CARBON NANOTUBES AS FILLER FOR ELECTROMAGNETIC INTERFERENCE APPLICATIONS

Jan Vácha

Technical University of Liberec, Studentská 2, 461 17 Liberec 1, Czech Republic
jan.vacha@tul.cz

Abstract: *This work examines the electrical properties of composite thermoplastic polymer matrix and carbon nanotubes. As basic matrix polybutylene terephthalate was used, to which nanoparticles in the weight percentage ratio were added. As filler multi-wall carbon nanotubes in various percentages by weight ratio were used. The nanocomposite was made by the Arburg injection molding machine. For evaluation of electrical behavior electromagnetic interference of the final composite materials with and without added nanofillers was measured. In this paper also mechanical properties are evaluated. These results are compared and discussed. Influence of conductive filler (multiwall carbon nanotube) on electrical and mechanical properties is evaluated and valid conclusions are deduced based on these findings.*

Keywords: *carbon nanotubes, nanocomposites, injection molding, electromagnetic interference*

1 INTRODUCTION

In nowadays, one of the most developing technologies is nanotechnology. Now it consists of four main areas - nanomaterials, nanoelectronics, molecular nanotechnology and microscopes working in the scale of nanometers. The same use is also in the high tech of nanocomposite materials, which today has properties that we previously could not imagine [1]. Growing application of these nanocomposites is in electrostatic discharge (ESD), electro-conductive (EC), electromagnetic interference (EMI) and radio frequency interference (RFI) applications. A conductive compound in manufactured products is dominated by injection moulding caused by fast growing demand for electronics goods and automotive components. Due to the ease of processing and improved heat dissipation properties, polymer nanocomposites with carbon nanotubes become attractive in the manufacture of automotive [2]. Carbon nanotubes have a many properties (mechanical and physical) that make them attractive for use in a broad spectrum of applications, especially as filler for nanocomposites. There are two kinds of carbon nanotubes: single-walled carbon nanotubes (SWCNTs) with one graphene layer and multi-walled carbon nanotubes (MWCNTs) with many graphene layers wrapped onto themselves, see Figure 1. Generally, an individual carbon nanotube is in a macromolecular structure with nanosized diameter and micrometer length. The diameter range for the SWNTs is between 0.4 and 5.6 nm [3], while that for MWNTs it is from several nanometers to several hundred nanometers. Their morphology depends very much on the production method and the treatment (for example, for dispersion purpose) before being put into the matrix [4].

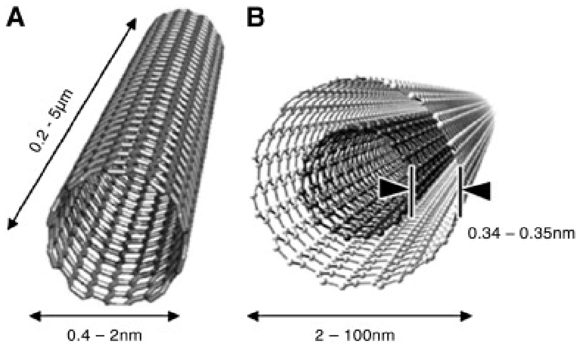

Figure 1 Scheme carbon nanotubes: single-wall carbon nanotube (SWCNT) and multi-wall carbon nanotube (MWCNT) [3]

However, CNTs have large specific surface area, bending fiber-like shape, and strong van der Waals interactions which are easy to make the CNTs agglomerate and entangled, and difficult to disperse in polymer. So, how to enhance the dispersibility of CNTs in polymer matrix has been one of the most concerns in the field of CNTs reinforced polymer-based composite materials. