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Non-solution Treatment Method of Carbon Nanotubes to Prepare Strong and Tough Polymer Nanocomposites

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ABSTRACT:

This paper demonstrated a simple approach for the development of advanced Nylon 12 composites by selectively modified multiwalled carbon nanotubes (MWCNTs). Prior mixing with Nylon 12, MWCNTs were modified by a non-solvent process namely plasma treatment in order to improve its dispersion in the nylon matrix and enhance the interfacial adhesion by increasing the compatibility. A new combination of plasma treatment have been found through extensive investigations that led the nanocomposites to be extremely strong and tough even at moderately low amount of CNTs loading. Addition of only 1 wt % of modified MWCNTs, improved the tensile strength, Young's modulus and elongation at break of the nanocomposites by ~ 65%, 61% and 68%, respectively. The FESEM images of fracture surfaces of nanocomposites showed excellent adhesion and dispersion of CNTs within the matrix, indicating the high merit of our selective plasma treatment process.

Keywords: Plasma, Interface, Young's modulus, Nanocomposite

1. INTRODUCTION:

The field of polymer nanocomposite is one of the most popular areas in current research due to its numerous potential applications in various engineering parts. In this context, carbon nanotubes (CNTs) based polymer composites provides a class of novel materials (nanocomposites) with superior mechanical, thermal, electrical and barrier properties suitable to replace many existing materials for engineering applications. Since first reported by Ijima in 1991,¹ CNTs have been largely utilizing in a wide variety of applications owing to their high aspect ratio, low mass density and unique mechanical, electrical, and thermal properties. However, to fully achieve these outstanding properties in composite materials, there are a number of issues that have to be resolved. These are (i) homogeneous dispersion of CNTs in the polymeric matrix and (ii) strong interfacial interactions with the matrix to attain efficient load transfer from the polymeric matrix to the CNTs. Because, the strong van der Waals forces that exist between each nanotubes, facilitate them to entangle tightly with each other or form clusters. This effect causes a bad scale of dispersion on being mixed with the polymer matrix. Hence, functionalization of CNTs is a promising way to prevent them from aggregation and improve their dispersion in polymer matrices.^{2,3} So far a large variety of approaches have been considered for functionalizing CNTs, which include noncovalent functionalization,⁴ covalent functionalization^{2,5} and polymer grafting.^{3,6} However, these methods usually utilize lots of chemical agents including many hazardous acids.⁹

Therefore, in the current piece of work we demonstrated a facile, non hazardous, fast and non-solvent based modification process for the surface modification of CNTs. The modification was done by radiofrequency (r.f) plasma treatment process using a unique combination of gasses i.e. oxygen and nitrogen. Comparing with the wet chemical methods used for CNT surface functionalization, plasma treatment has several advantages: (i) it is a simple, fast and homogeneous process (ii) it is an environmentally benign process as no hazardous chemical is utilized and (ii) using this process, a broad range of functional groups can be incorporated at the CNT surface, by variation of the process gas, and (iv) it can introduce functional groups to MWCNTs surface, without affecting the MWCNTs bulk properties.

Nylon 12 was chosen in this study since it a new class of polyamide with superior flexibility, high impact resistance, good mechanical properties at extreme temperatures, high thermal stability, low moisture absorption and good chemical resistance. The polymer nanocomposites were prepared by conventional melt processing technique as it is a fast, industrial friendly process and free of solvents and contaminants.

2. EXPERIMENTAL

2.1 Materials

The MWCNTs were purchased from Cheap Tubes, USA. The outer diameter was < 8 nm and length was in the range of 10-30 μm . Nylon 12 pellets were purchased from Sigma Aldrich, Singapore. The pellet size was 5 mm and density was 1.01 g/mL at 25 °C. Prior to melt blend, the Nylon pellets were dried in a vacuum oven for 8 h at 60 °C to remove residual moisture.

2.2 Plasma Functionalization of MWCNTs (*f*-MWCNTs)

Prior plasma modification, the raw MWCNTs were dispersed in DMF solution and treated by a 20 kHz ultrasonic processor for 10 min in order to break their inherent aggregation. After vacuum drying, the raw MWCNTs were placed into the plasma chamber and treated with the mixture of oxygen and nitrogen plasmas. The aim was to exclusively generate amide groups on CNTs along with other oxygen and nitrogen groups. The plasma power and exposure time was set to 400 W and 4 min respectively, in order to ensure good treatment. Plasma was conducted using a plasma generator supplied by March PX500 series, USA. The gas flow rate was set at 75 sccm (50sccm O₂ +25 sccm N₂) while the working pressure was 165 mTorr. The treated CNTs were then kept in air for 15-20 min to stabilize the surface changes.

