

Improving Tensile Strength and Toughness of Melt Processed Polyamide 6/Multiwalled Carbon Nanotube Composites by *In Situ* Polymerization and Filler Surface Functionalization

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ABSTRACT: The effect of processing method and condition on the dispersion status of multiwalled carbon nanotubes (MWCNTs), and mechanical properties of the MWCNT/polyamide 6 (PA6) composites are investigated. Different melt processing conditions are used to dilute the master batch produced by melt process or *in situ* polymerization. Both MWCNTs and carboxyl group functionalized MWCNTs (MWCNTs-COOH) are compounded with PA6 at different loadings (0.1, 0.25, 0.5, and 0.75 wt %) to study the effect of chemical modification of MWCNTs on the mechanical properties of the final composites. It is demonstrated

that chemical modification of MWCNTs has a positive effect on the strength of the composites as an increase of 5–10 MPa was observed. More importantly, a near 5 MPa increase in strength and more importantly, a maximum of 138% increase in strain at break were observed for the composites produced by *in situ* polymerization, indicating a toughening and strengthening effect of CNT on the composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 133–140, 2011

Key words: PA6; carbon nanotubes; strength toughness; nanocomposites; *in situ* polymerization; processing

INTRODUCTION

Several studies have been carried out in the literature to understand the effect of CNTs on different properties of CNT/polyamide 6 (PA6) composites,^{1–8} while the effect of filler dispersion on the mechanical properties has also been reported. As one of the first studies on CNT/PA6 composites, Meincke et al. fabricated composites by melt blending Chemical Vapor Deposition (CVD)-multiwalled carbon nanotubes (MWCNTs) with polyamide-6.⁹ The material was melting processed in a corotating twin screw extruder. An increase in modulus from 2.6 to 4.2 GPa was observed at a MWCNT content of 12.5 wt %, whereas the elongation at break decreased from 40% to 4%. The relative moderate increase they reported might be caused by poor dispersion of MWCNTs in the polymer matrix, as shown in their morphological study. Soon after, Zhang et al. reported a study¹⁰ on

CVD-MWCNT/PA6 composites. A simple melt mixing method was conducted in a Brabender twin-screw extruder, resulting in an impressive modulus increase from 0.4 to 1.24 GPa at 2 wt % loading. In addition, the yield strength increased from 18 to 47 MPa, with elongation at break only showing a decrease from 150% to 110%. Microscopy studies showed very good dispersion and adhesion, both responsible for the impressive properties. A comparison between the studies from Meincke et al. and Zhang et al. clearly stresses the importance of the quality of filler dispersion on the mechanical properties of the composites.

To improve the filler dispersion and interface between filler and matrix for the purpose of simultaneously strengthening and toughening a polymer matrix, the following study is carried out. The effect of processing condition on filler dispersion and mechanical properties of the composites are investigated. Different melt processing conditions are used to dilute the master batches produced by melt compounding and *in situ* polymerization, respectively. Both MWCNTs and MWCNTs-COOH are compounded with PA6 at different loadings to investigate the effect of chemical modification of MWCNT on the properties of the final composites.

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EXPERIMENTAL

Materials

PA6 (Technyl[®] C206; density of 1.14 g cm⁻³), produced by Rhodia Engineering Plastics S. A., is used as received (in pellets form). MWCNTs (purity of 90%) and MWCNTs-COOH (thin multiwalled, lot number: P 041206, purity of 95%) are kindly supplied by Nanocyl S.A. (Belgium). The diameter of these CNTs is 10 nm and the length is in the range of 1.5 μm according to the producer. A COOH content of less than 4% is reported by the producer for MWCNTs-COOH. ε-caprolactam with a purity of 99% was purchased from Fisher Scientific UK (C₆H₁₁NO) and used as received.

Sample preparation and materials characterization

Melt compounding

MWCNTs or MWCNTs-COOH were compounded with PA6 in a mini-extruder (DSM Micro 15) at 200°C. A masterbatch containing 3 wt % MWCNTs was compounded at the condition of 50 rpm for 5 min. Processing condition study was carried out at 100 rpm, 10 min; 130 rpm, 10 min; 160 rpm, 10 min; 200 rpm, 10 min; and 250 rpm, 15 min, respectively. In the case of dilution from *in situ* polymerization, a process condition study was carried out at 50 rpm, 5 min; 100 rpm, 10 min; 130 rpm, 10 min; 160 rpm, 10 min; and 200 rpm, 10 min, respectively. Nitrogen gas flow at a rate of 10 mL/min is used to avoid degradation of the polymer during compounding.

