Functionalization and Characterization of Carbon Nanotubes/Polypropylene Nanocomposite

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Abstract—Chemical and physical functionalization of multi-walled carbon nanotubes (MWCNT) has been commonly practiced to achieve better dispersion of carbon nanotubes (CNTs) in polymer matrix. This work describes various functionalization methods (acid-treatment, non-ionic surfactant treatment with TritonX-100), fabrication of MWCNT/PP nanocomposites via melt blending and characterization of mechanical properties. Microscopy analysis (FESEM, TEM, XPS) showed effective purification of MWCNTs under acid treatment, and better dispersion under both chemical and physical functionalization techniques combined, in their respective order. Tensile tests showed increase in tensile strength for the nanocomposites that contain MWCNTs up to 2 wt%. A decrease in tensile strength was seen in samples that contain 4 wt% of MWCNTs for both raw and Triton X-100 functionalized, signifying MWCNT degradation/rebundling at composition with higher content of MWCNTs. For the acid-treated MWCNTs, however, the tensile results showed slight improvement even at 4wt%, indicating effective dispersion of MWCNTs.

Keywords—Multi walled carbon nanotube (MWCNT), functionalization, dispersion, nanocomposite

I. INTRODUCTION

IN 1991, the discovery of CNTs by Iijima [1] has created a revolution in the world of nanomaterials engineering. Due to its wide range of potential uses, research after research has been done to create various polymer carbon nanocomposites. Shaffer and Windle [4] conducted the first study of using nanotubes as reinforcement of solution-based composites in 1999. Very little reinforcement was observed, as the storage modulus increased from approximately 6 GPa for the polymer to 12 GPa for the 60 wt% composite film. They managed to derive that it is easier to reinforce softer matrices, as better results were obtained above the polymer glass transition temperature. Using short fiber theory, the nanotube modulus and effective length obtained were 150 MPa and 35 nm, respectively. The low modulus value may be due to the difficulty in fitting a highly non-linear function such as Krenchel's rule of mixtures to a limited data set. As the first attempt, it was proven that the reinforcement was possible, albeit leaving much room for improvement and further research.

A. Melt Processing and Characterization of Mechanical Properties

Melt processing is a common alternative for preparing polymer nanotube composites, and is particularly effective for thermoplastic materials such as polypropylene.

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This technique takes advantage of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening [5, 6]. The advantages of this technique are its speed and simplicity, and its compatibility with standard industrial techniques. Bulk samples can then be fabricated by techniques such as compression molding, injection molding or extrusion. However it is important that processing conditions are optimized not just for different nanotube types, but for the whole range of polymer-nanotube combinations. This is because nanotubes can affect melt properties such as viscosity, resulting in unexpected polymer degradation under conditions of high shear rates [7].

Bikiaris et al. [8] studied the effects of acid treatment MWCNT on the mechanical stability of isotactic polypropylene. The MWCNT nanocomposites were prepared by melt-mixing, and four different nanotubes were used: untreated MWCNTs and acid treated (nitric acid and sulfuric acid) and refluxed for different times. As a result, the length of the MWCNTs progressively decreased as the treatment time was increased.

Bao and Tjong [9] prepared PP nanocomposites reinforced with 0.1, 0.3, 0.5 and 1.0 wt% MWCNTs using melt-compounding in a twin-screw extruder followed by injection molding. They altered the loading rate and temperature parameters of the twin-screw extruder to investigate their impacts on the mechanical properties. The mechanical properties of PP and PP/MWCNT nanocomposites obtained at a moderate cross-head speed of 10 mm min-1 under 18oC. The stiffness of PP increased dramatically by ~31% by adding 0.3 to 0.5 wt% MWCNTs. The storage modulus also detected an increase from 1.88 to 2.5 GPa, about 33% improvement over pure PP. In compliance with the loading rate and temperature parameters altered, they concluded that PP/MWCNTs nanocomposites tend to increase with increasing test temperatures, indicating that the reinforcing effect of MWCNTs in PP matrix is more pronounced at higher temperatures.

In 2009, Thiebaud [10] investigated the mechanical properties of PP/MWCNT composites in four different grades: 1 wt%, 2 wt%, 4 wt% and 8 wt%. The composites were fabricated using the melt-mixing method. It is observed that there was an increase of the Young's modulus and the stress at fracture with the MWCNT level while the strain to failure decreases significantly.

