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Kevlar Functionalized Carbon Nanotubes for Next-Generation Composites

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We report a sequential functionalization methodology for the covalent modification of multi-walled carbon nanotubes (MWNTs) with one and a half repeat units of the polymer poly-*p*-phenyleneterephthalamide (PPTA), Kevlar. Covalent attachment of PPTA monomer units, *p*-phenylenediamine (PDA) and terephthaloyl chloride (TPC), to the surface of MWNTs results in PPTA oligomer units forming an organic sheath around the nanotubes, PPTA-functionalized-MWNTs (PPTA-MWNTs). PPTA-MWNTs possess chemical functionality identical to that of PPTA, and thus provide nanoscale scaffolds which may be readily dispersed within a monomer solution and participate in the polymerization reaction to form a PPTA-MWNT/PPTA composite. We show that formation of PPTA in the presence of PPTA-MWNTs leads to a uniform dispersion of MWNTs within the polymer matrix, in contrast to aggregated masses of MWNTs in the case of pristine-MWNTs. The covalent attachment of oligomeric PPTA units to the surface of MWNTs represents the formation of a functional nanoscale building block which can be readily dispersed and integrated within the polymer PPTA to form a novel composite material. The implications of tuning the surface chemistries of carbon nanotubes (CNTs) to the chemistry of host polymer matrices are considered.

Introduction

Recent years have witnessed a multitude of reports demonstrating the advantages of using carbon nanotubes (CNTs) as 1D fillers in polymer composites.^{1–3} Many of these reports have documented remarkable advances in the formation of hybrid materials which exhibit extreme high modulus and strength values far exceeding those of conventional high performance materials.^{4–6} New synthetic methodologies for nanotube production now allow the preparation of ultrahigh aspect-ratio nanotubes which may be impregnated within polymer matrices to yield novel composites.^{7,8} Consequently, the paradigm shift in material properties promised by research involving

nanoscale structures is slowly becoming a realization.^{9–11} Some nanotube-based advances have utilized developments in the physical properties of carbon nanotubes, such as increases in length, control over diameter, and the ability to prepare precisely controlled arrays of free-standing nanotubes on a range of substrates.^{9,12,13} In parallel with this, progress has been made in the chemical functionalization of carbon nanotubes and their successful integration within polymer matrices to yield significantly improved composite materials.^{14–16}

Although much has been achieved, the issue of successfully integrating nanotubes within polymers at volume fractions whereby the efficiency of stress transfer between the tubes and the polymer matrix is optimized remains at large. Resolving this issue by combining optimized physical properties with precisely controlled chemical functionality would be expected to yield even further improvement in mechanical properties in such composites,

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whereas greater interfacial interaction would be expected to facilitate significantly improved electronic and thermal management characteristics of such materials.¹⁶ Toward this end, discrete molecules, polymerization initiators, and polymers have been grafted to and from the surface of carbon nanotubes.^{17–20} However, relatively few reports exist concerning the tailored grafting of short-chain analogues of the host polymer matrix to the surface of nanotubes. In this approach, nanotubes are specifically functionalized to adopt the chemical properties identical to those of the polymer, and furthermore, to allow surface bound reactive chemical groups to facilitate the nature of the interaction between tubes and matrix or substrate. In particular, CNTs functionalized specifically with chemistries identical to their intended host matrix of a composite are of interest.

One class of polymer that has commercial significance for the preparation of ultrahigh strength materials is poly aramids. Most notably, the poly aramid poly-*p*-phenylene terephthalamide (PPTA), Kevlar, has attracted interest in recent years concerning its integration with carbon nanotubes because of the extreme physical properties of both materials. Recent reports have described the physical combination of these materials to form composites.^{21,22} Unfortunately, such primitive physical mixing, although simple, has its drawbacks. It is well-known that basic physical integration of nanotubes and polymers allows formation of aggregates, which act as defect sites within polymers and may result in slippage between the materials. Highly desirable would therefore be the ability to structurally and chemically integrate and bind materials such as Kevlar and nanotubes together. We here report the successful achievement of this goal. Multi-walled carbon nanotubes (MWNTs) have been functionalized sequentially with PPTA monomer units to yield PPTA-functionalized MWNTs, allowing for not just a physical mixture of CNTs and Kevlar, but a structurally and chemically optimized multicomponent system suitable for next-generation composites (Figure 1).

The synthesis of PPTA resulting from the polycondensation of terephthaloyl chloride (TPC) and *p*-phenylenediamine (PDA) has been an established procedure since the early 1960s.²³ In the present study, multiwalled carbon nanotubes (MWNTs) were covalently functionalized by attaching alternating monomer units PDA and TPC to result in nanotubes surface functionalized with one and a half repeat units of the polymer PPTA, thus