Hot press

The extruded strands produced by the mini-extruder were cut into pellets and hot pressed into dog-bone shape, according to ASTM 638 at 240°C under 40 MPa for 3 min. A hold time of 15 min was used before the pressure is applied to melt the specimens. Samples were cooled down to room temperature using the water cooling system equipped with hot press.

SEM and optical microscopy

Morphological study of composites manufactured using different process conditions are carried out on JEOL JSM-6300F SEM on gold-coated, frozen fracture surface. The optical microscopy is carried out on the Olympus microscopy using reflection mode at room temperature.

Tensile test

Tensile testing of bulk composites is carried out on an Instron 5566 tensile test machine equipped with video extensometer. The gauge length and cross-

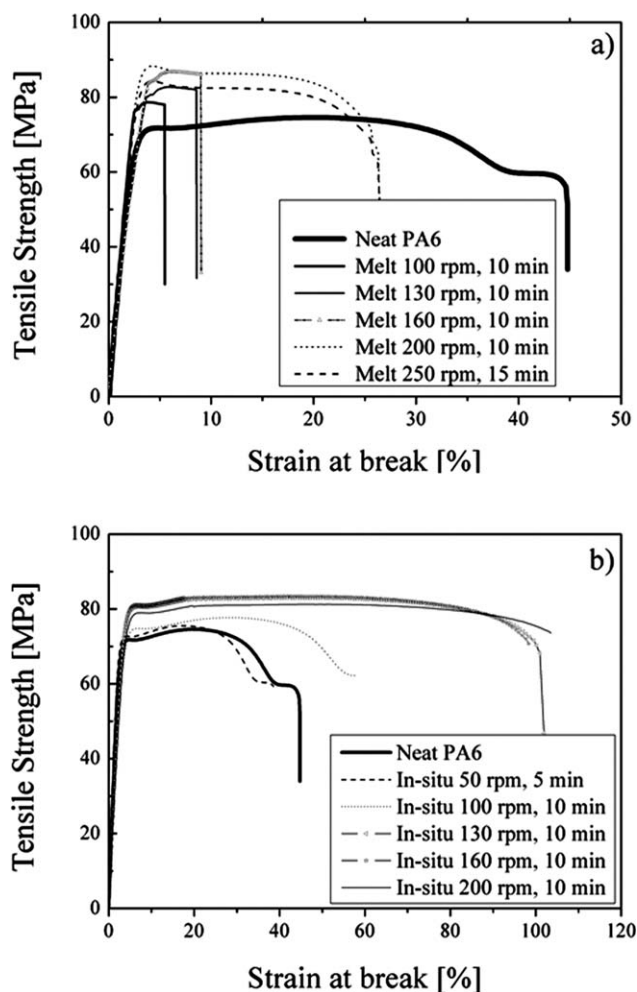


Figure 1 The stress–strain curves for 0.5 wt % MWCNT/PA6 composites processed at different conditions, (a) from melt processed master batch, (b) from *in situ* polymerized master batch.

head speed used for bulk composites was 30 mm and 10 mm/min, respectively.

Differential scanning calorimetry and thermogravimetric analysis

Differential scanning calorimetry (DSC) was performed under nitrogen gas flow in the range of 20–250°C by using a METTLER Toledo DSC 822[°]. Samples were heated to 250°C and held there for 5 min to remove the thermal history and were then cooled to 20°C. The DSC scanning rate was 10°C/min. Thermogravimetric analysis (TGA) was carried out under either air or nitrogen atmosphere in the temperature range of 20–1000°C by using a TA TGA Q500. The heating rate used was 20°C/min.

In situ polymerization

One gram MWCNTs or MWCNTs-COOH, 20 g ε-caprolactam, and 100 g distilled water were mixed

