

ELABORATION AND STUDY OF THE THERMO-MECHANICAL PROPERTIES OF AN ALIGNED CNT - POLYPROPYLENE NANO-COMPOSITE BY TWIN-SCREW MIXER

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Abstract. This study presents first the fabrication of a nanocomposite material based on Multi-Walled Carbon Nanotubes, and on a thermoplastic polymer matrix. First, a twin-screw mixer had been employed for preparing polypropylene nanocomposites loaded at 0.1, 1, 2, and 5wt% of MWCNT. Second, a characterization of rheological behavior for polypropylene as well as polypropylene/multi-walled carbon nanotube mixtures, at three temperatures (180, 200, and 220 °C,) has been carried out using cone and plate rheometer. Then, its thermo-mechanical properties have been studied. The work demonstrates how the addition of functionalized CNTs to a polypropylene will allow it to act as thermal conductor rather than as insulator.

1 INTRODUCTION

Incorporation of nanofiller such as carbon nanofiber, carbon nanotube (CNTs) has been successfully used to improve the matrix dominated and interlaminar properties [1,2]. CNTs exhibit unique structural properties such as exceptionally high specific stiffness and specific strength. Further addition of CNTs to the conventional fiber reinforced polymer composites has its own challenges [3,4]. The main challenge is to uniformly disperse them in the polymer matrix in order to obtain high interfacial area through which stress can be transferred from the weak matrix to the strong nanotubes [5]. Effective stress transfer through the CNTs/polymer interface is the key to obtain superior mechanical properties in the CNTs modified laminated composites [6]. In fact, polymer composites containing conducting fillers such as carbon black, carbon fiber, and metal fiber have been extensively investigated for various applications such as structural reinforcement, electromagnetic interference shielding, electronic packaging, radar absorption, heating element construction and high-charge storage capacitors [7-9].

Many researchers are interested in incorporating carbon nanotubes (CNTs) into polymers,

ceramics and metals to improve their mechanical properties by taking advantages of the superior physical, chemical and electronic properties of CNTs [10-12]. However, because CNTs have high aspect ratios and easily tangle with each other due to high surface energy and strong intrinsic van der Waals force [13,14], their uniform dispersion in a matrix is crucial for the manufacturing of sound nano-composites. The originality of the present study is the assessment of structural performance of these nanocomposites with a range of CNTs loading at various elevated temperature environments.

2 MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

The polymer matrix used to elaborate the nano-composites was a semicrystalline thermoplastic polypropylene (PP-EP548N) produced by Sabic Company[®] with melt flow Index (MFI) = 11g/10min (230 °C/2.16 kg) and density = 0.892g/mm³ (see Table 1). Commercially isotactic polypropylene (PP-EP548N) were supplied Multi-walled carbon nanotubes (MWCNTs) - NC7000 were purchased from Nanocyl Company[®] (Belgium) and were produced with purity higher than 90% and diameter range of 15-30 nm with typical length of 1-10 μ m.

Table 1: Material characteristics of Polypropylene

Material	Polypropylene (PP), P548N
Density [g/mm ³]	0.892
Transition temperature [°C]	-10
Melting temperature [°C]	155
Melt flow index (MFI) [g/10min]	[230°C/2.16kg]:11