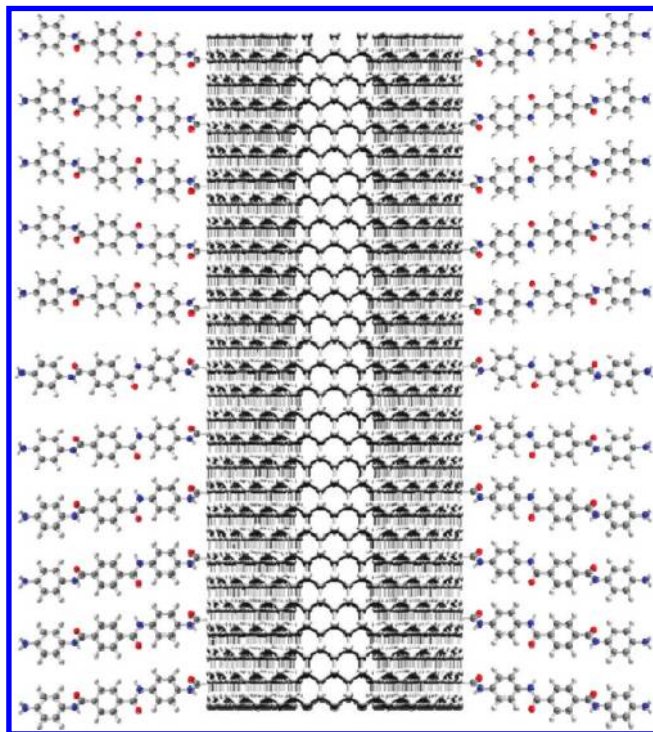


Figure 1. PPTA-functionalized MWNTs.

PPTA-oligomer-functionalized MWNTs. This step-by-step functionalization procedure represents a systematic methodology whereby a novel hybrid material is created that possesses chemical functionality identical to PPTA. It is postulated that such oligomers at the surface of the nanotubes facilitate interaction with a host polymer matrix via terminal amine functional groups and also via the tangential hydrogen bonding interactions and π – π interactions on account of the aramid functionality. To test this hypothesis, PPTA-MWNTs/PPTA and pristine-MWNTs/PPTA composites were prepared and characterized.

Experimental Section

MWNTs used in this study were arc-discharge produced, and were supplied by MER Corporation, Tucson, AZ. Terephthaloyl chloride was purchased from Fluka and was purified by exposure to thionyl chloride and recrystallized from hexanes prior to use. *N*-Methylpyrrolidinone (NMP) purum., absolute, over molecular sieves ($\text{H}_2\text{O} \leq 0.01\%$), $\geq 98\%$ (GC) was purchased from Sigma Aldrich and purified by vacuum distillation after drying over calcium hydride. Water (dd- H_2O) used for purification of oxidized MWNTs was deionized using a NANOpure purification system (Barnstead, USA). FT-IR spectra were recorded with a Nicolet 6700 using a Smart Orbit ATR accessory (Si Crystal). Raman spectra were recorded with a Renishaw inVia Raman Microscope using 633 and 534.5 nm excitation sources. Scanning electron microscopy (SEM) was conducted with a FEI Sirion XL30 scanning electron microscope (SEM). Palladium metal was evaporated onto composite samples to a thickness of approximately 10–15 nm to assist in the imaging of nonconductive regions by SEM. Samples for SEM analysis were prepared by dispersion of composite material in CH_2Cl_2 and the evaporation of a drop onto a piece of silicon wafer substrate. Transmission electron microscopy

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(TEM) was conducted with a JEOL 2010 Transmission electron microscope. Preparation of samples for TEM involved the deposition of a drop of a nanotube dispersion (DMF) onto a 2000 square mesh copper TEM grid, followed by several drops of to allowing wicking of the solvent and evaporation to dryness. Sonication was conducted using a Cole-Palmer Ultrasonic Bath 8890. All other chemicals and reagents were purchased from Sigma Aldrich and used as received. Schlenk apparatus used in this work was operated in conjunction with dry N_2 , at 4×10^{-3} Torr.

Preparation of PPTA-Functionalized MWNTs. Briefly, PPTA-functionalized MWNTs were prepared via the covalent attachment of PDA molecules to acid chloride functional groups at the surface of the MWNTs. Acid chloride functionalized MWNTs were prepared by the introduction of carboxylic acid functional groups at the surface of the MWNTs using established strong acid oxidative treatment^{24–28} and the subsequent conversion of the acid groups to acid chloride groups.²⁹ PDA monomer units were covalently bound to the acid chloride-MWNTs via amide formation. This was followed by a further covalent coupling of TPC monomer units and a final PDA coupling to the TPC groups to yield one and a half repeat units of PPTA at the surface of the MWNTs in a PDA-TPC-PDA-MWNT configuration, thus PPTA-MWNTs.

Preparation of Carboxylic-Acid-Functionalized MWNTs (COOH-MWNTs). MWNTs (0.5 g) were added to concentrated nitric acid (70%, 500 mL) and sonicated for 15 min to ensure adequate dispersion of the material. The nanotube suspension was refluxed at 130 °C for 24 h. The suspension of MWNTs was allowed to cool and was then filtered using a membrane filtration apparatus (Kimble, 90 mm) in conjunction with a Teflon filter (Millipore, Omnipore, 0.2 μ m), and washed thoroughly with water (DI)(3 L). The MWNTs were then dispersed into water (DI)(500 mL), to which $KMnO_4$ (1.50 g, 9.50×10^{-3} mol) was added under vigorous stirring. The suspension was cooled to 5 °C, and was acidified by the dropwise addition of $HClO_4$ (70%, 500 mL). Cooling was removed and the suspension allowed reach room temperature. An excess of citric acid-monohydrate (31 g, 0.148 mol) was added to the stirring suspension in order to quench the $KMnO_4$, this was evidenced by the color change of the suspension from a dark purple to a clear suspension of the MWNTs. The MWNTs were filtered as before, and washed thoroughly with water (DI)(10 L).

