HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 38(1). pp. 67-70 (2010)

MECHANICAL PROPERTIES OF POLYPROPYLENE/MULTI WALLED CARBON NANOTUBE COMPOSITES

A. SZENTES[1✉], G. HORVÁTH[1], CS. VARGA[2]

[1]Institutional Department of Chemical Engineering, University of Pannonia
H-8200 Veszprém, Egyetem u. 10., HUNGARY,
✉E-mail: szentesa@almos.uni-pannon.hu
[2]Institutional Department of Hydrocarbon and Coal Processing, University of Pannonia
H-8200 Veszprém, Egyetem u. 10., HUNGARY

Carbon nanotubes (CNTs) are promising additives for polymer composites due to their excellent special mechanical, electrical, and thermal properties. Polypropylene/multi walled carbon nanotube (PP/MWCNT) composites were produced in single and double screw extruders. The composites contained 0.5, 2, 3 and 5 wt% multi walled carbon nanotubes (MWCTN). For comparison, composites with carbon black as an additive instead of MWCNT have been made. The melt flow rate (MFR), flexural modulus, yield strength, tensile strength and heat deflection temperature (HDT) of the composites have been examined.

Keywords: carbon nanotubes, polypropilene, composites, mechanical properties

Introduction

Carbon nanotubes (CNTs) were discovered in the soot of arch discharge by Sumio Iijima in 1991 [1]. Carbon nanotubes are allotropes of carbon and members of the fullerene structural family. Carbon nanotubes are categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) [2]. MWCNTs consist in a variable number of graphene sheets rolled coaxially into a cylinder of nanometric diameter [3]. The interlayer distance in multi-walled nanotubes is close to the distance between graphene layers in graphite, approximately 0.34 nm. Typical diameter of MWCNTs are 10–20 nm, their typical length is above 20 µm.

Several production methods have been developed aiming at the production of carbon nanotubes in large scale, such as laser vaporization [4], electric arc discharge [5] and catalytic chemical vapor deposition of hydrocarbons over metal catalysts (CCVD technique) [6]. The first two methods are high temperature processes and can produce high quality nanotubes. However, the yields are poor and hence not adaptable for large-scale production. In contrast the CCVD technique is a very efficient method to produce multi-walled carbon nanotubes (MWCNTs) because this way could be a possibility to produce nanotubes at relatively low temperatures on a large scale at relatively low cost. This method is the most promising method to commercialize the carbon nanotubes growth. In CCVD method transition metals (Fe, Co or Ni) supported on oxides, zeolite or silica are used as catalyst precursor [7]. The combinations of transition metals and supports can be changed depending on the characteristics required, for example the size of the tubes. Bimetallic combinations of these transition metals are used for the synthesis of CNTs and the relatively high yield and quality have been explained by the characteristic behaviour of this alloy phase [8]. A very effective catalyst is a binary mixture of Co-Fe. Catalysts have been prepared by impregnation method using salts of Fe and Co.

CNTs are promising additives for polymer composites due to their excellent special mechanical, electrical, and thermal properties. The special mechanical properties are due to the strong bonding between the carbon atoms that form the carbene plane. The bond length is 0.142 nm which is lower than that in diamond (0.154 nm). The tensile strength of carbon nanotubes is high, 75-times higher than of steel filaments of the same size, and even 15-times higher than of carbon fibers. On the other hand, the density of carbon nanotubes is one sixth of steel. Their densities can be as low as 1.3 g/cm^3. These facts give excellent opprotunities to produce very strong materials with are light at the same time. Plastics enhanced with carbon nanotubes might be the new family of light and strong composites. [9]

Extrusion is the most effective and most important technology in polymer processing. This makes the thermoplastic polymer plastic, homogenizes its viscous melt, and degasifies it, if necessary. After this, the polymer is compressed, extruded in an open instrument of constant diamater and cooled down. Thus, polymer products of constant diameter can be produced in the desired legth, in continous run. [10]

Experimental

For the experiments, MWCNT products prepared by the Institutional Department of Chemical Engineering of the University of Pannonia were used. The MWCNT is unpurified, it contains the catalyst and the catalyst carrier in 10 wt%. According to transmission electron microscope (TEM) images, the diameter of the tubes is between 10 and 20 nm *(Fig. 1)*. The length of the tubes cannot be precisely measured. According to the scanning electron microscope (SEM) images, the length of the tubes is greater than 50 µm *(Fig. 2)*.