B. Current Advancement in Dispersion of CNTs

As CNTs are being used vastly as matrix reinforcement, more and more studies are being done to uncover more

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effective methods of dispersing CNTs to maximize its great potential. A burst of progress in the research of dispersing CNTs took place most aggressively in year 2010. Rausch et al. [11] investigated the dispersibility of unfunctionalized and three differently functionalized MWCNT in the presence of anionic, cationic and non-ionic surfactants.
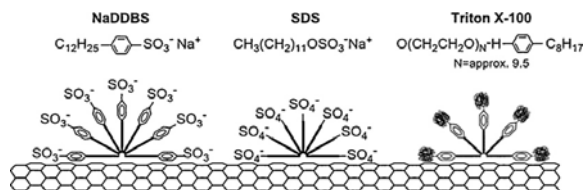

Fig. 1 Schematic representation of how surfactants may adsorb onto the nanotube surface. Reprinted from [12].

The mixtures were sonicated and cooled in water bath in different time intervals and recorded with UV-vis-spectrometer. It was found that at short sonication times the absorbance increases rapidly before leveling off at intermediate at higher sonication times. It was recommended that proper adjustment of the surfactant to CNT weight ratio is necessary for optimal exfoliation of the CNT.

Bai et al. [13] selected the Triton-X series surfactants with a same hydrophopic functional group and different hydrophilic polyethoxyl chain lengths to investigate their adsorption onto CNTs and their ability to stabilize CNT suspensions. The samples were shaken in a Gyrotory shaker at 200 rpm for 48 hours, and then underwent entrifugation at 3000g for 30 minutes. The samples were then filtered to remove the suspended CNTs but not significantly remove the surfactants. They discovered that adsorption capacities of the surfactants increased with decreasing hydrophilic chain length: Triton X-305 < Triton X-165 < Triton X-114 < Triton X-100. It was also found out that suspended CNT amounts in water were positively related to the adsorption capacities of the surfactants, but negatively with the hydrophilic fraction ratio of the X-series surfactants.

Comparative studies on dispersing multi-wall carbon nanotubes using two anionic surfactants (sodium dodecyl sulphate, SDS and sodium dodecyl benzosulfonate, SDBS) were also conducted [14]. CNTs were shorted by boiling in concentrated HNO_3 for 1 hour, and added to the surfactant solutions of different concentrations that are close to the critical micelle concentration (CMC) of both SDS and SDBS and sonicated for 5 hours at room temperature. The CNTs dispersions were then centrifuged to remove the precipitates and non-dispersed material. It was found that both dispersing agents form stable suspensions even below their CMC limit.

II. EXPERIMENTAL

A. Purification

An acid solution of H_2SO_4 and HNO_3 is mixed in a 3:1 ratio. To test the effect of ultrasonication time to the dispersion and purification of MWCNTs, the MWCNTs are ultrasonicated for 0.5, 2.75 and 5 hours respectively. Samples are then filtered with a microfiltration system, using a cellulose membrane filter of 0.47 μm pore size. Then the filtered MWCNTs are left to dry for 12 hours at room temperature, and then in a vacuum oven of 100oC for 5 hours. Samples are taken for FESEM and XPS analysis and the best sample is identified to be used for making of the nanocomposite.

B. Functionalization of raw MWCNT and purified MWCNTs

While anionic, cationic and nonionic surfactants have been used in previous studies to disperse CNTs, a nonionic surfactant was chosen for this experiment due to polypropylene's insolubility in water. Triton X-100 was used due to its availability in the market and previous studies have shown that it was an effective dispersing agent [14]. Both raw and purified MWCNTs from the previous process are then suspended in the Triton X-100 solution (5mg/ml), and sent for ultrasonication for 1 hour. The ratio of MWCNTs to surfactant is 1g MWCNT: 1.5g Triton X-100. The CNTs are filtered, washed and dried to be used for fabrication of the nanocomposite.

C. Fabrication of PP/MWCNT Nanocomposite

Melt-mixing was chosen over solution mixing due to time constraints and the first being a preferred choice for bulk production. It was also intended to combine the shear force of melt mixing with the functionalized MWCNTs to achieve better dispersion of MWCNTs. However, it was found that the functionalized MWCNTs form a hardened deposit after filtration and drying. A mortar grinder was used to grind the deposit into powder-form again before adding into the melt-mixer.