Preparation of Acid-Chloride-Functionalized MWNTs (COCl-MWNTs). COOH-MWNTs (0.100 g) were dried using a Schlenk line (24 h). Thionyl chloride (200 mL, 2.74 mol) was added to the dry COOH-MWNTs and sonicated (15 min) to allow complete dispersion of the COOH-MWNTs in the $SOCl_2$. The suspension was heated to 70 °C under N_2 with magnetic stirring for 24 h to allow conversion of the carboxylic acid to acid chloride groups. $SOCl_2$ and associated byproduct were removed by rotary evaporation followed by Schlenk drying (6 h).

Preparation of *p*-Phenylenediamine-Functionalized MWNTs (PDA-MWNTs). A solution of *p*-phenylenediamine(PDA)(0.50 g,

4.62×10^{-3} mol) in NMP(anhydrous) (200 mL) was added to COCl-MWNTs (0.100 g), prepared as described above. The solution was sonicated (15 min) to allow the complete dispersion of COCl-MWNTs in the PDA solution. The suspension was heated to 50 °C to promote optimum dispersion and exfoliation of the COCl-MWNTs within the solution and to promote the coupling of PDA at the surface of the COCl-MWNTs via amide formation. The appearance of the suspended material at this stage resembled a rich black oil-like material, giving preliminary indication to a favorable dispersion and reaction of the COCl-MWNTs in the suspension. The suspension was allowed stir for 12 h, throughout which intermittent sonication (5 min at 2 h intervals) was performed in order to ensure optimum dispersion of materials. PDA-MWNTs were then recovered by filtration (as described above) and were washed thoroughly with NMP (500 mL), ethanol (500 mL), and methanol (500 mL) to ensure complete removal of excess PDA.

Modification of PDA-MWNTs with Terephthaloyl Chloride (TPC) to form TPC-PDA-MWNTs. A solution of TPC (0.938 g, 4.62×10^{-3} mol) in NMP(anhydrous) was added to PDA-MWNTs (0.100 g) which had been dried using a Schlenk line (6 h). The PDA-MWNTs were sonicated (15 min) into suspension, and the material heated to 50 °C under magnetic stirring for 12 h to facilitate the covalent coupling of TPC to PDA-amino groups at the surface of the PDA-MWNTs (intermittent sonication, 5 min, every 2 h). The physical appearance of the suspension remained consistent with the previous step, i.e., a rich black suspension resembling an oil-like substance. The TPC-PDA-MWNT material was filtered (as described above) and was thoroughly washed with NMP(anhydrous)(1.5 L) to allow removal of unreacted TPC. The TPC-PDA-MWNTs were immediately transferred to a round-bottomed flask by sonicating the material off the Teflon filter membrane using NMP (30 mL).

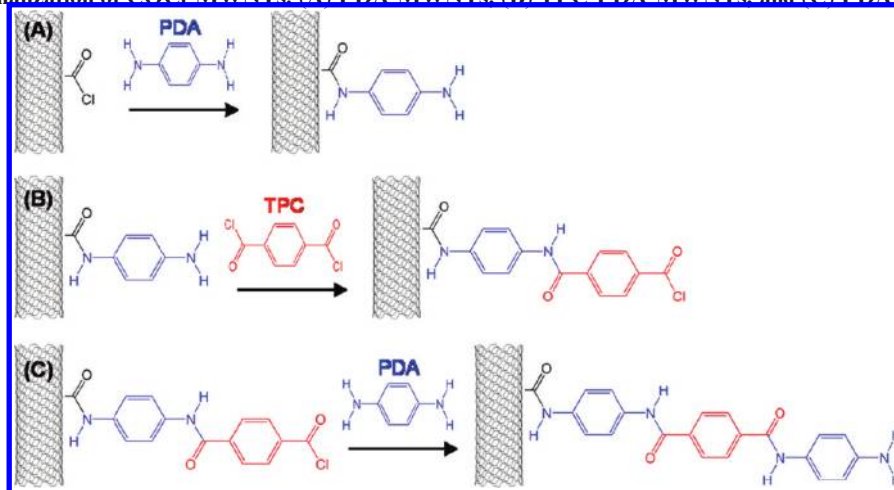
Modification of TPC-PDA-MWNTs with PDA to form PDA-TPC-PDA-MWNTs. A solution of PDA (0.50 g, 4.62×10^{-3} mol) in NMP(anhydrous) (200 mL) was added to TPC-PDA-MWNTs (0.100 g), prepared as described above. The material was sonicated (10 min) to ensure adequate dispersion of the MWNTs and resembled a rich black suspension as before. The suspension was heated to 50 °C and allowed to stir for 12 h, with intermittent sonication (5 min, every 2 h). The PDA-TPC-PDA-MWNTs were filtered and washed with NMP (500 mL), ethanol (500 mL), and methanol (500 mL) to ensure complete removal of excess PDA. As material which has been allow to form a cake on top of a filter membrane has the potential to trap unreacted materials, the material was redispersed in methanol (1 L) and filtered once more followed by washing with methanol (1 L). PDA-TPC-PDA-MWNTs were recovered from the filter and dried on a Schlenk line (6 h) before use.