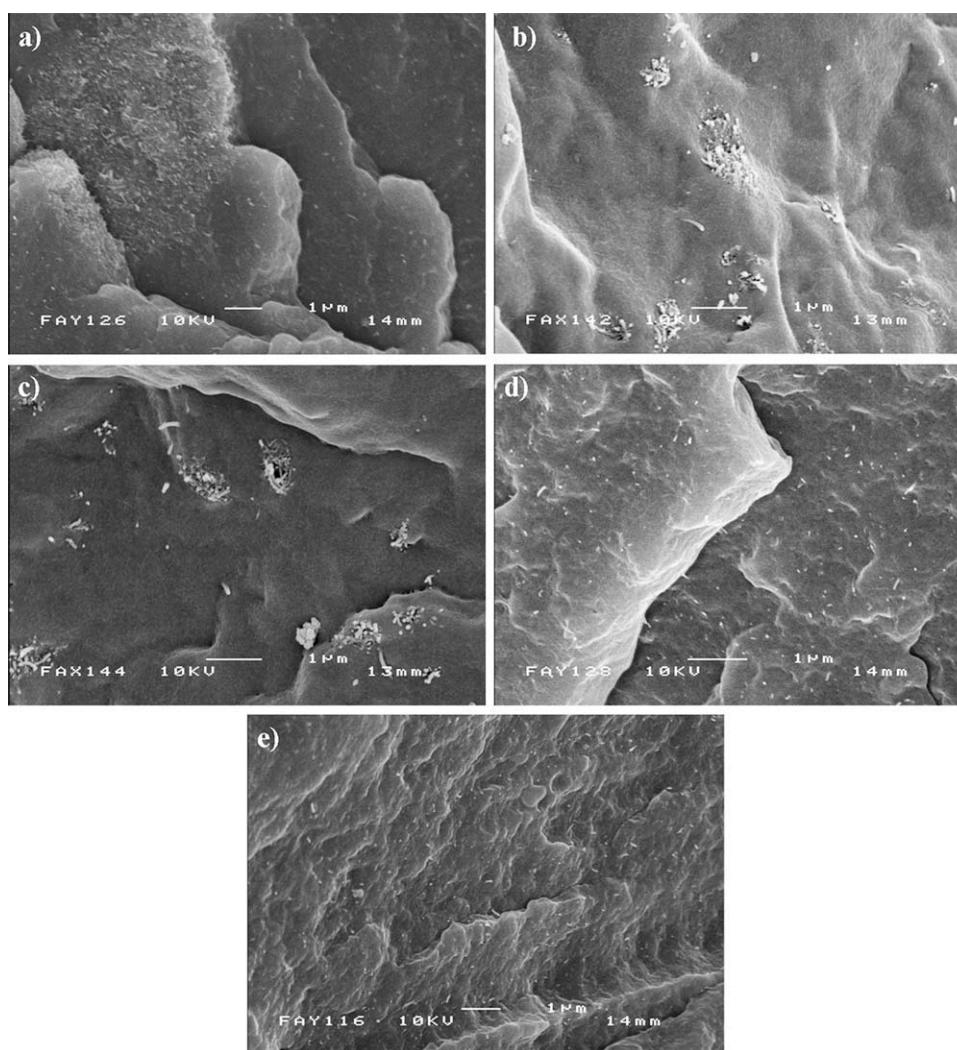


Figure 2 SEM graph showing the dispersion quality of MWCNT/PA6 composites containing 0.5 wt % MWCNTs processed at (a) 100 rpm, 10 min; (b) 130 rpm, 10 min; (c) 160 rpm, 10 min; (d) 200 rpm, 10 min; and (e) 250 rpm, 15 min, respectively.

and ultrasonicated for 30 min to form a master solution. Then the master solution and additional 350 g ϵ -caprolactam were mixed in a closed autoclave for the polymerization. The polymerization temperature was maintained at 230°C for 6 h. Flowing nitrogen was used to exhaust water during the process. The products were removed from the autoclave and pelletized, extracted in water at 80°C for 12 h, and then dried in vacuum oven for 12 h. As a result, CNT/PA6 composites containing 3 wt % MWCNTs or MWCNTs-COOH were obtained.

RESULTS AND DISCUSSIONS

Processing condition study

Different melt processing conditions are used to dilute the master batches produced by melt compounding and *in situ* polymerization, respectively.

The effect of processing condition on the dispersion status of fillers and mechanical properties of the composites are investigated. The objective of the processing condition study is to choose the optimum condition to process the composites containing different filler contents. As shown in Figure 1, the stress-strain curves of PA6/MWCNT composites diluted down at different conditions from master batches produced by both melt compounding and *in situ* polymerization are plotted.