Polypropylene and the MWCNTs are mixed using the Haake Rheomix 600 mixer under temperatures of 200ºC, mixing speed of 30 rpm and a mixing duration of 15 minutes. The polypropylene was allowed to be melted for 5 minutes prior to adding the MWCNTs, in 0.5, 1.0, 2.0 and 4.0 wt%. Subsequently, the mixure is granulated into pellets and directly injection molded with the Krauss Maffei 40 Tonne injection molding machine into dog bone samples, adhering to the standard of ASTM D638. The injection molding parameters are as follows; barrel temperature: 205 – 220ºC, mould temperature: 25ºC, pressure: 800 bar, speed: 60 rpm.

D. Characterization and Mechanical Testing of Composites

Transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM) , and XPS are used to check the MWCNT configuration after purification under acid treatment. Unlike the light microscope, the TEM and FESEM use electrons instead of light. The electrons function as "light source" and their much lower wavelength makes it possible to get a resolution of a few angstroms (10-10 m). As a result, these electron microscopes are able to provide small area crystallographic information of the nanocomposite.

XPS is used to determine the composition of materials/elements in the MWCNTs. The FESEM, XPS and TEM analysis are done in the university's Central Research Laboratory.

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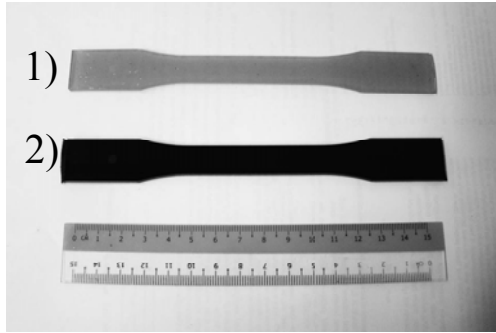Vol:5, No:10, 2011

Fig. 2 Dogbone specimens according to ASTM D638 standards; (1)
Pure PP, (2) MWCNT/PP nanocomposite.

For mechanical tests, universal testing machine (UTM) was
used to conduct tensile tests onto the fabricated MWCNT/PP
composite. Results of these tests show the characterization of
the mechanical properties of the composite materials in forms
of shear-strain graphs.

III. RESULTS

A. Fesem/Tem Results

The samples were sent for FESEM and XPS inspection,
with a clear distinction of purification and shortening of
MWCNTs in different ultrasonication times. Not much
difference can be seen on the structure of MWCNTs after 0.5
hours of ultrasonication, but more obvious changes are found
from the samples that have undergone ultrasonication for 2.75
(as shown in Fig 3) hours and 5 hours. At 5 hours, the
MWCNTs are severely shortened and dispersed, with the risk
of the MWCNTs being damaged under prolonged acid
treatment.

XPS results (Table 1) show that the Fe catalyst was
eliminated and Ni was reduced significantly after acid
treatment. However, oxidation also occurred more
aggressively under longer periods of ultrasonication. Based on
our reference [11], the optimum parameter obtained is the
ultrasonication time of 2.75 hours, in 150 ml of acid solution,
whereby a sufficient amount of Ni was reduced without a
drastic oxidation of carbon. The presence of sulfur is due to
the acid treatment, and can be removed with thorough
washing. TEM micrographs in Figure 4 confirm the
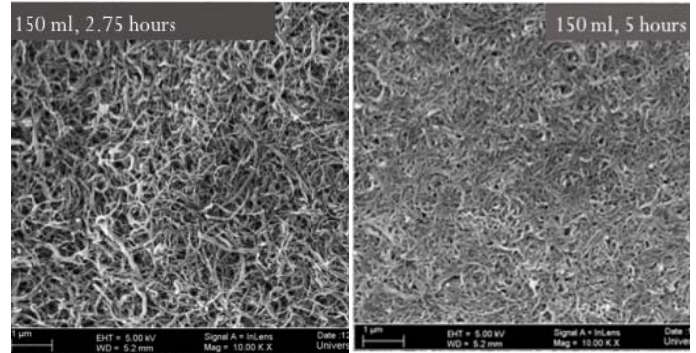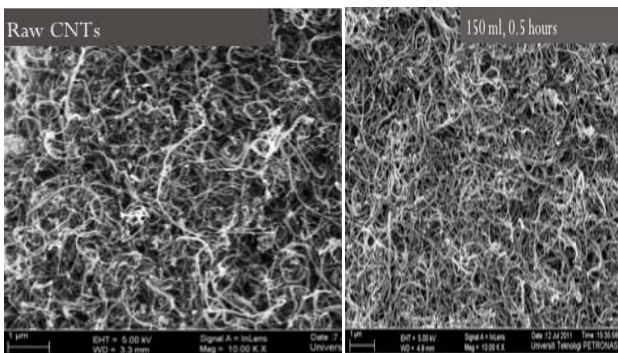effectiveness of purification of the MWCNTs.