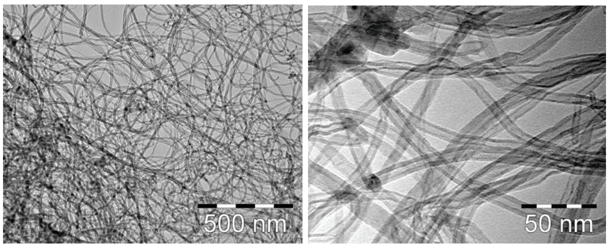

Figure 1: TEM images of multi walled carbon nanotubes

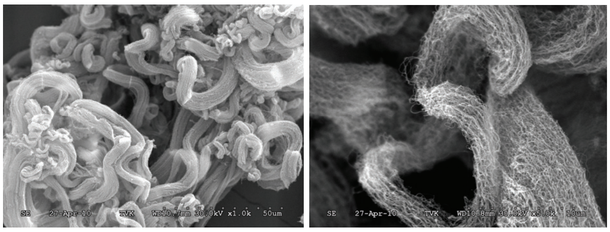

Figure 2: SEM images of multi walled carbon nanotubes

Polypropylene-based (PP) composites were prepared with a Brabender-type single screw extruder (SSE, zone temperatures: 1: 195 °C, 2: 200 °C, 3: 205 °C, 4: 210 °C, revolutions per minute: 40), and with a Werner & Pfleiderer-type double screw extruder (DSE, zone temperatures: 1: 195 °C, 2: 205 °C, 3: 210 °C, 4: 210 °C, 5: 210 °C, 6: 210 °C revolutions per minute: 100), to decide which method gives better results. The composites contain MWCNT or carbon black (C) in different quantities (0.5 2 3 and 5 wt%). The composites were also prepared with carbon black to make sure that the change in properties is because of the CNTs. The composites with the carbon black additive were prepared with the double screw extruder. The content of the composites is summarized in *Table 1*.

The normalized specimens with dimensions of 10 mm x 4 mm x 80 mm were produced with injection moulding (temperature: 180 °C, injection melt rate: 0.011 m/s, cooling time: 30 s) for the normalized examinations.

The melt flow rate (MFR, patent: ISO 1133, 230 °C, 2,16 kg), the flexural modulus (patent: ISO 178), the yield strength (patent: ISO 527), the tensile strength (patent: ISO 527) and the heat deflection temperature (HDT, patent: ISO 75) have been measured.

Table 1: The content of the composites

Sample code	PP (wt%)	MWCNT (wt%)	C (wt%)
PP	100		
PP/CNT/SSE/0.5	99.5	0.5	
PP/CNT/SSE/2	98	2	
PP/CNT/SSE/3	97	3	
PP/CNT/SSE/5	95	5	
PP/CNT/DSE/0.5	99.5	0.5	
PP/CNT/DSE/2	98	2	
PP/CNT/DSE/3	97	3	
PP/CNT/DSE/5	95	5	
PP/C/DSE/0.5	99.5		0.5
PP/C/DSE/2	98		2
PP/C/DSE/3	97		3
PP/C/DSE/5	95		5

Results

Fig 3 shows the effect of different additive contents on the MFR of PP/MWCNT and PP/carbon black melts. The MFR decreased with increasing CNT-content for PP/MWCNT composites prepared with both extruders. The value of MFR decreased more for samples prepared with the double screw extruder (PP/CNT/DSE) than for samples prepared with the single screw extruder (PP/CNT/SSE). This might be explained by the fact that a better homogeneity can be reached with the double screw extruder, than with the single screw extruder. The MFR values of samples containing carbon black did not change significantly.

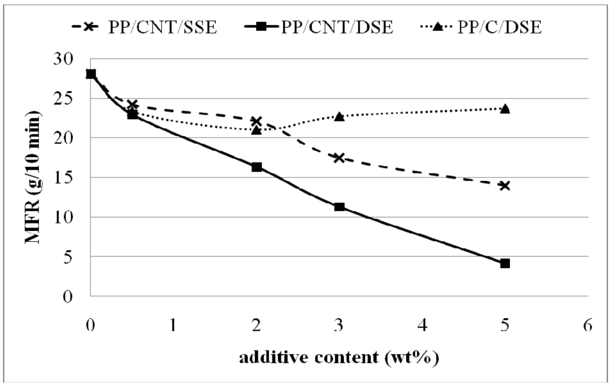

Figure 3: Effects of different additive contents on the MFR of PP/MWCNT and PP/carbon black melts

The value of the flexural modulus is indicative of the sample's flexibility. *Fig 4* shows the effect of different additive contents on the felexular modulus of PP/MWCNT and PP/carbon black composites. By increasing the MWCNT-content, one expects the flexural modulus to increase, too. As shown in Fig. 4, in the case of PP/MWCNT composites produced with the double screw extruder (PP/CNT/DSE), the value of the flexural modulus inreased significantly. As compared to polypropylene, the flexural modulus of the composite produced with the double screw extruder and which contains 5 wt%

MWCNT (PP/CNT/DSE/5) increased by 64%. An 18% increase is measured in the case of the composite produced with the single screw extruder. By increasing the concentration, the values are significantly better with the double screw extruder, compared to the single screw extruder. In the case of the carbon black additive (PP/C/DSE), the flexural modulus increased by approx. 30%, irrespective of the amount of additive.