For melt-based processes, composites produced under the condition of 200 rpm 10 min and 250 rpm 15 min showed higher strain at break than other conditions. This indicates that a better dispersion is achieved for composites processed at these conditions as aggregations [Figs. 2(a–c) and 4(a–c)] can initiate crack growth, leading to a reduction in strain at break for the composites processed at 100 rpm, 10 min; 130 rpm, 10 min; and 160 rpm, 10 min. It is

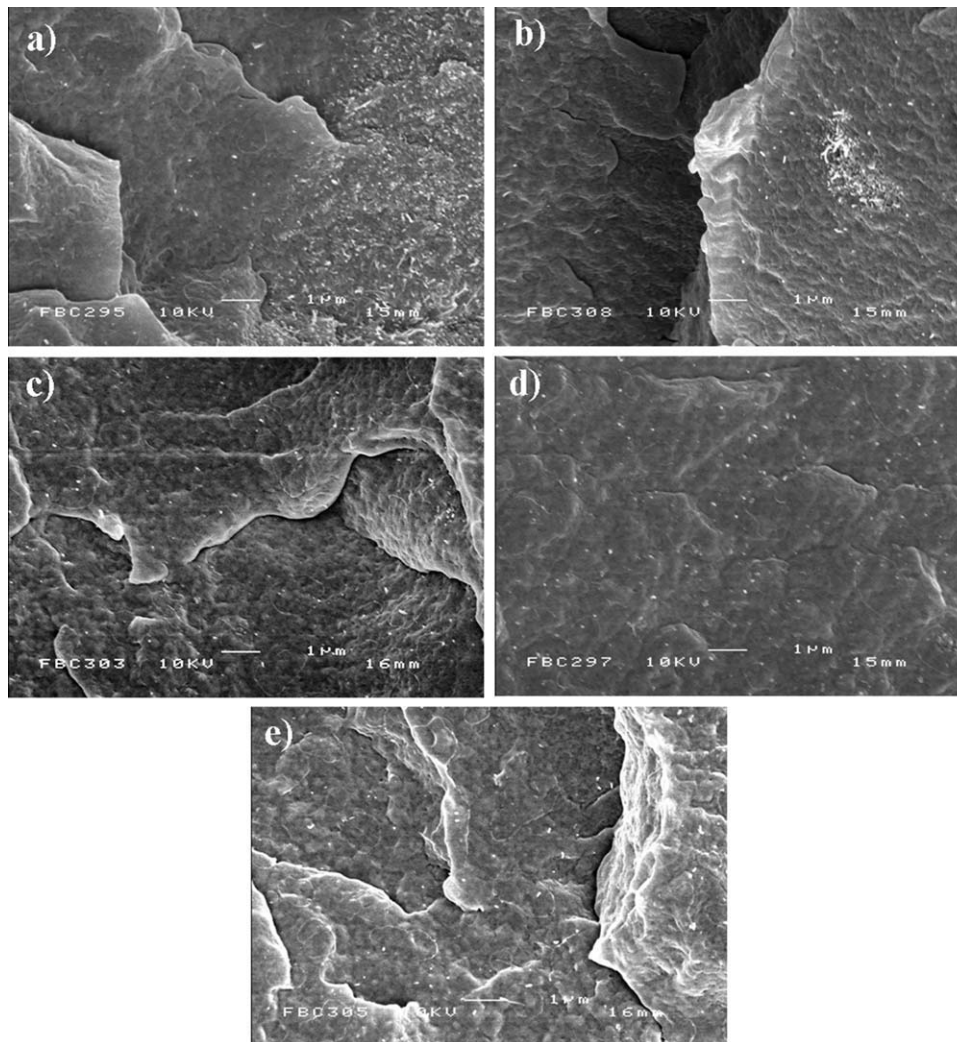


Figure 3 SEM graphs showing MWCNT/PA6 composites containing 0.5 wt % MWCNTs diluted at the conditions of (a) 50 rpm, 5 min; (b) 100 rpm, 10 min; (c) 130 rpm, 10 min; (d) 160 rpm, 10 min; (e) 200 rpm, 10 min.

confirmed in Figures 2(d,e) and 4(d,e) that a good dispersion is achieved in the composites processed under the condition of 200 rpm, 10 min and 250 rpm 15 min. A relative poorer dispersion is obtained for composites processed at 100 rpm 10 min; 130 rpm, 10 min; and 160 rpm, 10 min. To keep the processing condition as “mild” as possible to avoid polymer degradation and tube length shortening, 200 rpm and 10 min is chosen as the condition to finally process the CNT/PA6 composites based on melt compounding containing different loadings of CNT for further investigation.

