11], consisting of two coaxial concentric tubes, could be considered as the preferable reinforcing filler in polymer matrices; they possess mechanical properties, structural and thermal stability which are superior to SWNTs [12]. Furthermore, chemical moieties which are selectively introduced on the outer tubes [13] provide effective anchoring sites for strong bonding with polymers, while the optical properties of the inner tube of the DWNTs remain unchanged. It is noteworthy that the chemical moieties introduced on the sidewalls of the DWNTs strongly affect the individualized species of DWNTs in dimethylformamide (DMF). Furthermore, we demonstrate that DWNTs which have been individually dispersed in polyimide prepared by combining the chemical modification of the tubes and an in-situ polymerization process contributed to the largely enhanced mechanical, thermal and electrical properties of polyimide composites while sustaining their transparency.

In this study, we have used highly pure and crystalline DWNTs having the inner and outer diameters of ca. 0.9 and 1.6 nm [10], prepared by the catalytic chemical vapor deposition and a subsequent purification process. In order to improve dispersability of the DWNTs and activate the surface sites, we have selectively introduced three types of chemical moieties (carboxylic, benzylicisocyanate and phenylisocyanate groups) on the sidewall of the DWNT [14]. To understand the effects of the dispersion quality of DWNTs within the polyimide, non-isolated and isolated DWNT solutions in DMF were prepared under strong sonication and centrifuge (**Fig. S1 (a)**). Finally, *in-situ* polymerized polyimide films (**Fig. S1 (b)**) were evaluated in terms of their mechanical and thermal properties as well as electrical conductivity ([see detailed experimental](#)).

Low-frequency Raman spectra of pristine and chemically functionalized DWNTs were measured in order to observe the changes in the radial breathing mode (RBM) (**Fig. 1 (a)**). Even though there was no significant change for the peaks at ca. 270 and 324 cm^{-1} , which correspond to the inner tubes, the RBM frequencies below 220 cm^{-1} originating from the outer tubes of DWNTs are clearly depressed for chemically modified DWNTs since the chemical moieties covalently bonded to the carbon atoms of the nanotube selectively modify the van Hove singularities of the outer tubes [9]. In the case of DWNTs with carboxyl groups, the intermolecular hydrogen bonds between adjacent tubes cause the upshift of the RBM (associated with the outer tube) because no distinctive change was observed in the size of bundle (ca. 50 nm) between the pristine and the carboxyl groups-introduced DWNTs (**Fig. 1 (b, c)**). On the other hand, the phenylisocyanate and benzylisocyanate groups on the sidewall of the DWNT give rise to strong π - π interaction between adjacent tubes, and result in the formation of large bundles with sizes ranging from 60 to 80 nm in diameter (**Fig. 1 (d, e)**). However, the absence of changes in the RBM frequency for the large bundled DWNT sample suggests the loosely packed nanotubes (or weak intertube interaction) within the bundle due to the presence of long chemical moieties.

We have examined, using optical spectroscopy [15], the dispersability of pure and chemically modified DWNTs in DMF. The weak and flat absorption spectrum of the pure DWNTs is reflected by its low dispersability due to its intrinsic hydrophobic nature, while the chemical modification clearly improved the dispersion status of DWNTs in DMF (**Fig. 2 (a)**). Moreover, the phenylisocyanate and benzylisocyanate groups-decorated DWNTs exhibited the well-resolved sharp absorption peaks due to their excitonic transitions between van Hove singularities, thus indicating that they are individually dispersed in DMF. The absorption peaks located at 500-800 nm could be assigned to the E_{22}^S of the inner tubes while the absorption peaks between 900 and 1300 nm correspond to the E_{22}^S of the outer tubes. For

comparison, the bundled or non-isolated DWNTs exhibited broad and weak absorption spectra due to the superposition of electronic transitions (**Fig. S2**) [15]. In order to identify the individualized DWNTs in DMF, we have obtained photoluminescence (PL) maps of the carboxyl- and phenylisocyanate-attached DWNT solutions (**Fig. 2 (b, c)**). The carboxyl group-decorated DWNT solution exhibited strong PL peaks, which are assigned to the inner tubes with chiralities $(10,2)$, $(8,3)$, $(7,5)$ and $(6,5)$. After attaching phenylisocyanate groups, the individualized species were changed to the large sized tubes having the inner tubes with chiralities $(10,2)$, $(9,4)$ and $(8,6)$. This result strongly indicates the possibility for the diameter-dependent separation of DWNTs by varying the chemical moieties on their outer tubes.