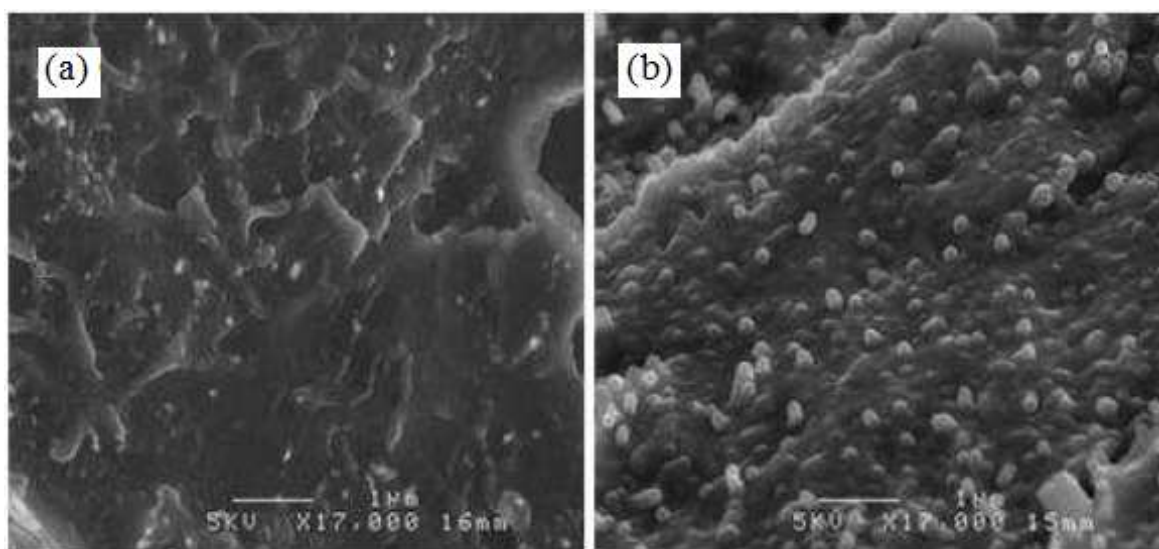


Figure 1: Dispersion of (a) 0.1%, (b) 0.5% MWCNT in nano-composite.

Figure 1 indicates the dispersion state of MWCNTs in the PP matrix of 0.1% and 5% nano-composites. The MWCNTs are mostly isolated from each other and uniformly distributed throughout the matrix of 0.1% MWCNT-composite whereas in 5% MWCNT-composites, local bunches of CNTs are found which form agglomerates as shown in Fig. 1b. The reduction of strength at higher MWCNT content can be attributed towards formation of these agglomerates, reducing the total CNTs/matrix interfacial area.

2.2 Nano-composites preparation

All Prior to the preparation of nano-composites, all of the materials were dried in an oven for 24 h at 80 °C to facilitate the dispersion of CNTs particles into the PP. Firstly PP was introduced in the a Brabender® mixer with a pair of rotor blades (see Fig.2); after the melting of the PP, CNTs were then carried out in. For the melt mixing process, the rotation speed and temperature of the mixing chamber were set at 30 rpm and 180 °C, respectively, and the blending continued for 30 min. After pelletizing, blend granules will be used in the injection process. In order to prepare tensile specimens for measurement of mechanical properties, the mixture PP loaded with the CNTs was injected into a die mould cavities.

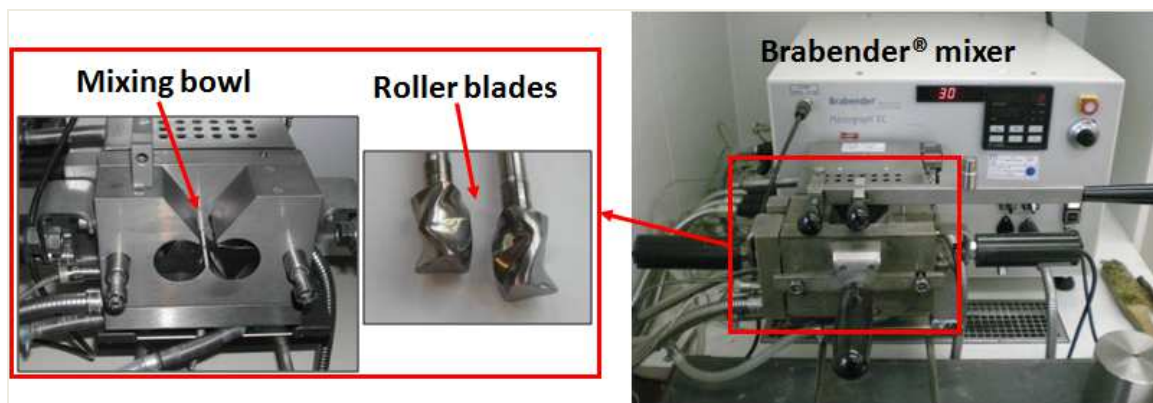


Figure 2: Photograph of Brabender® mixer and its internal structure.