For *in situ* polymerization based CNT/PA6 composites, the mechanical property in terms of strain at break for the composites processed under different conditions is shown in Figure 1. As discussed previously, it indicates that MWCNTs are well dispersed at process conditions of 130 rpm, 10 min; 160 rpm, 10 min; and 200 rpm, 10 min. Figures 3 and 4(f-j) shows the morphology of the composites containing

0.5 wt % MWCNTs processed under the conditions of (a) 50 rpm, 5 min, (b) 100 rpm, 10 min, (c) 130 rpm, 10 min (d) 160 rpm, 10 min and (e) 200 rpm, 10 min, respectively. It shows that poor dispersion of MWCNTs is obtained in the composites processed under the condition of 50 rpm, 5 min and 100 rpm 10 min. Nevertheless, dispersion is much better for composites processed under the condition of 130 rpm, 10 min; 160 rpm, 10 min; and 200 rpm, 10 min. These morphological results are in good agreement with the results obtained from mechanical tests. Therefore, the process condition for dilution of masterbatches from *in situ* polymerization is chosen as: 130 rpm, 10 min again to avoid possible polymer degradation and tube length shortening during mixing.

By comparing the process conditions needed to achieve good dispersion of MWCNT in PA6 matrix, one can observe that a higher mixing rate (thus, higher shear rate) is needed to process the composites based on melt compounding rather than *in situ*

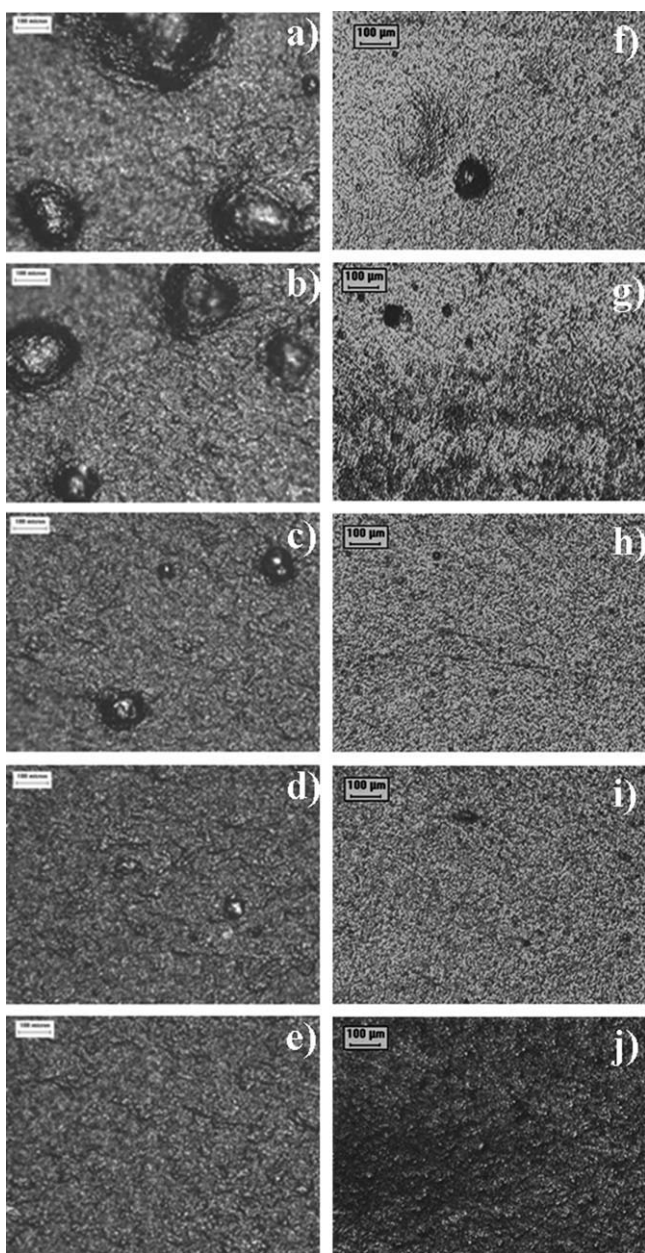


Figure 4 Optical microscopy pictures showing the dispersion state of filler in a mm scale (scale bar: 100 μm) of melt processed composites under the condition of: (a) 100 rpm, 10 min; (b) 130 rpm, 10 min; (c) 160 rpm, 10 min; (d) 200 rpm, 10 min, and (e) 250 rpm, 15 min. The composites diluted from master batches produced by *in situ* polymerization at the condition of: (f) 50 rpm, 5 min; (g) 100 rpm, 10 min; (h) 130 rpm, 10 min; (i) 160 rpm, 10 min; (j) 200 rpm, 10 min.

polymerization. Therefore, it can be concluded that dispersion of MWCNTs in the masterbatch can be achieved better through an *in situ* polymerization process than a melt compounding process.