Regarding in-situ polymerized DWNTs- (ca. 0.1 wt %) reinforced polyimide in a form of film (ca. 1.51 μm), we have carried out systematic analysis on the DWNT-reinforced polyimide films in order to understand the influence of chemical moieties on the sidewall as well as the degree of dispersion of the DWNTs. Individually dispersed DWNTs do not perturb transparency while the non-isolated tubes are randomly aggregated and thus deteriorate the visual appearance of the polyimide film (**Fig. 3 (a-c)**). As shown in **Table 1** and **Fig. 3 (d)**, the chemically modified and isolated DWNTs lead to the increased modulus, tensile strength, elongation-at-break of polyimide nanocomposites. Among these, phenylisocyanate groups on the DWNTs contribute to the largest enhancement in the modulus and the tensile strengths from 933 and 109 to 1644 and 156 MPa, as well as the doubled elongation-at-break. This is due to the presence of individually dispersed DWNTs within the polyimide and the ensured strong bonding strength between tubes and polyimide. More specifically, long chemical moieties containing benzene rings attached on the outer tubes of the DWNTs impart the ability to loosen and eventually individualize bundled tubes in DMF and then provide the strong interactions with the polyimide backbone via π - π interactions. As additional effects of

individually reinforced DWNTs in polyimide, we observed the improved thermal stability and electrical conductivity (**Fig. S4 and Table 1**).

In summary, we have presented a novel route to the fabrication of polyimide composite film reinforced with individually dispersed DWNTs based on the introduction of chemical moieties of the outer tubes combined with an in-situ polymerization. It has been demonstrated that individually reinforced DWNTs make the polyimide stronger and more ductile without any deterioration of transparency. In addition, we suggested the possibility of the diameter-dependent separation of DWNTs by changing the chemical moieties introduced on the outer tubes of the DWNTs. It is envisaged that our developed DWNTs-reinforced polyimide composites will find uses in electronic devices, transparent conducting film and complex aerospace parts.

Experimental

Synthesis and functionalization of DWNTs:

The synthesis of DWNTs was carried out by a catalytic chemical vapor deposition method utilizing a conditioning catalyst (Mo/Al₂O₃) at one end of the furnace, and the nanotube catalyst (Fe/MgO) in the middle part of the furnace. The highly pure and crystalline DWNTs were successfully prepared and the subsequent oxidative purification process. The high-purity of DWNTs (20 mg) were treated in a mixture of HNO₃ (70%, 10 ml) at 50 °C for 12 h to increase the amount of carboxylic acids. After being dispersed in N,N'-dimethylformamide (DMF, 40 ml) under stirring, the acid-treated DWNTs (DWNT-COOH) were reacted with benzyl isocyanate and phenyl isocyanate in a dry argon atmosphere at 50 °C for 24 h.

After being dispersed in DMF under stirring, three samples having different dispersion states were prepared by controlling sonication and ultracentrifugation parameters. The pristine and chemically functionalized DWNTs (2 mg) were dispersed in 100 ml under strong

ultrasonication (US-300T, NIHONSEIKI KAISHA LTD.). We designated this tube solution as non-isolated DWNT solution because dispersed tubes in DMF consist of isolated and bundled tubes. Subsequently, the sonicated solutions were subjected to ultracentrifuge (Optima MAX-XP, Beckman Coulter, 9,000 g, 5 °C) for 1 hr in order to prepare completely isolated tubes in DMF (isolated DWNT solution). **Fig. S1 (a)** describes the schematic method to prepare non-isolated and isolated DWNT solutions. Finally, isolated DWNT solutions were condensed to have same concentration of tubes (ca. 2 mg of tubes in DMF) to non-isolated DWNT solution.

In-situ polymerization nanocomposites of polyimide (polyamic acid) with chemically modified DWNTs:

The precursor for polyimide (polyamic acid (PAA)) was synthesized using pyromellitic dihydride (PMDA) and 4,4'-oxydianiline (ODA) as starting materials. First, the ODA 1.156 g (0.530×10^{-2} mol) was completely dissolved into a three-neck flask containing of DMF (100 ml) and DWNTs (2 mg) in nitrogen at room temperature and stirred for 12 h. PMDA 1.061 g (0.530×10^{-2} mol) was added into the ODA/DWNTs solution to prepare PAA/DWNTs composites. The PAA/DWNTs films were obtained by solution cast method, and the residual solvent was completely removed using vacuum dryer at 50 °C for 3 days. Then PAA/DWNTs films were cured at 100 °C in vacuum for 1 h to form DWNTs-reinforced polyimide films having a thickness of ca. 0.51 μm and 0.1 wt % of DWNT with regard to polyimide. A schematic description for in-situ polymerization procedure is shown in **Fig. S1 (b)**.