Fig. 3 FESEM images (magnification 10K) of MWCNTs after acid
treatment under different ultrasonication hours; clockwise from top-
left; raw CNTs, 0.5 hours, 2.75 hours, 5 hours

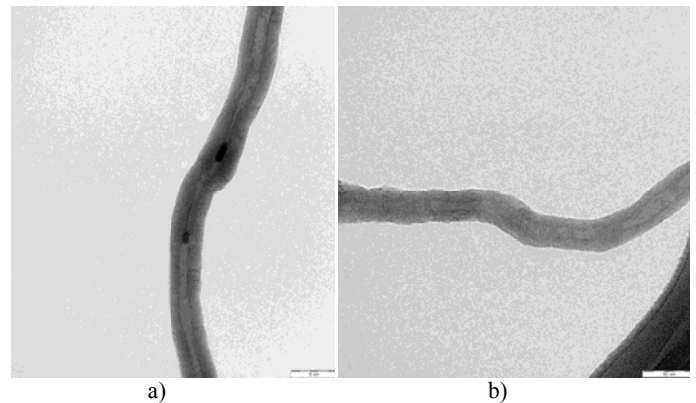a)   b)

Fig. 4 TEM micrographs; a) Impurities contained in raw MWCNTs,
b) purified MWCNTs after 2.75 hours of acid treatment

TABLE I
XPS RESULTS AFTER ACID TREATMENT UNDER DIFFERENT
ULTRASONICATION HOURS

| Element	Weight %	Atomic %
0.5hours ultrasonication		
C	94.22	96.52
O	4.04	3.11
Fe	0.46	0.10
Ni	1.29	0.27
2.75 hours ultrasonication		
C	90.56	93.40
O	7.95	6.16
Fe	-	-
S	0.73	0.28
Ni	0.76	0.16
5 hours ultrasonication		
C	88.93	91.82
O	10.26	7.95
Fe	-	-
S	0.32	0.12
Ni	0.50	0.10

B. Mechanical Tests

Tensile test with the rate of 20mm/min was performed onto
the dog-bone specimens adhering to ASTM D638 standards,
and stress-strain graphs were obtained as shown in Figure 5.
The resulting tensile strength and Young's modulus are
obtained as in Table 2. From the tensile test, it is observed
that the PP nanocomposites exhibit higher mechanical
performance with increasing MWCNT content up to 2 wt%
for all samples.

For samples containing raw and MWCNTs without acid
treatment experience a slight decrease in tensile strength at

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4%. This confirms studies that show that partial tensile strain can be transferred to MWCNTs embedded in PP matrix under tensile stress in low MWCNTs content. However, further addition of MWCNTs causes agglomerates of MWCNTs to form in the PP matrix and defects appear in the polymer matrix due to poor MWCNT dispersion by melt mixing. [15] Samples with MWCNTs that underwent acid treatment on the other hand showed encouraging results with continuous increase of tensile strength even at 4wt% of MWCNTs content. This shows that purified and shortened MWCNTs continue to achieve good dispersion within the polymer matrix. There was no significant improvement for solely Triton X-100 functionalized MWCNTs, however. This is due to the removal of the surfactant during the filtration and washing process, making the functionalization process almost redundant. Physical functionalization can only be effective when suspended or coated in the surfactant that is compatible with the matrix. Therefore, this project has been unsuccessful in dispersing MWCNTs using Triton X-100 under melt-mixing process. An alternative approach is suggested for future experiments.