2.3 Characterizations

The morphology of CNTs nano-particles and nano-composites were examined by scanning electron microscopy. The rheological analyses were carried out using rheometer HAAKE MARS III with a cone and plate geometry with the diameter of 35 mm and the cone angle of 2°. The test temperature is set from 180 to 220 °C beyond the melting temperature of polypropylene and below its degradation temperature. The shear rate has been chosen in a range from 10^{-1} to 10^2 s^{-1} . Dynamic measurements of rheological properties were carried out using the HAAKE MARS III using parallel plate geometry (25 mm diameter and 1 mm gap). Frequency sweeps from 0.1 to 100 rad/s were performed. For rheological measurements, PP/CNTs samples were tested within the linear viscoelastic strain range. Thermogravimetric/differential thermal analysis (TG/DTA) of PP/CNTs nano-composite were carried out using a thermobalance Setaram® thermal analyzer from room temperature to 500 °C, at a rate of 10 °C/min in a continuous argon flow.

3 RESULTS AND DISCUSSION

In this paper, different loading ratio of the CNTs have been selected to elaborate the PP/CNTs nano-composite by melt mixing process. The curves in figure 3 shows the final mixing torque variation of the PP and PP/CNTs nano-composite (loading ratio from 0.1 to 5 wt.%), vs. mixing time. Uniform mixing is achieved when the torque reaches a steady state value. From the results, it reveals that:

- the addition of the CNTs can increase effectively the final mixing torque of the nano-composites which means the addition of CNTs decreases the fluidity of the nano-composite;
- increasing the CNTs content can increase the final mixing torque, when the CNTs content is below to 1wt.%, there is no evident difference comparing to the pure PP; when the CNTs content is beyond 1wt.%, an evident increase of the mixing torque for the nano-composite is observed.

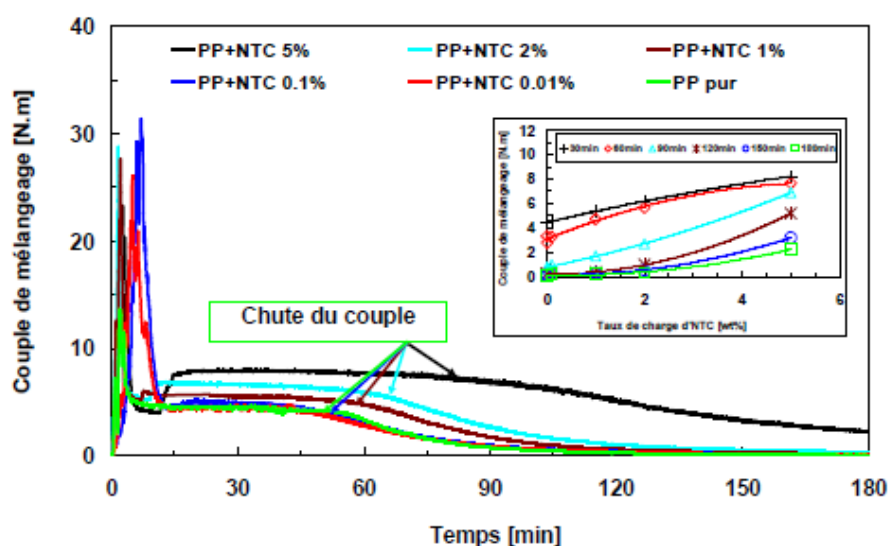


Figure 3: Mixing torque vs. time for PP and PP/CNTs nano-composites at 180°C during 30 min.

Figure 4 illustrates the influence of the CNTs loading ratio to the nano-composites shear viscosity tested at 220°C, the viscosity of composite increases clearly with a rise of the CNTs loading ratio from 0.1% to 1% (For the CNTs loading ratio of 10%, the viscosity is too high beyond the measurement range of the rheometer). Finally, the conclusion can be obtained that increasing the temperature and shear rate can decrease effectively the viscosity of CNTs/PP nano-composites and improve their capacity of filling the mould cavities, but increasing the CNTs loading ratio results in the rise of the nano-composites viscosity which is not conducive to the cavities filling.

Figure 5, it is shown that the storage modulus and loss modulus of the CNTs/PP nano-composites increases lightly with the increase in MWCNT up to 5 wt%. The results shown in Fig. 5 indicate that increasing CNTs concentration leads to a transition from convex to concave curves. Therefore, at sufficiently high concentrations the elastic modulus tends to level off as frequency goes to zero.