2.3 Synthesis of Nylon 12/*f*-MWNT Composites

Nylon 12/*f*-MWNT nanocomposites were prepared by melt blending of Nylon 12 with the *f*-MWNTs. The melt blending was performed by a Hakke MiniLab internal mixer at 185°C for 6 min with a screw speed of 70 rpm. During mixing nitrogen gas was purged inside to avoid the degradation of Nylon. The extruded strips were then hot pressed at 185°C for 3 min under 10MPa to prepare the film with a thickness of approximately 0.3 mm. Composites prepared with only 1 wt% of *f*-MWCNTs and compared with composites reinforced with similar amount of raw MWCNTs.

2.4 Measurements

Fourier transform infrared (FTIR) spectroscopic measurements were performed using a FTIR spectrometer (Perkin-Elmer GX, USA). The FTIR spectra of raw MWCNTs and plasma modified MWCNTs were obtained by mixing a small amount of the materials in KBR pellets. X-ray photoelectron spectroscopy (XPS) measurements were taken using Kratos Axis Ultra XPS spectrometer equipped with a monochromatic Al K α X-ray excitation source. The structural changes between the raw and functionalized MWCNTs were investigated by a Confocal Raman microscope (WITec CRM200 using 488 nm laser). The surface morphology of the tensile fractured samples of the nanocomposites were observed by scanning electron microscopy (JEOL 6400F). Tensile tests were carried out by a Instron Micro Tester 5848 at room temperature at crosshead speed of 50 mm/min. Thermal stability of the nanocomposites was investigated using a thermal gravimetric analyzer (TGA 2950, TA Instruments) from 30 to 600 °C at a heating rate of 10 °C min⁻¹ under dry air atmosphere.

3. RESULTS AND DISCUSSION

The FTIR spectra for the *f*-MWCNTs and raw MWCNTs are shown in Fig. 1. As can be seen, the FTIR spectra of the raw MWCNTs show very low intensity bands at 3442, 1588, 1668 and 1182cm⁻¹, corresponding to the C-C-O stretching, -C=C, -C=O stretching, and -OH groups, respectively.⁷ Though, after plasma treatment the *f*-MWCNTs show same characteristic peaks, however the intensity of those peaks are radically increased. Moreover, a new peak can be observed at 1551 cm⁻¹, which is probably due to the formation of new amide groups. These results clearly suggest the efficiency of the oxygen+nitrogen plasma treatment which created numerous functional groups (-OH, -COOH, -C=O, -NH₂, -CONH₂, -C=NH, -C \equiv N, and etc.) on MWCNTs surface.

Fig. 2 shows the XPS survey and high resolution C1s profiles of the *f*-MWCNTs and raw MWCNTs. The survey spectra were investigated to identify the elements present on the surface of MWCNTs as well as to perform the quantitative analysis. The survey spectra of *f*-MWCNTs and raw MWCNTs are shown Fig. 2a and b, respectively. The peak at 284.7 and 532.2 eV corresponds to C1s and O1s respectively.⁸ In case of raw MWCNTs, a very intense carbon is detected along with a small oxygen peak. The appearance of small oxygen peak in raw MWCNTs is probably due to the mild surface oxidation that occurs during synthesis process. From the XPS survey spectra of *f*-MWCNTs, it can be clearly noticed that the height of O1s peak dramatically increased as compared to the raw MWCNTs sample. At the same time, a nitrogen peak clearly appears at a binding energy of 400.1 eV. This indicates the existence and formation of both oxygen and nitrogen functional groups on the MWCNT surfaces as a result of that particular plasma treatment. The atom compositions of raw MWCNTs are 96.88% C and 3.12 % O. After plasma treatment the C content is decreased to 77.30 % while the O and N content increased to 17.60 and 5.10 %, respectively.

The Raman spectra was employed next to identify changes in raw and *f*-MWCNTs since it is a very valuable tool for the characterization of carbon-based nanostructures. It can be seen from Fig. 3 that both the Raman spectra display two characteristic bands at 1351 (D-band) and 1576 (G-band). The D band indicates disordered or amorphous carbons, while the G band is related to the graphite in-plane or ordered carbons in the MWCNTs.⁸ Therefore, the relative intensity of the D-band is proportional to the amount of defects in the *f*-MWCNTs sample. As can be seen, both the samples have similar spectral pattern, but the intensity ratio of D band and G band, I_D/I_G , is different, suggesting some definite structural changes of MWCNTs. It can be noticed that I_D/I_G of the *f*-MWCNTs (Fig. 3b) is higher (0.53) than that of the raw MWCNTs (0.22), indicating the presence of more defects in the crystal structure. This result once again attributed the generation of functional groups on MWCNTs as identified by FTIR and XPS spectra above.

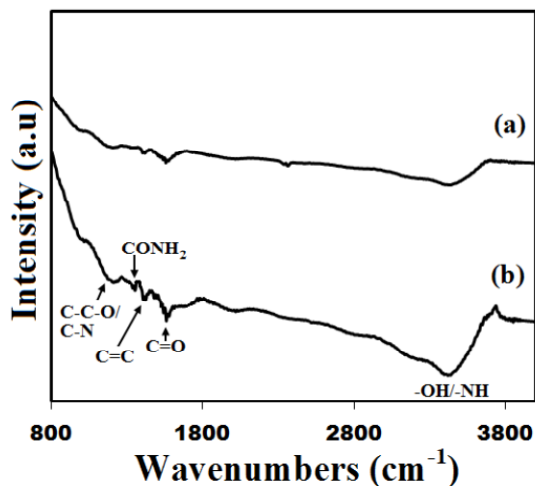


Fig. 1 FTIR spectra of (a) raw CNT and (b) *f*-MWCNTs.

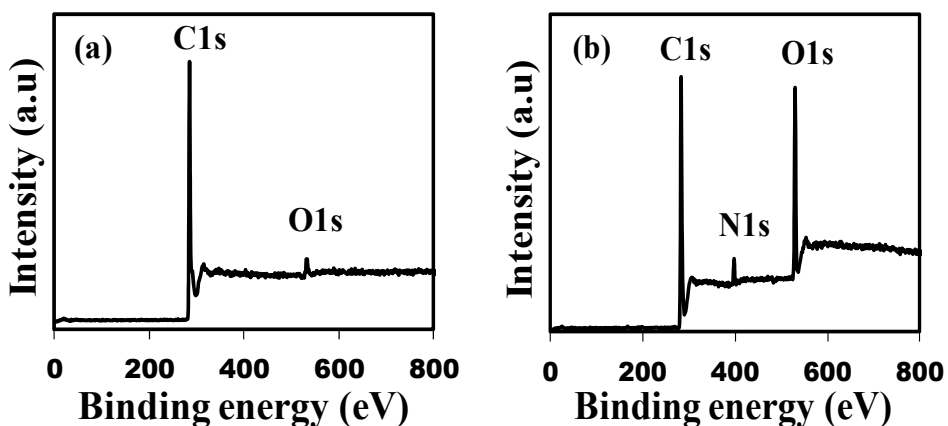


Fig. 2 XPS survey spectra of (a) raw MWCNT and (b) *f*-MWCNTs.

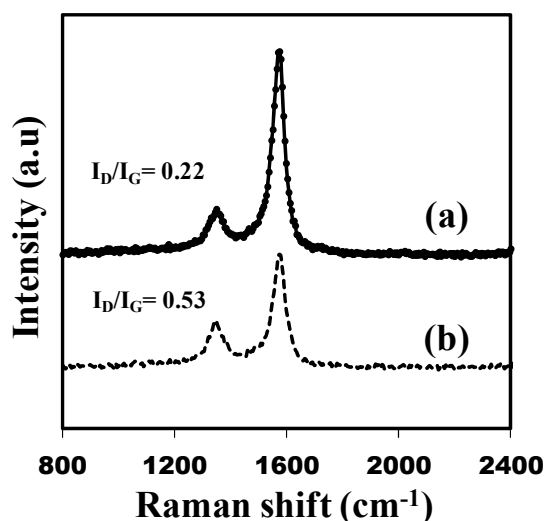


Fig. 3 Raman spectra for (a) raw MWCNT and (b) *f*-MWCNTs.

The mechanical, thermal and morphological properties of the Nylon12/*f*-MWCNTs composites are presented next to understand the effects of plasma surface treatment. Fig. 4 shows the stress-strain curve of the nanocomposites obtained by tensile test. It is apparent that the addition of *f*-MWCNTs dramatically increased the tensile strength and Young's modulus (*E*) of the Nylon 12 matrix as compared to the raw MWCNTs with same amount. Moreover, the plasma treated MWCNTs contained nanocomposites showed a large increase in the elongation at break. The Tensile strength and Young's modulus of neat Nylon 12 are found to be 48.35 MPa and 420 MPa, respectively. While these values increase to up to 74 MPa and 630 MPa with the addition of only 1 wt % *f*-MWCNTs. On the other hand, addition of same amount of raw MWCNTs did not show much improvement in their tensile strength and Young's modulus values. Table 1 represents the typical tensile values of all the nanocomposites. It was found that addition of 1 wt % *f*-MWCNTs improves the tensile strength and Young's modulus of the Nylon matrix by ~ 25% and 29% as compared to the raw MWCNT based one. Such large improvements in tensile properties associated with the long elongation at break of the Nylon12/*f*-MWCNTs nanocomposites can be attributed due to strong interfacial adhesion (hydrogen bonding) between the surface functional groups of MWCNTs and the amide bonds in Nylon 12. Moreover, this can also be attributed by the improved compatibilization between Nylon 12 and *f*-MWCNTs since both of them contain lots of amide groups on their structures. The toughness of the Nylon12/*f*-MWCNTs composite was measured from the area under the stress-strain curve. In composite materials, the strain at break and toughness are extremely dependent on the degree of filler dispersion and their interfacial adhesion with the matrix.

Table 1. Mechanical properties of Nylon 12/MWCNTs composites (results are average of 5 samples).

Sample	Tensile strength (MPa)	Young's Modulus (MPa)
Nylon 12	48.35 (±3.5)	420 (±15.2)
Nylon 12/1 wt% Raw MWCNTs	58.81 (±3.3)	490 (±16.1)
Nylon 12/1 wt% <i>f</i> -MWCNTs	73.78 (±4.0)	630 (±16.5)

To investigate the dispersion of MWCNTs within the polymer matrix, the surface morphologies of the fractured nanocomposites (cryo-fractured) are presented in Fig. 5. It is apparent from Fig. 5b that the dispersion of raw MWCNTs is very poor in the Nylon 12 matrix and the CNTs are weakly adhered with the matrix. Moreover, the raw CNTs are appeared in the form of bundles. This low quality dispersion is believed to be the cause of unfunctionalized surfaces

which insist them to form aggregation owing to the intertubular strong van der Waals forces. In contrast, the micrograph of Nylon12/*f*-MWCNTs clearly shows the homogeneous dispersion of *f*-MWCNTs in the polymer matrix where the nanotubes are tightly embedded into the matrix. There are no agglomerates can be seen in the micrographs, rather the nanotubes are uniformly distributed throughout and appear as individual tubes. Such well dispersion and strong adhesion of *f*-MWCNTs with Nylon 12 is believed to be the cause of specific and efficient surface functionalization which facilitates to improve the higher matrix-filler molecular level compatibility. These observations once again point out the necessity of proper surface treatment of CNTs in the fabrication of advanced polymer nanocomposites.