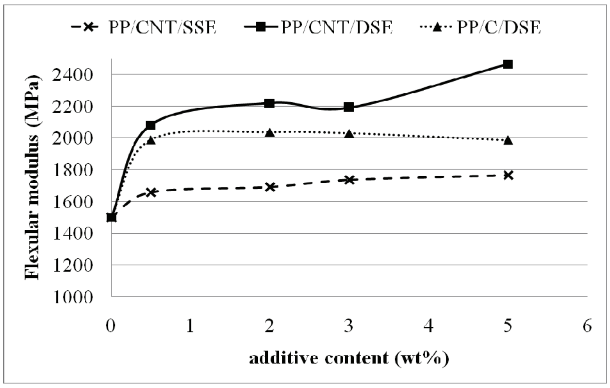

Figure 4: Effects of different additive contents on the felexular modulus of PP/MWCNT and PP/carbon black composites

The yield strength is the highest tensile stress that the sample is able to withstand during the tensile measurement. For certain materials, such as polypropylene, the value of the yield strength is different from the value of the tensile strength. *Fig 5* shows the effect of different additive contents on the yield strength of PP/MWCNT and PP/carbon black composites. For the MWCNT composites produced with the double screw extruder (PP/CNT/DSE), the yield strength increases with the CNT content, whereas this value decreases above 0.5 wt% MWCNT content for the composites produced with the single screw extruder (PP/CNT/SSE). The value of the yield strengtjh is 36.3 MPa for the sample containing 5 wt% MWCNT produced with the single screw extruder (PP/CNT/SSE/5), which is identical to the sample's tensile strength. In the case of the carbon black additive (PP/C/DSE), the tensile strength increases with 10%, irrespective of the amount of the additive.

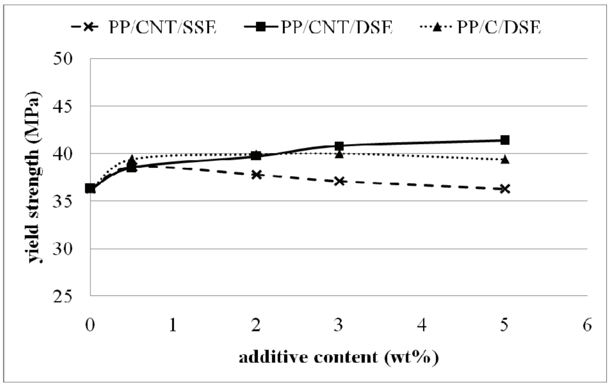

Figure 5: Effects of different additive contents on the yield strength of PP/MWCNT and PP/carbon black composites

Fig 6 shows the effect of different additive contents on the tensile strength of PP/MWCNT and PP/carbon black composites. The tensile strength is the stress under which the sample is torn. The tensile strength increases with the increasing percentage of the additive. The composite produced with the double screw extruder that contains 0.5 wt% MWCNT (PP/CNT/DSE/0.5) has an outstanding tensile strength of 36.7 MPa which means an increase of 36% as compared to the blank polymer (PP). The tensile strength values increased slightly for the composites containing carbon black, but this increase is significantly small compared ot the MWCNT composites. The composite containing 5 wt% carbon black has the same tensile strength as the 0.5 wt% MWCNT composite produced with the single screw extruder (PP/CNT/SSE/0.5), which is 30.7 MPa.

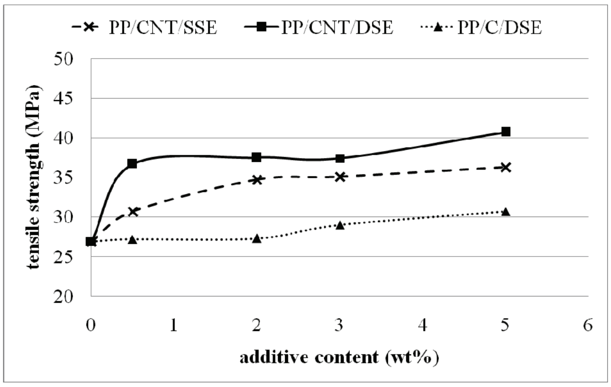

Figure 6: Effects of different additive contents on the the tensile strength of PP/MWCNT and PP/carbon black composites

The ability of the materials to withstand heat can be measured by HDT (heat-deflection) measurements. *Fig 7* shows the effect of different additive contents on the heat deflection temperature of PP/MWCNT and PP/carbon black composites.