Thermal properties

Thermal properties of CNT/PA6 composites are characterized by DSC and TGA. Figure 5 shows the

DCS crystallization curve at a cooling rate of $10^\circ\text{C}/\text{min}$: (a) MWCNT/PA6 and (b) MWCNTs-COOH/PA6. It is shown that MWCNTs and MWCNTs-COOH have clear nucleating effects on PA6 as shown by the clear increase in both crystallization temperature and crystallinity. However, both crystallization temperature and crystallinity did not further increase above 0.25 wt % filler loading. Another important information which needs mentioning is the observation that CNT/PA6 composites have two crystallization exotherms of similar shape as the crystallization curves reported in literature.¹¹ The second crystallization exotherm is caused by adding MWCNTs into the matrix.

Thermal stability of the nanocomposites is also investigated. There are few mechanisms suggested in literature about improvement of thermal stability in CNT/polymer composites. Neither MWCNTs nor MWCNTs-COOH have improved the thermal stability of the PA6 matrix. However, better improvement is shown in air. The temperature at maximum degradation rate are $442\text{--}462^\circ\text{C}$ and 464°C for neat PA6, 1 wt % MWCNTs and 1 wt % MWCNTs-COOH, respectively. Both MWCNTs and MWCNTs-COOH filled composites have a higher temperature at maximum degradation rate in air than neat PA6 in nitrogen. This improvement is more significant than the result demonstrated by Li et al.,¹² where a similar two-step degradation process is obtained for both neat PA6 and the composites in air.

Mechanical properties—Effect of filler loading and chemical modification

Mechanical properties for the composites based on melt compounding containing different loadings of MWCNTs or MWCNTs-COOH are shown in Figure 6. It is clear that the best mechanical properties in terms of Young's modulus and tensile strength are achieved at loadings between 0.1 wt % and 0.25 wt %. As discussed in our previous work,¹³ for the same processing condition, the composites containing higher filler loadings led to poorer dispersion of CNTs in the matrix. Therefore, CNT aggregates that can act as crack initiators during deformation, which results in the best mechanical performance, is obtained for composites containing relative low filler content. The effect of chemical functionalization of MWCNTs on the mechanical performance of the composites is pronounced in a higher tensile strength and lower strain compared with the same content of raw MWCNTs. It indicates that the interface between MWCNT and PA6 is improved by -COOH group attached on the MWCNTs.

For *in situ* polymerization based composites, the masterbatch produced by *in situ* polymerization is diluted into different loadings under process

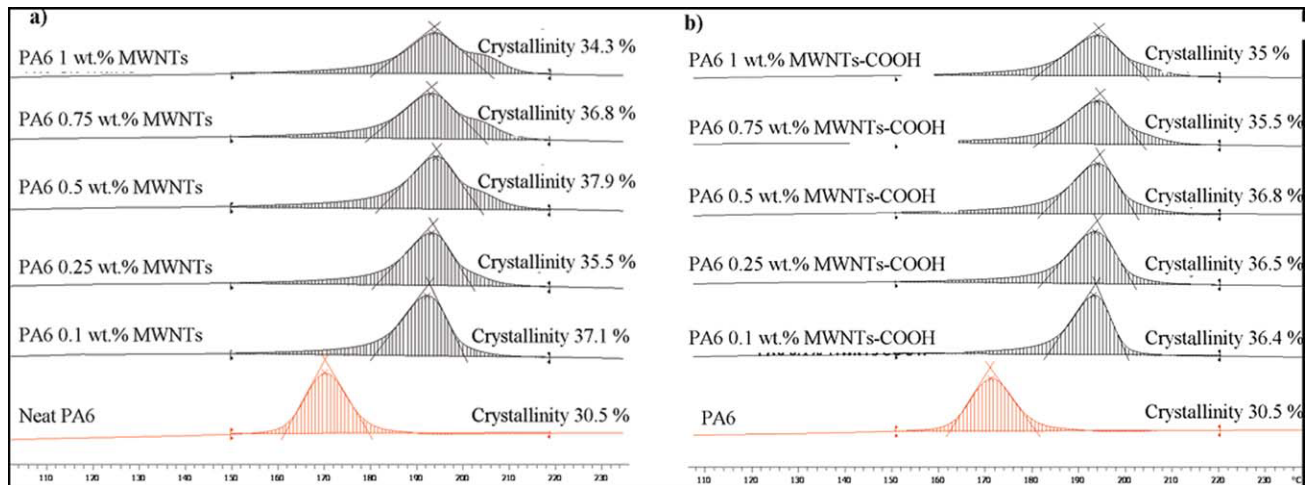


Figure 5 DSC crystallization curves from (a) MWCNTs/PA6 and (b) MWCNTs-COOH/PA6 at cool rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