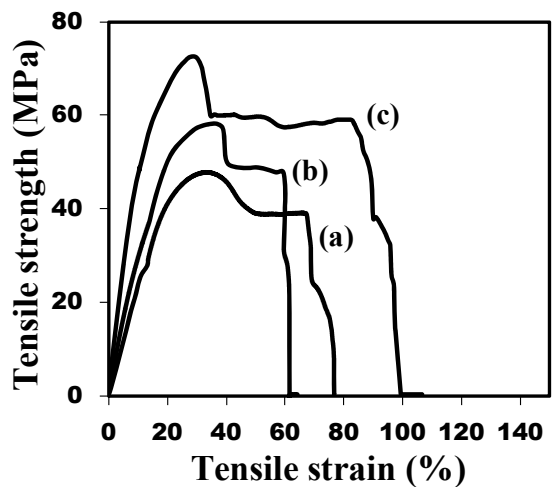


Fig. 4 Stress-strain curves of Nylon 12 and the nanocomposites

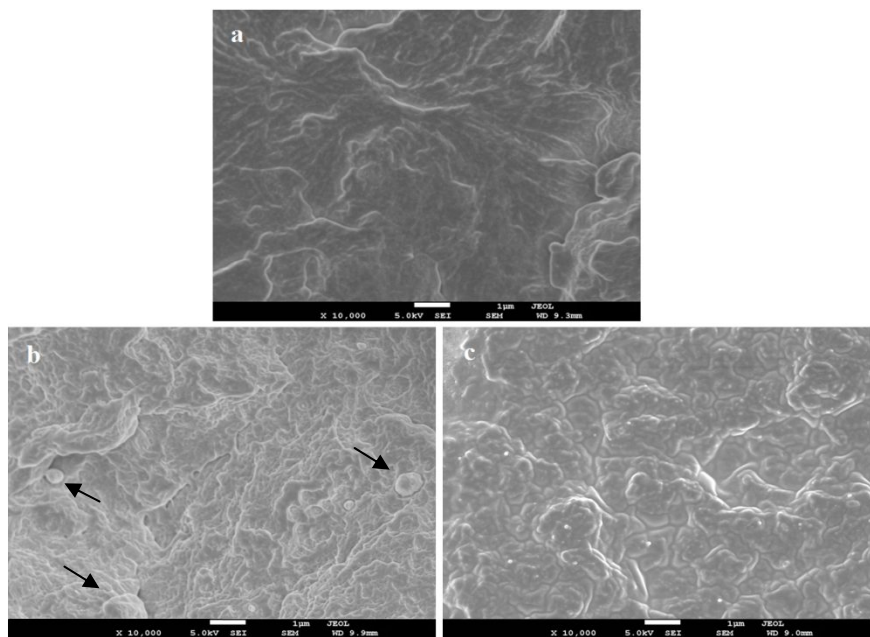


Fig. 5 FESEM images of the cross-sectional fracture of: (a) neat Nylon 12, (b) Nylon 12/1% raw MWCNTs, and (c) Nylon 12/1% *f*-MWCNTs.

To investigate the role of *f*-MWCNTs in the thermal stability of the Nylon 12 matrix, TGA measurements were carried out, and the results are shown in Fig. 6. The onset decomposition temperature (T_d) is considered at 5 % weight loss in our system. From the TGA curve of net Nylon 12, it was noticed that the 5 % and 50 % decomposition occurred at 404

°C and 448 °C, respectively. It can be clearly seen that the decomposition temperature of the neat Nylon 12 is noticeably improved (by 9.2°C at $T_d=5$) with the addition of 1wt % *f*-MWCNTs, while the raw CNTs showed a little difference (2.4°C). The improved thermal stability by *f*-MWCNTs can be attributed due to their strong interfacial interaction and homogeneous dispersion within the matrix which is act as good thermal insulation barriers, thus delaying the decomposition temperature by preventing the diffusion of the degraded volatile products out of the matrix.

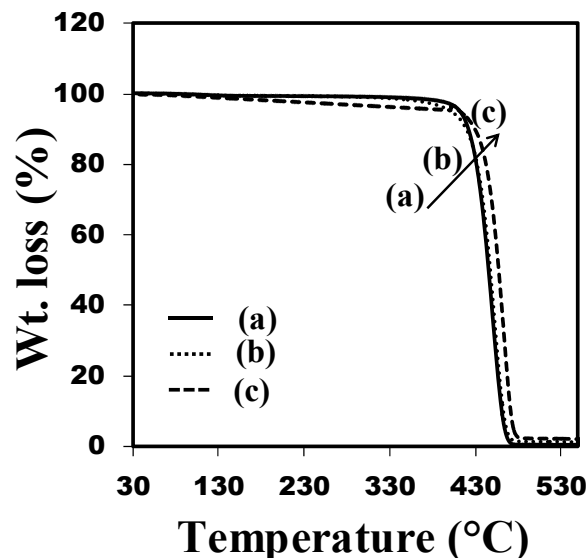


Fig. 6 TGA curves for (a) neat Nylon 12, (b) Nylon 12/1% raw MWCNTs, and (c) Nylon 12/1% *f*-MWCNTs.

4. CONCLUSIONS

In conclusion, multiwalled carbon nanotubes have been successfully functionalized by a fast, uniform and nonhazardous dry chemistry process. Precisely, oxygen and nitrogen plasma were used to exclusively generate amide groups onto the MWCNTs surface along with other oxygen+nitrogen groups. This was to achieve excellent molecular level bonding and miscibility between the matrix and fillers as both of them possesses the same surface chemistry. FTIR, XPS and Raman spectroscopy analysis supported the successful accomplishment of the surface functionalization process. The resulting *f*-MWCNTs reinforced Nylon 12 composites showed tremendous improvements in mechanical and thermal properties over the composites filled with the raw MWCNTs. The overall improvements in above properties for Nylon12/*f*-MWCNTs nanocomposites are mainly due to the fine dispersion and strong interfacial adhesion of nanotubes within the matrix. The well dispersion and good wetting of *f*-MWNT in the polymer matrix has also been confirmed by FESEM images. Finally, this approach is promising for use in the preparation of high-performance Nylon nanocomposites for many structural applications.

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