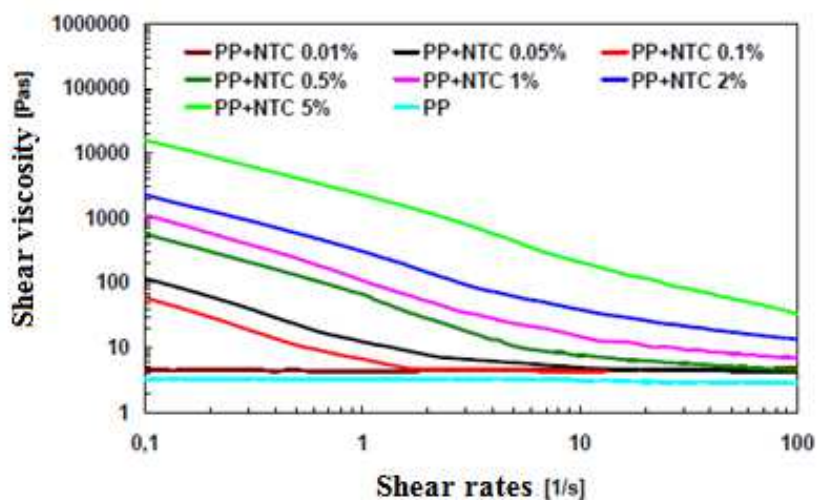


Figure 4: The shear viscosity of PP loaded respectively with 0.1 and 1wt% CNTs vs. shear rate at 220°C.

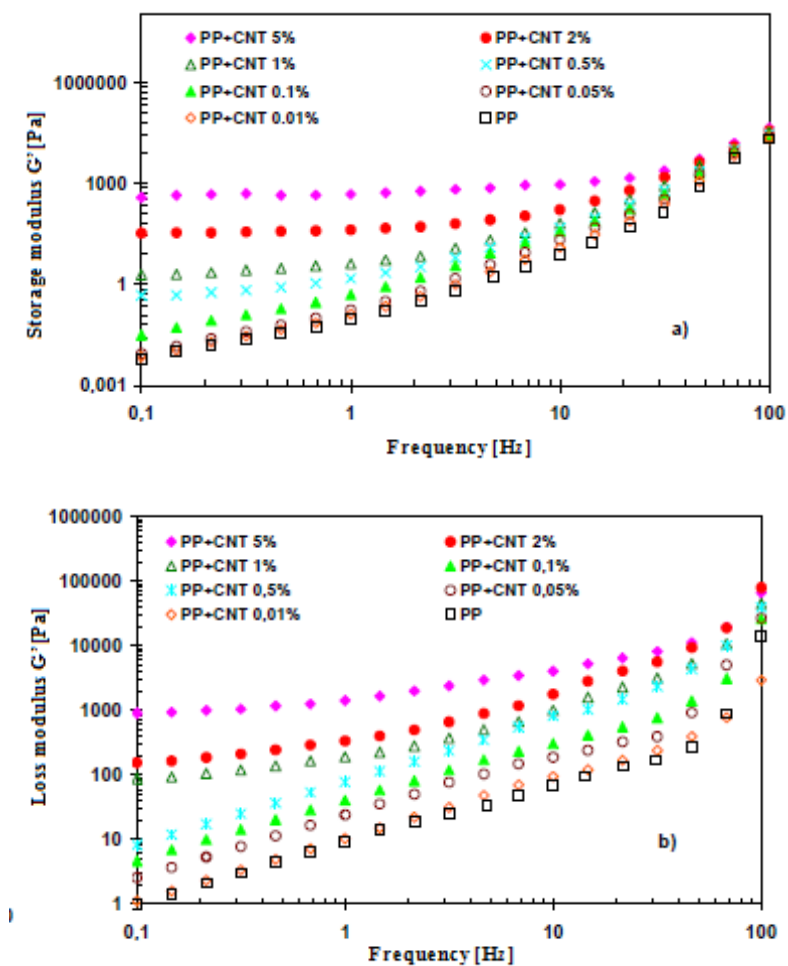


Figure 5: Variation of the viscoelastic modulus with frequency for the indicated compositions (180 °C).