Preparation of PPTA/MWNT and PPTA/PPTA-MWNT Composites. The polycondensation between TPC and PDA to form PPTA, was based on published experimental details and was carried out in the presence of MWNTs to result in 1 wt % MWNT-impregnated PPTA composites.^{23,30} For comparative purposes, composites of PPTA with pristine as-received MWNTs (p-MWNTs), denoted PPTA/p-MWNTs, and PPTA with PDA-TPC-PDA-MWNTs (PPTA-MWNTs), denoted PPTA/PPTA-MWNTs, were prepared. Briefly, *p*-phenylenediamine (PDA)(5.28 g, 4.88×10^{-2} mol) was dissolved in NMP (50 mL), and the solution cooled to 3 °C under magnetic stirring. MWNTs (either p-MWNTs or PPTA-MWNTs, 0.100 g) were

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Scheme 1. Functionalization of COCl-MWNTs: (A) PDA-MWNTs, (B) TPC-PDA-MWNTs, and (C) PDA-TPC-PDA-MWNTs



added to the stirring solution and sonicated (10 min) to ensure dispersion of the material. A solution of TPC (9.92 g, 4.88×10^{-2} mol) in NMP was added to the stirring MWNTs/PDA solution. This resulted in the immediate formation of the polymer PPTA, evidenced by the formation of a pastelike opaque yellow-green material. The material was filtered using membrane filtration equipment, and was washed by NMP (500 mL) and methanol (500 mL) to ensure removal of the reaction byproduct, HCl. The resultant material was vacuum-dried using Schlenk apparatus (6 h) and yielded ca. ~ 10.2 g of MWNT-impregnated-PPTA.

Results

The preparation of PPTA-functionalized-MWNT was achieved by the sequential covalent attachment of PPTA monomers, PDA, and TPC to the surface of acid chloride-functionalized MWNTs, as depicted in Scheme 1. The oxidation of MWNTs to introduce surface bound functional groups using strong acid is a well-established methodology.^{24–28} This solution-based oxidative procedure with MWNTs is particularly attractive as it is readily scalable and results in reproducible surface functionalization of nanotubes. Contrary to popular belief, this procedure can be tuned to yield negligible damage to the nanotubes, by using carefully controlled reaction conditions together with an appropriate choice of nanotube. Indeed, typical commercial arc-grown MWNTs such as those used in this study commonly have over 20 walls so that even if harsh oxidative treatment were to alter the structure of an outer wall, the effect on the total MWNT integrity is negligible.

In view of this, here we employ strong acid oxidation treatment which is known to introduce carboxy, hydroxyl and carbonyl groups at the surface of MWNTs in the approximate ratio 4:2:1, respectively.²⁷ Consequently, we also perform a second oxidative treatment using acidified potassium permanganate in order to oxidize hydroxyl and carbonyl groups to carboxylic acid that can be employed for covalent coupling chemistry.²⁸ The structural integrity of the MWNTs was characterized using TEM following acid oxidation and was found to remain intact (Figure 2a), whereas Raman spectroscopy was also

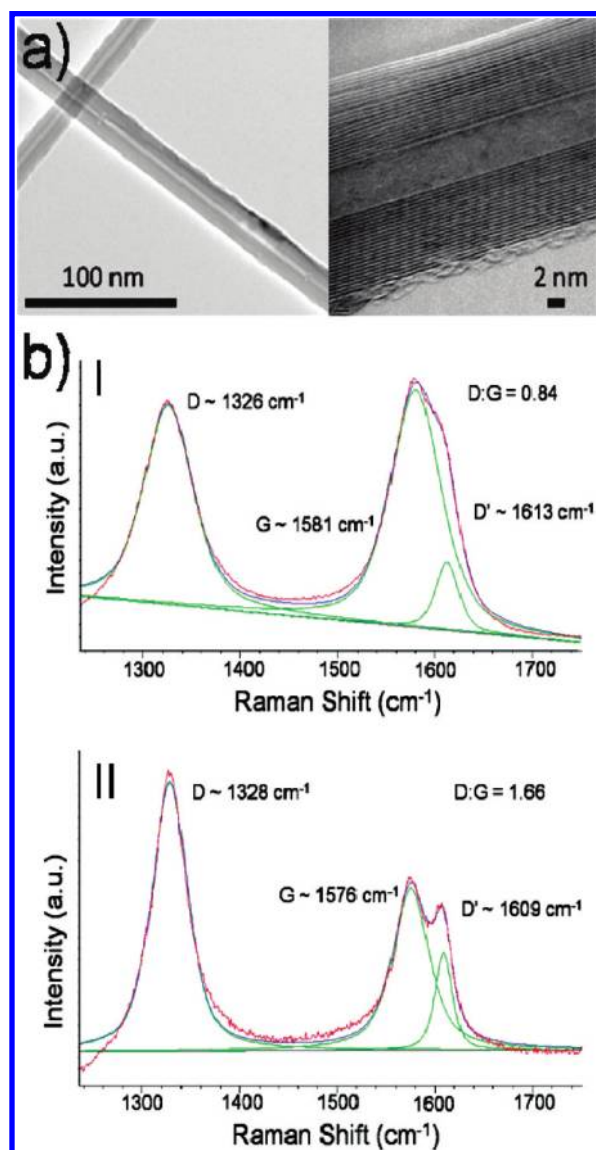


Figure 2. (a) TEM images of representative MWNTs following acid oxidation procedure. (b) Raman spectra of (I) pristine-MWNTs and (II) PDA-TPC-PDA-MWNTs.