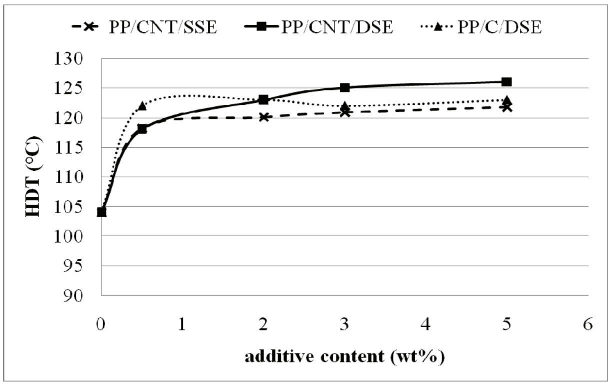

Figure 7: Effects of different additive contents on the the heat deflection temperature of PP/MWCNT and PP/carbon black composites

The blank polypropylene sample (PP) has an HDT temperature of 104 °C, which is significantly lower than for the composites containing additives. The value of the HDT temperature increases with increasing the MWCNT contents. The HDT temperature is 118 °C at 0.5 wt%

MWCNT (PP/CNT/SSE/0.5 and PP/CNT/DSE/0.5). The HDT temperature is 4 °C higher for the MWCNT composites produced with the double screw extruder (PP/CNT/DSE/2, PP/CNT/DSE/3 and PP/CNT/DSE/5) than for the composites of the same content produced with the single screw extruder (PP/CNT/SSE/2, PP/CNT/SSE/3 and PP/CNT/SSE/5).

It can be concluded, that the properties of the composites produced with the single and the double screw extruder with 0.5 wt% MWCNT content are nearly the same in the most cases, but with increasing MWCNT content, the composites made with the double screw extruder have better properties. The same mechanical value can be reached with lower MWCNT content with the double screw extruder, than with the single screw extruder. The reason for this is the double screw extruder's better homogenizing ability. According to the measurement results it can be concluded, that the double screw extruder is more appropriate for the production of the PP/MWCNT composites. The composites are more homogeneous, the dispersion of the CNT in the polymer matrix is significantly better than in the case of the single screw extruder. The composites containing carbon black were prepared with the double screw extruder. It can be seen that the amount of carbon black does not affect significantly the mechanical properties of the composite.

Conclusions

Polypropylene/multi walled carbon nanotube composites were produced in single and double screw extruders. The composites contained 0.5, 2, 3 and 5 wt% multi-walled carbon nanotube. For comparison, composites with carbon black as an additive instead of MWCNT have been made. The melt flow rate (MFR), flexural modulus, yield strength, tensile strength and heat deflection temperature (HDT) of the composites have been examined.

It can be concluded, that the properties of the composites produced with the single and the double screw extruder with 0.5 wt% MWCNT content are nearly the same in the most cases, but with increasing MWCNT content, the composites made with the double screw extruder have better properties. The same mechanical value can be reached with lower MWCNT content with the double screw extruder, than with the single screw extruder. The reason for this is the double screw extruder's better homogenizing ability. According to the measurement results it can be concluded, that the double screw extruder is more appropriate for the production of the PP/MWCNT composites. The composites containing carbon black were prepared with the double screw extruder. It can be seen that the amount of carbon black does not affect significantly the mechanical properties of the composite.

ACKNOWLEDGMENT

We acknowledge the financial support of this work by the Hungarian State and the European Union under the TAMOP-4.2.1/B-09/1/KONV-2010-0003 project.

REFERENCES

1. S. IJIMA: Nature, 354, 1991, 56.
2. S. IJIMA, T. ICHIHASHI: Nature, 360, 1993, 603.
3. L. P. BIRÓ, J. GYULAI, PH. LAMBIN, J. B. NAGY, S. LAZARESCU, G. I. MÁRK, A. FONSECA, P. R. SURJÁN, ZS. SZEKERES, P. A. THIRY, A. A. LUCAS: Carbon, 36, 1998, 689.
4. Y. SAITO, M. OKUDA, M. TOMITA, T. HAYASHI: Chem. Phys. Lett., 236, 1995, 419.
5. T. W. EBBESEN, P. M. AJAYAN: Nature, 358, 1992, 220.
6. W. Z. LI, S. S. XIE, L. X. QIAN et al.: Science, 274, 1996, 1701.
7. K. HERNADI, Z. KÓNYA, A. SISKA, J. KISS, A. OSZKÓ, J. B. NAGY, I. KIRICSI: Materials Chemistry and Physics, 77, 2003, 536–541.
8. Z. KÓNYA, J. KISS, A. OSZKÓ, A. SISKA, I. KIRICSI: Phys. Chem. Chem. Phys., 3, 2001, 155.
9. J. N. COLEMAN, U. KHAN, W. J. BLAU, Y. K. GUN'KO: Carbon, 44, 2006, 1624.
10. Z. SPITALSKY, D. TASIS, K. PAPAGELIS, C. GALIOTIS: Progress in Polymer Science, 35, 2010, 357.