Thermo-gravimetric analysis (TGA) was performed on nano-composites at all concentrations to obtain additional confirmation of both the CNTs content and the structure of the nano-composite, as well as to determine the effects of the CNTs on the thermal stability of the nano-composite. TGA was carried out under a argon atmosphere. The resulting curves are shown in Fig. 6a. In the case of nano-composite, an initial 98% weight loss at > 350 °C revealed the oxidation of amorphous carbon present in the sample and also attributed to the decomposition of PP and was degraded completely at 430 °C. This method can determine the actual CNTs content in the nano-composites. The degradation temperature of the nano-composites increased with CNTs content. A maximum increase of 35 °C was observed for the 5 wt.% nano-composite. This indicates also that the thermal stability of the PP nanoparticles was improved by the addition of CNTs. The incorporation of nano-particles CNTs on PP matrix resulted in an increase in crystallization temperature (T_c). In the case of pristine PP matrix, the T_c was observed at 95 °C and was shifted to 120 °C for the 5 wt.% nano-composite. Such an effect on the T_c obtained there are also observed on the glass transition (T_g) and melting temperatures (T_f).

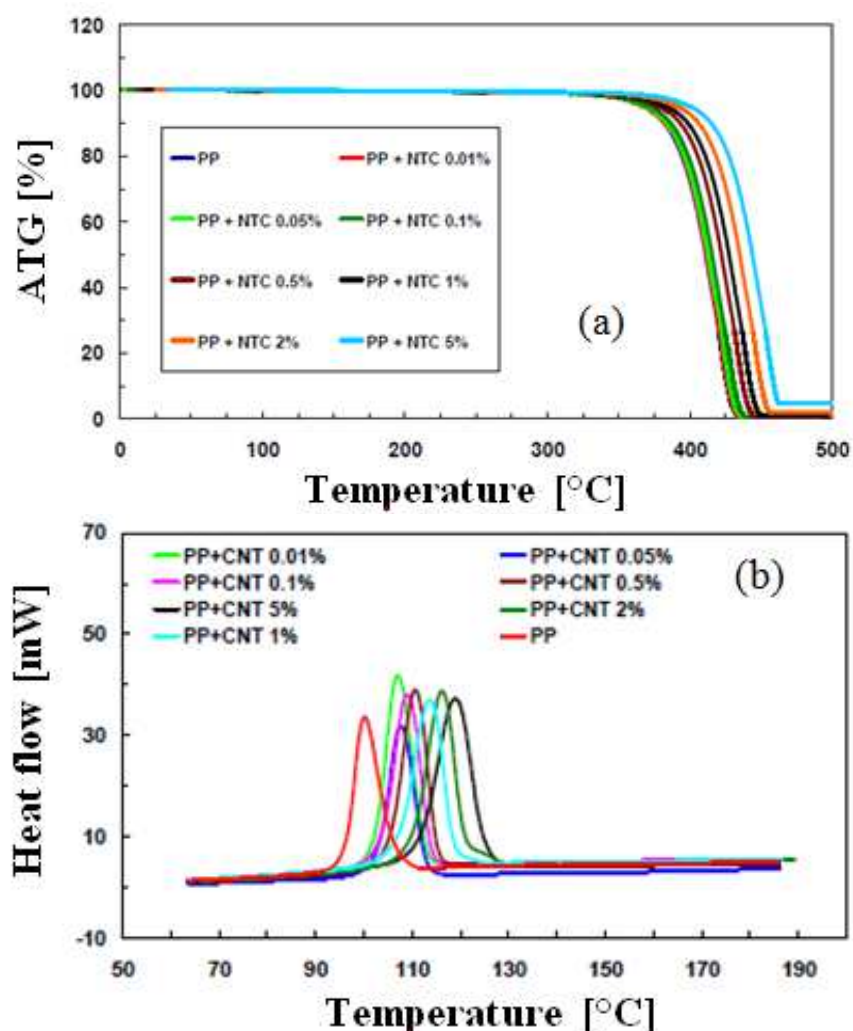


Figure 6: Thermal properties of the CNTs/PP nano-composite: (a) TGA and (b) DSC analysis.