performed to characterize the MWNTs following oxidative treatment (Figure 2b). TEM of MWNTs following

the oxidative treatment shows that the overall structural integrity of the nanotubes is intact (Figure 2a). The overall multiwalled structure of the nanotubes was unaffected by the acid oxidation. It is speculated that only several outermost walls may become substantially oxidized at defect sites, dislocations and regions of strain in the nanotube lattice. From the TEM imaging, it is clearly seen that underlying walls appear completely unaffected, and thus importantly retain the intrinsic mechanical properties of the nanotube.

Raman spectroscopy of both pristine-MWNTs (p-MWNTs) and carboxy-MWNTs (COOH-MWNTs) indicated a significant difference between the MWNTs ($\lambda = 633$ nm). The spectrum of p-MWNTs shows a characteristic tangential-mode G peak at 1581 cm^{-1} , a D' shoulder at 1613 cm^{-1} , and a disorder D peak at 1326 cm^{-1} (Figure 2b, I). The spectrum of the COOH-MWNTs shows the tangential mode G peak, now at 1576 cm^{-1} has significantly decreased in intensity relative to the disorder peak D at 1328 cm^{-1} (Figure 2b, II). The D' peak at 1609 cm^{-1} has increased in intensity, which is known to indicate disorder in nanotubes,³¹ and is comparable in size to the G peak. The $I_{\text{D}}/I_{\text{G}}$ ratio increases upon functionalization from 0.84 to 1.66 indicating an extensive increase in the number of defects in the nanotubes. Such changes are of course fully expected. It is particularly gratifying that spectroscopic evidence together with the TEM data of Figure 1, indicates beneficial modification of the MWNTs surface following oxidation, and that, despite this, the nanotube core remains structurally intact. In view of the present study and the aim to extensively functionalize the surface of the MWNTs, for our purposes this experimental procedure was deemed optimal. Following oxidative treatment, carboxy-functionalized MWNTs (COOH-MWNTs) were converted to the corresponding acid chloride-MWNTs (COCl-MWNTs) to allow efficient, catalyst-free, amide formation in organic solvents.²⁹ PDA was coupled to the surface of the COCl-MWNTs via amide formation to yield PDA-MWNTs, as shown in Scheme 1a. Subsequent coupling of TPC to PDA-MWNTs using identical methodology was performed to yield TPC-PDA-MWNTs, Scheme 1b. Finally, PDA was coupled to acid chloride groups at the terminal positions of the TPC-PDA-MWNTs to yield PDA-TPC-PDA-MWNTs, Scheme 1c. Thus, PDA-TPC-PDA-MWNTs, hereafter referred to in general terms as PPTA-MWNTs, represent a hybrid material of PPTA oligomer units covalently bound to the surface of the MWNTs.

The functionalization of COCl-MWNTs with PDA and TPC molecules was characterized by FT-IR spectroscopy (Figure 3). Relative to the comparatively featureless spectrum of pristine MWNTs (p-MWNTs) (Figure 3a), the spectrum of PDA-MWNTs exhibits clear indication of the covalent coupling of PDA molecules to the surface bound acid chloride groups of the

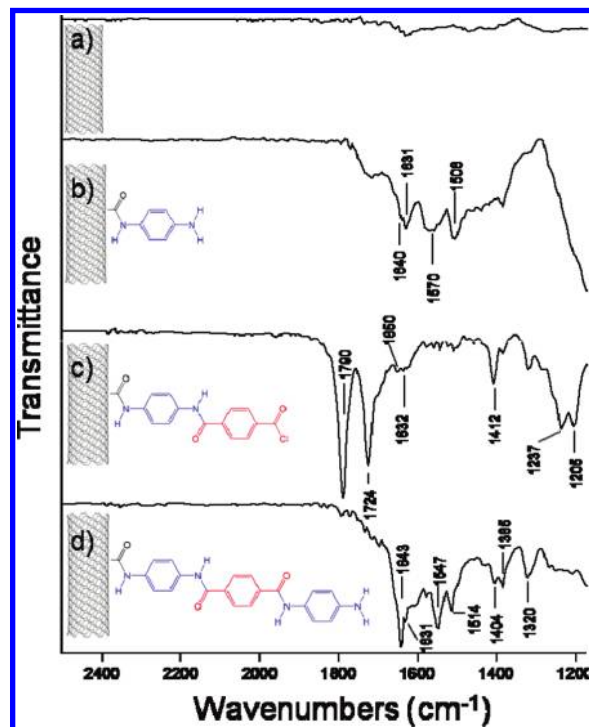


Figure 3. FT-IR Spectra of (a) pristine-MWNTs, (b) PDA-MWNTs, (c) TPC-PDA-MWNTs, and (d) PDA-TPC-PDA-MWNTs following sequential functionalization by PDA and TPC units.