condition of 130 rpm for 10 min. The mechanical properties of MWCNT/PA6 composites and MWCNT-COOH/PA6 composites are shown in Figure 7. The properties maintained unchanged above 0.25 wt % filler loading. Functionalization seemed to have a positive effect on the tensile properties of the composites since it improves the interaction between CNT and matrix, as discussed previously. Figure 7(c) shows that the strain at break is increased by adding more filler into the matrix. Interestingly, this indicates an increase in toughness with the addition of CNTs into the composites. This could be caused by increased bonding between filler and matrix, whereas a good dispersion is created in the *in situ* polymerized masterbatch. Another possible explanation could be based on the fact that less destructive processing conditions are used for the *in situ* polymerized composites compared with the melt compounded ones, hence, MWCNT lengths are more preserved in the earlier case. This could lead to an increase in strain at break because of better crack bridging effects. Therefore, a significant strengthening and toughening effect is achieved for composites processed by *in situ* polymerization and melt compounding. In addition, it is well known that nanofillers could act as nuclear agent in semicrystalline polymers.^{13–15} The resulting increase in crystallinity (Fig. 5) could also be partially responsible for the increase in mechanical properties. Here, the increase in crystallinity for the nanocomposites is around 5%. It is rather moderate compared with the values reported in literature.^{14,15} Therefore, the improvement in mechanical performance is not mainly contributed by the increase in matrix crystallinity. In contrast with the increase in crystallinity, a decrease in crystallinity has been reported in polymer matrix caused by adding different nanofillers.^{16,17} It is caused by the reduced chain mobility in the system

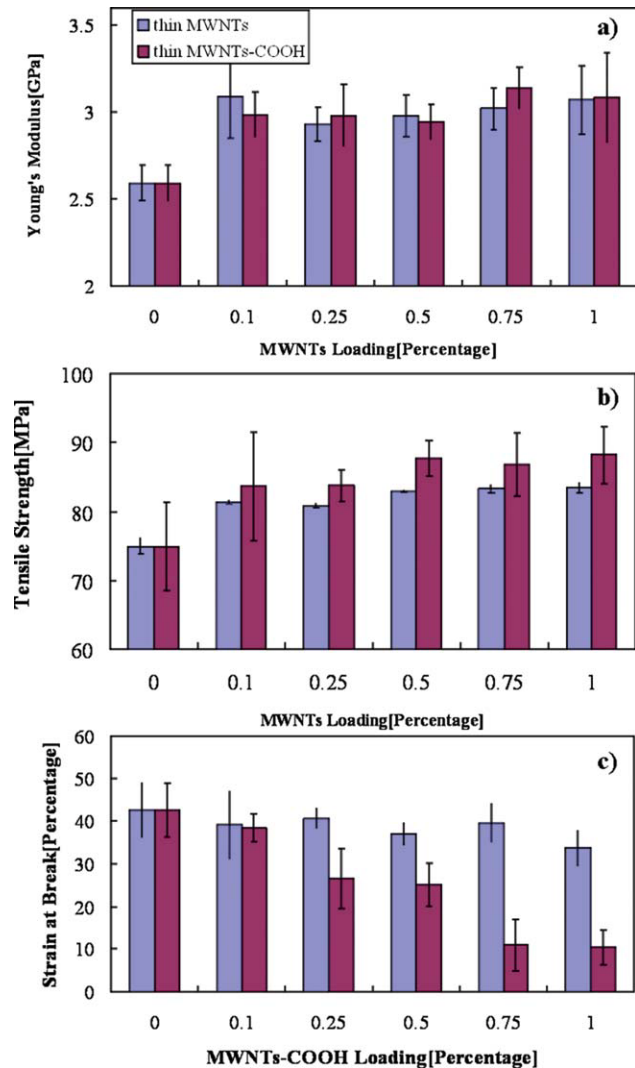


Figure 6 Mechanical properties of melt process based MWCNT/PA6 composites and MWCNT-COOH/PA6 composites in terms of (a) Young's modulus, (b) tensile strength, and (c) strain at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