TABLE II
TENSILE TEST RESULTS

Sample	Tensile Strength (MPa)	Percentage Increase (%)	Remarks
PP	28.96	-	
PP + 0.5wt% R	30.31	4.64	R: Raw MWCNT
PP + 1.0wt% R	32.47	12.11	TX: Triton X-100 functionalized MWCNT;
PP + 2.0wt% R	33.32	15.04	
PP + 4.0wt% R	32.56	12.42	A-TX: Acid-treated and Triton X-100 functionalized MWCNT
PP + 0.5wt% TX	31.62	9.18	
PP + 1.0wt% TX	32.12	10.88	
PP + 2.0wt% TX	33.69	16.32	
PP + 4.0wt% TX	33.36	15.16	
PP + 0.5wt% A-TX	30.83	6.45	
PP + 1.0wt% A-TX	32.90	13.59	
PP + 2.0wt% A-TX	33.63	16.09	
PP + 4.0wt% A-TX	33.98	17.32	
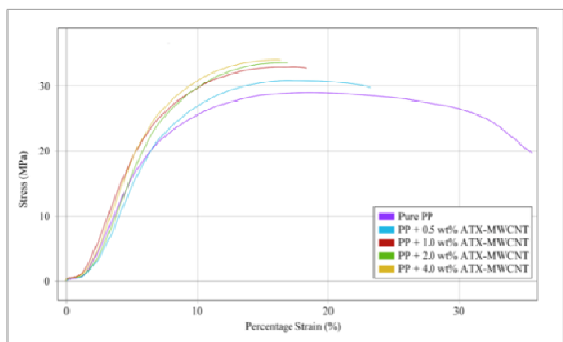
a) Triton X-100 functionalized MWCNTs
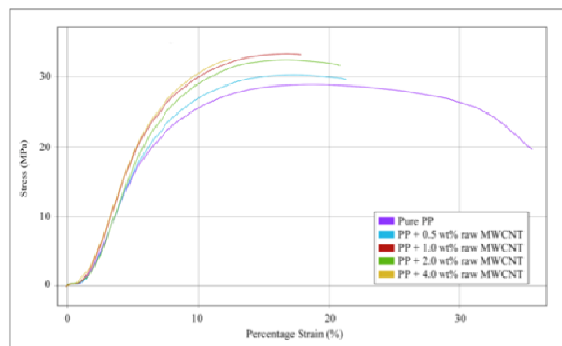
b) acid-treated and Triton X-100 functionalized MWCNTs
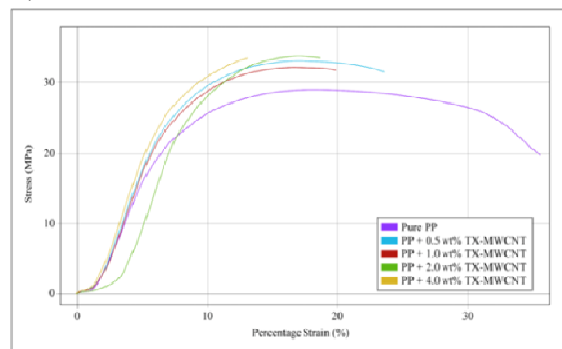
c) Compared to pure Polypropylene
Fig. 5 Stress-strain curves for Raw MWCNTs

IV. CONCLUSIONS

Based on the results obtained, it can be seen that acid treatment effectively removes and reduces catalysts in MWCNTs, as well as shortening the tubes. However, prolonged treatment can also damage the MWCNTs, forming amorphous carbon around the walls as well as reducing its mechanical properties. Throughout the experiments, it was concluded that 2.75 hours was the optimum ultrasonication time to purify the MWCNTs.

Also, it has been proven that purification and shortening of MWCNTs contribute to more effective dispersion of MWCNTs in the polymer matrix. The shortening of MWCNTs enables the MWCNTs to be dispersed more effectively in the PP matrix by delaying agglomeration to higher loadings.

The as-bought raw MWCNTs had inconsistent diameter and did not adhere to the specifications as provided by the supplier. XPS results (Table 1) showed a high amount of catalyst in the MWCNTs. The MWCNTs that were filtered and dried form a hardened deposit, which could cause uneven dispersion in mixing with the PP matrix during melt-mixing. While the hardened deposit was successfully grinded into powder-form with the mortar grinder, the grinding also resulted in damage to the MWCNTs by causing more open ends.MWCNTs were also exposed to foreign materials during two stages of the experiment, due to improper cleaning of the mortar grinder and granulator.

For future considerations, higher quality MWCNTs and new and clean equipment should be used for this experiment. Also, solution processing may prove to be a better alternative for more prominent test results.

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