COCl-MWNTs (Figure 3b). The appearance of a broad-band centered at 1631 cm^{-1} with a distinctive shoulder at 1640 cm^{-1} is believed to be a combination of the N–H bend of the free amino group coupled with the amide I C=O absorption. A broadband centered at 1570 cm^{-1} is attributed to the amide II N–H absorption, while the band at 1508 cm^{-1} indicates the C=C absorption of the aromatic ring. The appearance of these bands and the fact that N–H bands are present due to both amine and amide groups give firm evidence for the covalent attachment of PDA molecules at the surface of the MWNTs. Following subsequent coupling of TPC to PDA terminal amino groups via amide formation, TPC-MWNTs were characterized. The appearance of intense bands at 1790 and 1724 cm^{-1} are indicative of the C=O of an acid chloride in both free and hydrogen bound states (Figure 3c). Bands at 1650 and 1632 cm^{-1} are due to the amide I C=O stretch and the amide II N–H bend, respectively. The aromatic C=C stretching band is found at 1412 cm^{-1} , whereas two equivalent bands at 1237 and 1205 cm^{-1} are indicative of the two forms of *p*-disubstituted benzene rings which collectively support the assertion of the covalent modification of PDA-MWNTs with TPC to form TPC-PDA-MWNTs.

Further coupling of PDA to the terminal acid chloride groups of the TPC-PDA-MWNTs was performed. In contrast to the spectrum of the TPC-PDA-MWNTs (Figure 3c), where the C=O stretch of the acid chloride groups appear as intense bands, in the case of PDA-TPC-PDA-MWNTs (Figure 3d), these bands are absent and have been replaced by the sharp amide I C=O absorption at 1643 cm^{-1} with a shoulder at 1631 cm^{-1} of the amide II

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N–H absorption. The N–H bend of the terminal amino group of the PDA molecule is seen at 1547 cm^{-1} , whereas the sharp absorption of the aromatic C=C stretching is seen at 1514 cm^{-1} . Bands at 1404 and 1385 cm^{-1} are due to the aromatic C–H bend, whereas a band at 1320 cm^{-1} is due to the phenyl C–N stretch. Notably, the amide I band has increased in intensity as might be expected

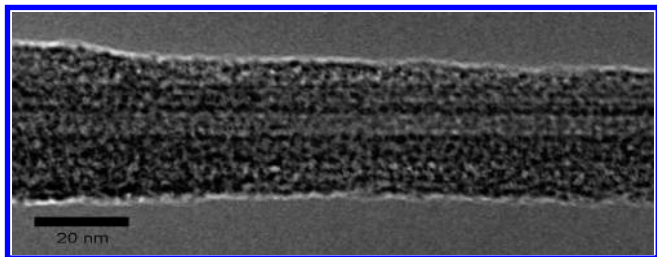


Figure 4. PDA-TPC-PDA-functionalized MWNT, indicating a monolayer of PPTA-oligomer material surrounding the MWNT.

because of both the presence of additional amide functional groups and the increased vibrational freedom of molecules subsequently bound to the surface of MWNTs. This effect is well-known in the case of ligands bound to the substrates and nanoparticles, where groups α to the surface are often weak or indistinguishable, whereas ω groups are typically well-defined.³² Thus, the combined FT-IR spectroscopic evidence supports the assertion that the covalent step-by-step functionalization of MWNTs with PDA and TPC units had been successful. HR-TEM was used to image the surface of the PDA-TPC-PDA-MWNTs following functionalization and shows a significant amount of organic material at the surface of the MWNTs (Figure 4; also see the Supporting Information, Figures S4–6). This feature is encouraging as it indicates that the surface of the MWNTs has been extensively functionalized at defect sites to yield a dense monolayer of PPTA oligomers. Such a high degree of surface