The stress-strain plots for samples with CNTs loading at various in-situ temperatures are shown in Fig. 7a. The service temperature of these materials is limited in accordance with their melting temperature (T_f). Hence the maximum in-situ testing temperature was so chosen that it is under to the T_f of the nano-composites. The impact of various CNTs loading on nano-composites can be noticed from Fig. 7b. The properties obtained from these stress-strain plots are then reported in Table 2. Addition of 1% MWCNT into the nano-composites resulted in enhancement of both modulus and strength by 14.6% and 39.7% respectively when tested at room temperature as shown in Fig. 7b. This huge increment in strength might be attributed to the efficient stress transfer from the polymer matrix to the stiff MWCNT through the subtle S/polymer interface.

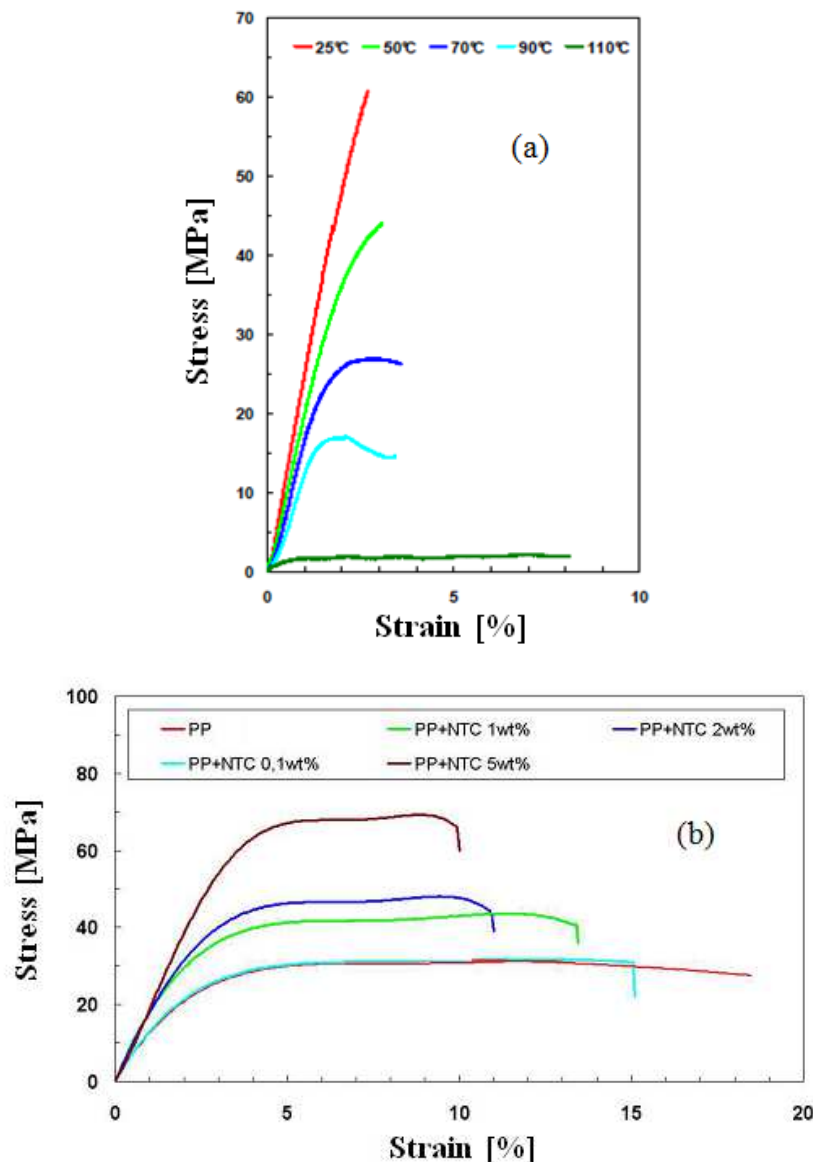


Figure 7: Stress-strain curves for nano-composites at: (a) different temperatures and (b) room temperatures with various CNT contents.

