Properties of PP/MWCNT-COOH /PP composites made by melt mixing versus solution cast /melt mixing methods

I Reinholds1, Z Roja1, J Zicans2, R Merijs Meri2, J Bitenieks2

1 Faculty of Chemistry of University of Latvia, 48 Valdemara Str., Riga, Latvia
2 Institute of Polymer Materials, Riga Technical University, 14 Azenes Str. 14, Riga, Latvia
E-mail: ingars.reinholds@lu.lv

Abstract. An approach on improvement of the properties of polypropylene / carbon nanotube (PP/CNT) composites is reported. PP blend compositions with carboxylic acid functionalized multi-walled carbon nanotubes (MWCNT-COOH) at filler content 1.0 wt.% were researched. One part of the composites was manufactured by direct thermoplastic mixing PP with the filler, but the other one was made from solution casted masterbatch with the following thermoplastic mixing. An increase of mechanical properties (Young’s modulus, storage modulus and tensile strength), compared to an increase of glass transition temperature indicated a reinforcement effect of CNTs on PP matrix, determined from the tensile tests and differential mechanical analysis (DMA), while the elongation was reduced, compared to PP matrix. By differential scanning calorimetry (DSC) analysis, the effect of nanofiller on the reorganization of PP crystallites was observed. A noticeable enhanced effect on increase of the crystallization temperature was indicated for masterbatch manufactured composite. An increase of thermal stability was also observed, compared to pristine PP and the composite made by direct thermoplastic mixing PP with the filler.

1. Introduction
As one of the most used thermoplastic polymers, isotactic polypropylene, has many benefits in industrial applications due to its low cost, recyclability, noteworthy mechanical properties and the thermal resistance determined by its tacticity. From this point, it is a prospective material for manufacturing reinforced nanocomposites with novel properties. Single and multi-walled (SWCNT, MWCNT) carbon allotropic nanofillers and their modified forms have many benefits on the improvement of mechanical, electrical, thermal and other properties of polymer materials [1-2]. For sufficient enhancement of PP nanocomposite properties due to the reinforcing effect, the carbon nanofiller should be well dispersed in PP matrix [2-3]. Melt mixing is the most common method used for manufacturing composites of PP with macro and nano fillers [3]. The physical properties of such materials depend directly on the content of nanofiller, as an increase of its content can lead to reduction of performance due to agglomeration. The Van der Waals interaction forces of filler are too strong to be disrupted by the mechanical mixing [4]. The aim of the present work was to investigate the physical properties of composites made from isotactic PP and the carboxyl group functionalized MWCNTs by the direct thermoplastic mixing and by the formation of blends from PP/CNT masterbatches made by solution mixing and sonification both the components in o-xylene and to study extensively the dispersion of filler particles by the change of mechanical and thermal properties.
2. Materials and investigation methods

2.1. Materials

As the matrix, isotactic PP of trademark Moplen HP456J supplied by LyondellBasell Industries (density 0.905 g/cm$^3$, melt flow index 3.0 g/10 min) was used. Industrial grade carboxylic group functionalized multi-walled carbon nanotubes (MWCNT-COOH) of trademark TNIMC4 supplied by Chengdu Organic Chemicals (carboxylic acid content 1.55 wt.%, density 2.1 g/cm$^3$) synthesized by chemical vapor deposition (CVD) were applied as fillers. Reagent grade solutions of o-xylene (Alfa Aesar) and methanol (Penta) were used for masterbatch preparation.

The sample description for creation PP/1 wt.% MWCNT-COOH composite from masterbatch (composite B) is as follows: PP properly weighted using analytical weights was added to 100 mL of o-xylene in Erlenmeyer flask. The solution was heated in glycerol bath equipped with temperature measurement for 30 minutes at 125 °C with 1,000 rpm. In the second flask, MWCNT-COOH was added to the second portion of 100 mL of o-xylene followed by the mixing at 1,000 rpm for 15 minutes at room temperature and for 30 minutes in an ultrasound bath (ULTRASONS 3000515, 50/60 Hz, 4000 W). The solution of filler dispersion in o-xylene was heated at 125 °C for about 5 minutes and added to the mixture of PP/ solution followed by heating up to 10 minutes at 130 °C. The hot mixture was sonificated for 5 min in ultrasound bath followed by the heating for 5 min at 130 °C, repeated by twice. The following mixture was poured by portions in 500 mL of cold methanol, followed by a rapid stirring for 5 minutes. The masterbatch was filtered by membrane filter (Millipore VVLP, 0.1 µm) and desiccated at 80 °C for 24 h. Then in was crashed to the powder and added to PP followed by thermoplastic mixing of a total duration of 6 min on twin roll-mills at 190 °C, which was also used for the direct mixing PP with the filler (composite A). The plates for all compositions were obtained by compression molding at 180 °C and a pressure of 5 MPa with a transverse cross section 60 × 0.5 mm.

2.2. Methods

Differential scanning calorimetric measurements were carried out with Mettler Toledo DSC 1/200W under a nitrogen atmosphere. DSC scans were performed in a temperature range of 25 to 200 °C at a constant heating rate of 10 °C/min. The first heating cycle was used to eliminate prior thermal history. The cooling and the second heating scans were analyzed. The average weight range of samples was 10 mg. Results were calculated by applied software Mettler Graph Ware TA72 PS. 5.

Thermogravimetric analysis (TGA1/SF) was carried out by Mettler TG-50 equipment at temperature range from 25 to 600 °C at a heating speed of 10 °C/min under a nitrogen atmosphere.