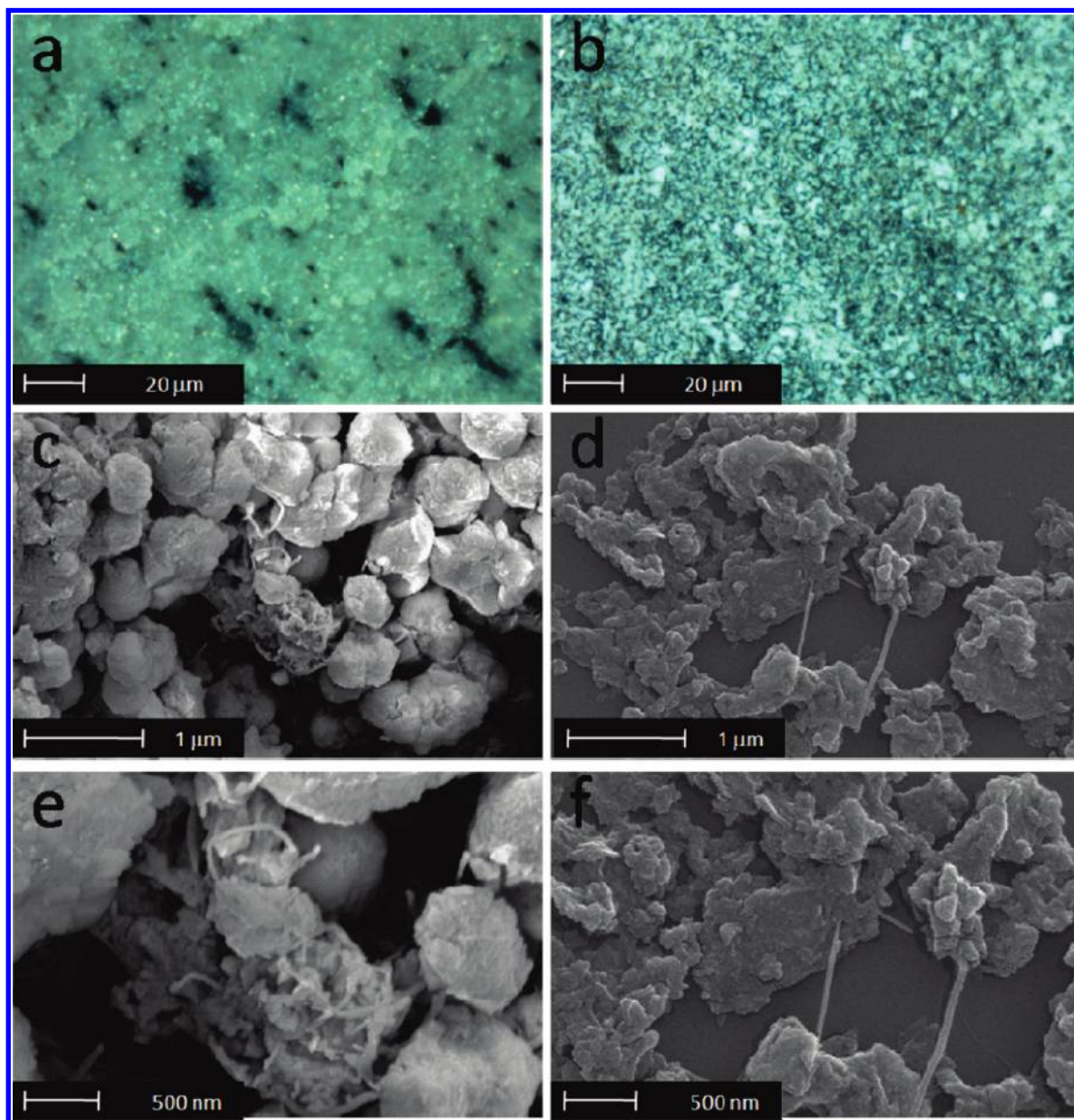


Figure 5. Optical and SEM images of (a, c, e) *p*-MWNT/PPTA composite and (b, d, f) PPTA-MWNT/Kevlar.

functionalization is expected to be optimal for the potential integration of functionalized MWNTs within a host polymer matrix such as PPTA, Kevlar.

To test this hypothesis, we prepared poly-*p*-phenylene terephthalamide (PPTA), Kevlar, using a procedure based on literature preparative methods in the presence of both p-MWNTs and PPTA-MWNTs.³⁰ As the PPTA-MWNTs possess surface chemistry identical to that of the PPTA host matrix, it was expected that the PPTA-MWNTs would be integrated within the PPTA. Alternatively, p-MWNTs, possessing little or no surface functionality, might be expected to aggregate among themselves and form insoluble nanotube regions within the PPTA matrix. Such behavior of MWNTs within polymer matrices is extremely common and has been the underpinning motivation for a multitude of nanotube-polymer composite studies aimed at preventing such behavior. In this case, 1 wt % MWNT-PPTA composites were prepared by forming PPTA in the presence of p-MWNTs and PPTA-MWNTs. Optical images of the composites indicated distinct differences between the materials (Figure 5a,b). PPTA is opaque yellow in color, whereas the composites of p-MWNTs/PPTA and PPTA-MWNTs/PPTA were gray and olive-green in color, respectively. The fact that the materials were markedly different in appearance gave some preliminary indication that the MWNTs had been distributed differently within the polymer matrix. Optical images of the p-MWNTs/PPTA and PPTA-MWNTs/PPTA composites at 500 \times magnification show macroscopic aggregates of MWNTs in the case of the p-MWNTs (black regions in Figure 5a), which were absent in the case of the PPTA-MWNTs (Figure 5b).

SEM images of the materials deposited onto a piece of silicon wafer indicated that large aggregates of MWNTs existed on top of large PPTA regions in the case of the p-MWNTs (Figure 5c). While in the case of the PPTA-MWNTs, individual MWNTs were observed to be embedded within the PPTA matrix, and were not found as aggregates within the material (Figure 5d). The entire morphology of the samples was notably different as can be seen from the SEM images. We speculate that in the case of the p-MWNTs, PPTA was formed independently from the MWNTs that were present. In the case of the PPTA-MWNTs, PPTA-MWNTs were found to be embedded within the Kevlar matrix that exhibits markedly different grain size and morphology because of the size regime of the MWNTs that the PPTA had formed around. Images e and f in Figure 5 show the materials at higher magnification, which clearly shows the p-MWNT aggregates in the case of the p-MWNTs/PPTA (e) and individual PPTA-MWNTs protruding from within sheets of the PPTA material (f). We hypothesize that in the latter case, this is possible because of the intrinsic interaction between the materials on account of their identical surface chemistry.