Structural characterizations:

The Fourier transform infrared (FT-IR) spectroscopic measurements were performed to identify a structure of PAA, PI synthesized and functionalized DWNTs using IR Prestige-21

(Shimadzu) equipped with attenuated total reflectance. Raman, absorption spectra and photoluminescence map were obtained using Kaiser HoloLab5000 system (532 laser line), UV-VIS-NIR spectrophotometer (Shimadzu soildspec-3700) and Shimadzu NIR-PL system. The macro-morphology of chemically functionalized DWNTs was observed using a field emission scanning microscopy (FE-SEM) (JSM6335Fs). We also carried out thermogravimetric analysis (Shimadzu DTG-60/60). The samples were scanned from 0 to 900 °C with the heating rate of 2 °C/min in argon. Electrical conductivity measurement was carried out using the 1M6ex ZAHNER electric analyzer. A standard four probe method was used to measure the electrical conductivity for all of the composites films at ambient conditions of 25 °C. Mechanical properties of the specimens were evaluated at room temperature according to ASTM D638 test method using tensile tester (UTM LR50K; JJ Lloyd, Centre for Materials Research, University of London, London, UK) for a dog-bone type dumb-bell specimen. The dimensions of the specimens were 60 (length) × 10 (width) × 10 (narrow portion length) × 3 (narrow portion width) × 0.50 (thickness) mm. We have used the following measurement conditions: gauge length = 25 mm; crosshead speed = 10 mm/min; load cell = 2.5 kN. At least three samples were tested and the average was used.

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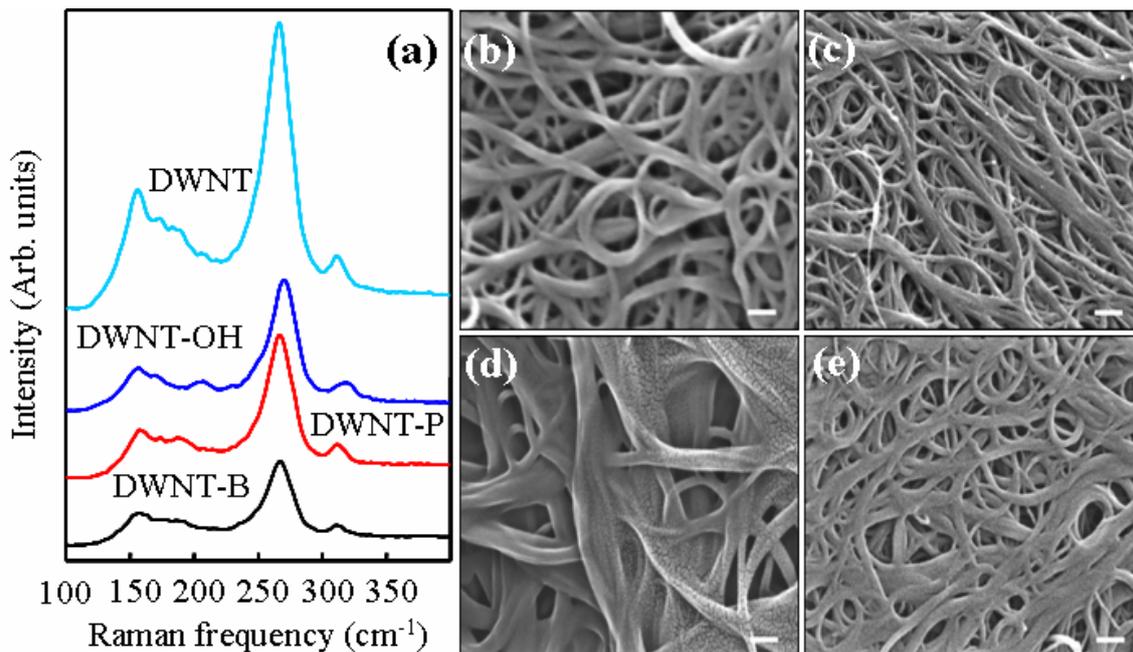


Figure 1. (a) Low frequency Raman spectra of pristine and chemically modified DWNTs (excitation laser = 532 nm), and FE-SEM images of pristine (b), chemically modified DWNTs having carboxyl acid (c), phenylisocyanate group (d), and benzylisocyanate group (e). Scale bars: (b-e), 100 nm.