Table 2: Properties of nano-composites with varying CNT content at room temperatures

CNT content (%)	Young Modulus [GPa]	Resistance a la traction [MPa]
0.0	1.37±0.02	31.06±0.02
0.1	1.43±0.03	31.37±0.03
1.0	1.57±0.05	43.36±0.04
2.0	1.63±0.04	47.53±0.02
5.0	1.89±0.03	68.90±0.02

6 CONCLUSIONS

Homogenous multi-wall carbon nanotube/polypropylene nano-composites have been fabricated using a twin-screw Brabender[®] mixer. Based on experimental investigations of impact behaviour of PP filled with multi-walled carbon nano-tubes (CNTs), the following conclusions can be drawn:

- From the results of the rheological properties of the PP/MWCNT nano-composites, the increase in the viscosity was observed, that may be due to the increase inhomogeneous dispersion of the MWCNT in the PP matrix. The rheological properties of these nano-composites blends were investigated under shear flows. Our small-amplitude dynamic shear rheological studies showed that both the complex viscosity increase monotonically with increasing MWNT content,
- Introduction of CNTs to the PP system can enhance the thermal stability of nano-composites due to an interaction between the outer walls of the CNTs and PP lattices. Moreover, the formation of a barrier of CNT inhibits mass transfer and provides thermal insulation to shield the underlying polymer from the heat source,
- Tensile test measurements show that the tensile strength and Young modulus increases dramatically with the nanotube loading, while the draw-down ratio (drawability) significantly decreases. The addition of MWNTs to PP improves the mechanical, thermal, and wear properties of an already low performance matrix, without harming important characteristics, such as thermal and chemical resistance.

REFERENCES

- [1] Wang, B-C. Zhou, X. Ma, K-M. Fabrication and properties of CNTs/carbon fabric hybrid multiscale composites processed via resin transfer molding technique, *Compos Part B Eng* (2013) **46**:123-131.
- [2] Fiedler, B. Gojny, FH. Wichmann, MHG. Nolte, MCM. Schulte, K. Fundamental aspects of nano-reinforced composites, *Compos Sci Technol* (2006) **66**:3115-3125.
- [3] Siddiqui, NA. Khan, SU. Ma, PC. Li, CY. Kim, J-K. Manufacturing and characterization of carbon fibre/epoxy composite prepregs containing carbon nanotubes, *Compos Part Appl Sci Manuf* (2011) **42**:1412-1420.

- [4] Ma, P-C. Siddiqui, NA. Marom, G. Kim, J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review, *Compos Part Appl Sci Manuf* (2010) **41**:1345-1367.
- [5] Li, Q. Zaiser, M. Koutsos, V. Carbon nanotube/epoxy resin composites using a block copolymer as a dispersing agent, *Phys Status Solidi Appl Res* (2004) **201**:89-91.
- [6] Ma, P-C. Zheng, Q-B. Mäder, E. Kim, J-K. Behavior of load transfer in functionalized carbon nanotube/epoxy nanocomposites, *Polymer* (2012) **53**:6081-6089.
- [7] Al-Saleh, M. Sundararaj, U. Electromagnetic interference (EMI) shielding effectiveness of PP/PS polymer blends containing high structure carbon black, *Macromol Mater Eng* (2008) **293**:621-630
- [8] Kim, MG. Moon, JB. Kim, CG. Effect of CNT functionalization on crack resistance of a carbon/epoxy composite at a cryogenic temperature, *Composites Part A* (2012) **43**:1620-6127.
- [9] Theilmann, P. Chu, KM. Bandaru, PR. Asbeck, P. Park, SH. Optimisation of microwave absorption of carbon nanotube composites through use of carboxyl-epoxide functional group linkages, *Electron Lett* (2012) **48**:638-648.
- [10] Curtin, WA. Sheldon, BW. CNT-reinforced ceramics and metals, *Mater Today* (2004) 7:44-53.
- [11] Li, QQ. Rottmair, CA. Singer, RF. CNT reinforced light metal composites produced by melt stirring and by high pressure die casting, *Compos Sci Technol* (2010) 70:2242-2249.
- [12] Neubauer, E. Kitzmantel, M. Hulman, M. Angerer, P. Potential and challenges of metal-matrix-composites reinforced with carbon nanofibers and carbon nanotubes, *Compos Sci Technol* (2010) **70**:2228-2236.
- [13] Calvert, P. Nanotube composites-a recipe for strength. *Nature* (1999) **399**:210-221.
- [14] Coleman, JN. Khan, U. YK. Gun'ko, Mechanical reinforcement of polymers using carbon nanotubes, *Adv Mater* (2006) **18**:689-706.