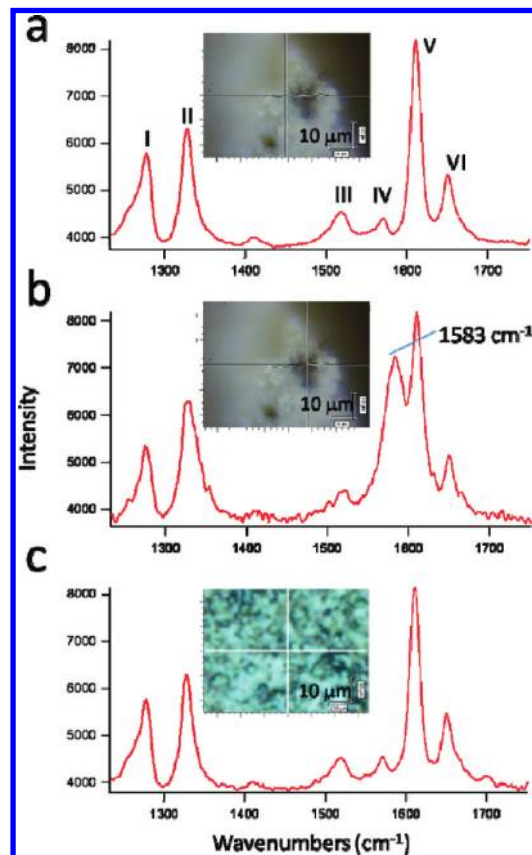


Figure 6. Raman spectra with optical insets of (a) a PPTA region within the p-MWNTs/PPTA composite, (b) an aggregate of *p*-MWNTs within the p-MWNTs/PPTA composite, (c) a representative area of the PPTA-MWNT/PPTA composite.

Raman mapping of the composite materials also was used to spectroscopically identify the regions in the MWNTs/PPTA composites ($\lambda = 514.5$ nm). In the case of the p-MWNT/PPTA composite, Figure 6a shows the Raman bands corresponding to a region of PPTA material, as indicated by the optical image in the inset. The bands labeled I–VI correspond exactly with values reported in the literature for PPTA.³³ Figure 6b shows the bands corresponding to an aggregate of p-MWNTs within the PPTA matrix as shown in the inset. Clearly evident is the appearance of a band at 1583 cm^{-1} , which is identified as the G-band characteristic of MWNTs. Such regions were indistinguishable in the case of the PPTA-MWNTs/PPTA material, whose spectrum was dominated by the PPTA bands, Figure 6c. It is indeed gratifying that bands due to MWNTs are not observed in this latter case, corresponding with good integration and dispersion of MWNTs within the PPTA matrix.

Summary

From the analysis of the MWNTs composites, it is evident that the PPT-MWNTs are considerably better dispersed in the PPTA matrix than the p-MWNTs. We attribute this to the extensive functionalization of the surface of the MWNTs with PPTA oligomers. Thus, the

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high degree of functionality obtained, because of the initial strong acid oxidation employed, is a critical step to allow for the dispersion of the PPTA-MWNTs into the PPTA matrix. This high degree of functionalization is evidenced by the TEM micrograph (Figure 3) showing a sheath of organic material surrounding a MWNT. Had only a low amount of functionalization been achieved, results similar to the pristine-MWNTs (aggregation instead of dispersion within the PPTA matrix) would be expected. If incorporated into a bulk polymer matrix, these aggregates would most likely act as defect points for fracture upon stressing the composite, thereby undermining the original intent of polymer reinforcement. The design and preparation of PPTA-MWNTs has also highlighted the fact that due to the identical chemistries of both the MWNTs and the host PPTA matrix, that the MWNTs are not only expected to disperse within the polymer matrix, but are also expected to participate in the polymerization reaction itself. This feature is particularly attractive, as it means that MWNTs may be both covalently and noncovalently bound within the polymer matrix. The implications of this are of much interest for further studies involving the mechanical testing of PPTA fibers impregnated with PPTA-MWNTs.

In conclusion, we have demonstrated the controlled sequential functionalization of MWNTs with monomer units of poly-*p*-phenylene terephthalamide (PPTA), Kevlar. We have shown using spectroscopy that the surface of MWNTs is amenable to extensive functionalization and that the specific chemical functionality of the MWNTs can accurately be controlled. The preparation of 1 wt %

MWNT/PPTA composites was demonstrated and it was shown that the functionalization of MWNTs with PPTA oligomer units facilitated integration of the PPTA-MWNTs within the PPTA matrix. This was in stark contrast to pristine-MWNTs which exhibited no-such affinity for the PPTA material and existed as aggregates within the polymer matrix. The preparation of PPTA-MWNTs constitutes a hybrid material which possesses the chemical functionality of PPTA integrated with the physical properties of a MWNT scaffold. This approach toward nanotube functionalization provides the basis for further investigation of the preparation of PPTA-nanotube composite materials and the analysis of the properties of such materials. These results represent a rational approach toward the creation of functionalized nanoscale building blocks, whereby the interaction and integration of these materials with other materials and substrates can be accurately controlled and not dictated by random surface interactions.

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Supporting Information Available: Additional FT-IR spectroscopic data available for functionalized MWNTs (PDA-MWNTs, TPC-PDA-MWNTs, PDA-TPC-PDA-MWNTs); HR-TEM images of PPTA-MWNTs (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.