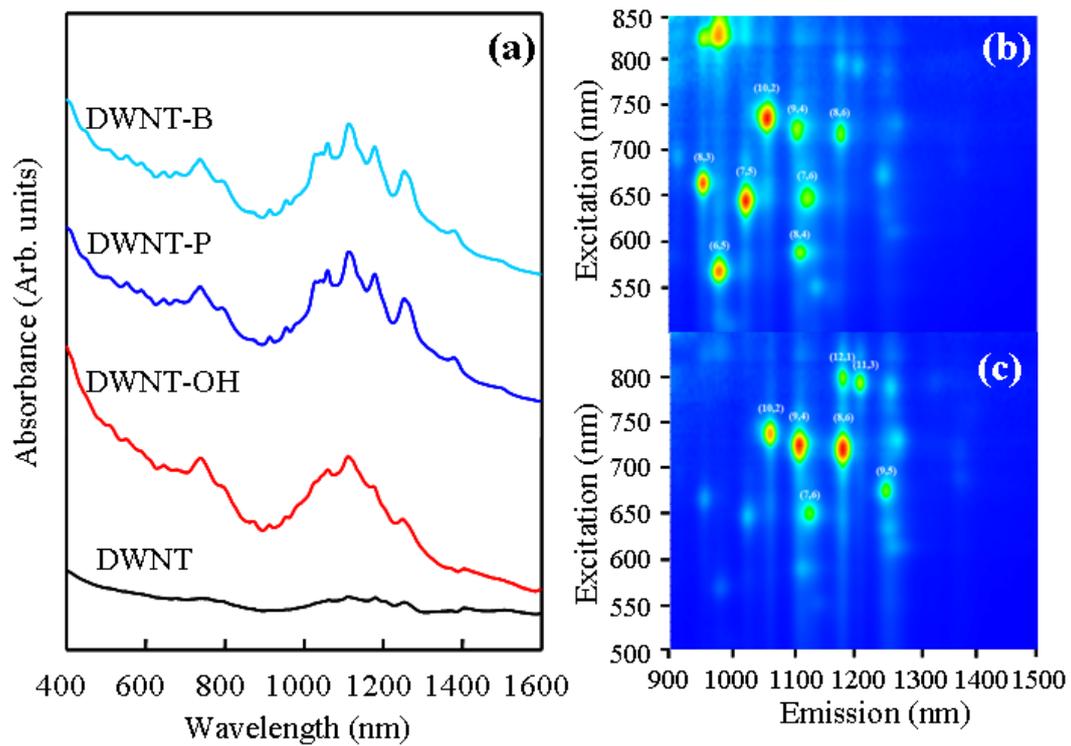


Figure 2. (a) UV-vis absorption spectra of pure and chemically modified DWNTs, Photoluminescence maps of DWNTs having carboxyl group (b) and phenylisocyanate group (c).

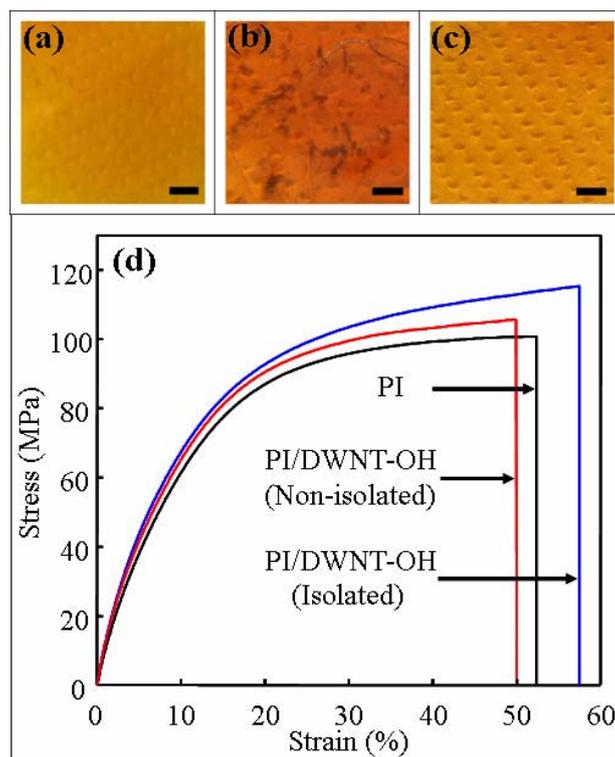


Figure 3. Visual appearances of pure polyimide (a), non-isolated DWNTs/polyimide (b) and isolated DWNTs/polyimide (c) films; note that film transparency strongly depend on dispersion quality. (d) Typical stress-strain curves of pure polyimide and chemically modified DWNTs-reinforced polyimide films. Scale bars: (a-c), 1 cm.

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Here we propose double walled carbon nanotubes, consisting of two concentric coaxial tubes, as the preferable reinforcing filler in polymers. Chemical moieties which are selectively introduced on the outer tubes impart the ability to individualize and provide effective anchoring sites for strong bonding with polymers, while the optical properties of the inner tubes of the double walled carbon nanotubes remain unchanged.

Keyword (Carbon Nanotubes, Nanostructures, Polymer composites)

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