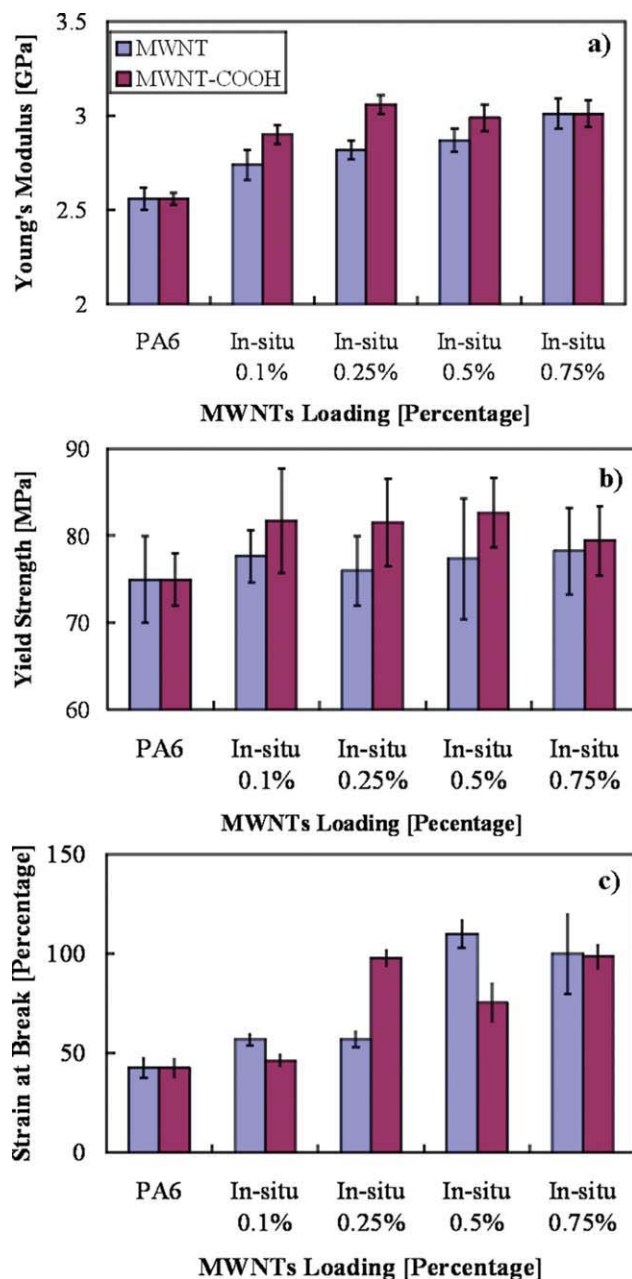


Figure 7 Mechanical properties in terms of Young's modulus (a), yield strength, (b) strain at break, and (c) for the composites diluted from *in situ* polymerized masterbatch processed at 130 rpm, 10 min containing either MWCNTs or MWCNTs-COOH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

because of the interactions between functional groups. In the current study, an increase in crystallinity is observed because of the nucleation effect of MWCNTs on PA6 matrix. Compared with the results in literature, it may be caused by the weaker interactions in the current system than the ones studied in literature.

The molecular weight of the polymerized PA6 might also play a role on the mechanical properties of the composites, as the molecular weight of the

PA6 obtained in the lab is often lower than the one produced in industry. Nevertheless, it should be noted that the content of polymerized PA6 in the final composites is from 3.2 to 25 wt %. It may only have insignificant effect on mechanical performance of the composites. Future work will be carried out on the molecular weight of such a polymerized PA6.

The potential of CNTs for toughening polymer composites is discussed in detail in literature,¹⁸ where the high aspect ratio, nanometer size, and high strength of the CNTs makes them a good candidate for toughening polymer composites compared with carbon fibers. However, high reinforcement content, high alignment, high interface strengths, and structural hierarchies are often needed to fully utilize the toughening potential of these materials as in natural biocomposites such as bone.¹⁹ Future work is needed to create hierarchical nanocomposites to produce high toughness and strength composites.

Conclusions

To achieve strengthening and toughening in polymer matrices, CNT/PA6 composites are produced by simple melt compounding and *in situ* polymerization routes. Different melt processing conditions are used to dilute master batches produced by melt compounding and *in situ* polymerization, respectively. The effect of processing conditions on the dispersion state of the fillers and the resulting mechanical properties of the composites are investigated. Chemical modification of MWCNTs has resulted in a 5–10 MPa increase in the strength of the composites. More interestingly, a maximum of 138% increase in strain at break and 5 MPa increase in strength were observed for the composites produced by *in situ* polymerization, indicating a toughening and strengthening effect of CNT on the composites.

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