Tensile tests of composite specimens were performed at 23±2 °C on a Tinius Olsen HIKS UTM at a deformation speed of 1 mm/min for determination of Young’s modulus (E) and at a deformation speed of 50 mm/min for stress-strain characteristics, e.g. stress at yield ($\sigma_y$), tensile strength ($\sigma_B$) and deformation at break ($\epsilon_B$) in accordance to ISO 527-2 standard. At least 8 parallel specimens were tested.

Dynamic mechanical analysis (DMA) was done by Mettler DMA/SDTA861e equipment within the temperature range from -40 to 100 °C at a heating speed of 10 °C/min, using nitrogen as a carrier gas.

3. Results and discussion

The average results of stress-strain properties for pristine PP and PP/MWCNT-COOH composites with the filler content 1 wt.% measured at room temperature are compared in Table 1. The addition of carbon nanotubes by direct mixing in PP matrix and by manufacturing through the masterbatch technique affect an increase of the Young’s modulus by 9.4 % and by 22 % compared to pristine PP, indicating an increase of MWCNT distribution in polymer matrix for the last ones.
However, the elongation at break decreases as well as the stress at break for composites, while the yield stress increases by 14% for masterbatch manufactured composite, indicating an increase of the nanofillers distribution in PP matrix, acting as the reinforcing filler (Table 1).

Table 1. Mechanical properties of PP and PP/MWCNT-COOH composites.

| Sample     | E (MPa)   | \(\sigma_Y\) (MPa) | \(\sigma_B\) (MPa) | \(\varepsilon_B\) (%) |
|------------|-----------|--------------------|--------------------|-----------------------|
| PP         | 1380±100  | 34.5±0.5           | 42±2               | 700±100               |
| Composite A| 1510±100  | 33.5±0.5           | 26.5±0.5           | 19±8                  |
| Composite B| 1690±100  | 39.5±0.5           | 37±2               | 16±6                  |

E – the Young’s modulus, \(\sigma_Y\) – yield stress, \(\sigma_B\) – stress at break, \(\varepsilon_B\) – elongation at break.

The investigation of DSC cooling scans indicate a notable increase of PP crystallization temperature by 6 and by 11°C for composites A and B compared to pristine PP due to the CNTs nucleating effect (Figure 1a) with an enhanced behavior for masterbatch compounded composite, that also indicates a reduction in melting temperature, due to an decrease of the arrangement of crystallites in the PP matrix in the presence of distributed CNTs (Figure 1b). The degree of crystallinity for B composite increased from 42% for pristine PP and A composite to 48% for B composition.

Figure 1. DSC curves of cooling (a) and the 2nd heating scan (b) for pristine PP, PP/MWCNT-COOH composites (filler content 1 wt.%) made by direct thermoplastic mixing (A) and made from masterbatch (B).

The measurements of storage modulus (E’) by DMA indicate an increase of storage modulus of PP in the presence of the filler at higher extent for masterbatch manufactured composite (Figure 2a).

Figure 2. DTA curves of the storage modulus (a) and the mechanical loss factor (b) for pristine PP, PP/MWCNT-COOH composites (filler content 1 wt.%) made by direct thermoplastic mixing (A) and made from masterbatch (B).
It should be noted that MWCNT nanofiller affects an increase of storage modulus at lower temperatures by 1.14 and by 1.27 times for A and B composites compared to pristine PP, affecting an increase of crack resistance of PP matrix that is beneficial for this material [2]. However, the storage modulus increase also at room temperature by 1.26 and by 1.21 times due to the reinforced effect of the nanofiller dispersion in PP also indicated by the shift of the mechanical loss factor curves to higher temperatures and an increase of Ps glass transition temperatures in the presence of nanofillers.

In Figure 3a the profiles of TGA curves related to the materials obtained are shown. There is notable a shift of the curves of PP/MWCNT-COOH nanocomposites to higher values of degradation temperature in relation to those corresponding to pristine PP. However, the masterbatch made composite may include PP fragments of reduced PP crystallinity of lower thermal stability, affecting the small peak in Figure 3b, corresponding to the first derivative of TGA. Meanwhile, the filler particles affect an increase of $T_{\text{max}}$ values by 6 °C and 16 °C for composites A and B, indicating an increase of the filler distribution in PP matrix for masterbatch manufactured composites (Figure 3b).

![Figure 3. TGA curves (a) and the first derivatives (b) for pristine PP, PP/MWCNT-COOH composites (filler content 1 wt.%) made by direct thermoplastic mixing (A) and made from masterbatch (B).](image)

4. Conclusions

An experimental investigation on the effect of functionalized MWCNT filler interaction with PP matrix at MWCNT-COOH content equal to 1 wt.% was done. The method of manufacturing nanocomposites by a complex solution mixing and thermoplastic mixing method was done, showing an enhanced effect of mechanical and thermal properties for made nanocomposites compared to pristine PP and even to composite made by the direct thermoplastic mixing. The changes of structure indicated an increase of crystallization temperature that could indicate a nucleating effect of filler nanoparticles also affecting a reduced thermal destruction compared to pristine PP. The future experiments should be continued in order to better explain the changes of composite morphology especially at higher content of nanofiller in contrast to manufacturing method evaluation of composites.

Acknowledgements: This work was supported by The National Research Program of Latvia in Materials Science No.6.

References
[1] Breuer O Sundararaj U 2004 Polymer composites 25 630-645
[2] Bikaris D 2010 Materials 3 2884-2946
[3] Han Z D Fino A 2011 Progress in Polymer Science 36 914-944
[4] Zhorin V A Muhina L L Razumovskaya I V 2008 Polym Deg Stabil 93 952-967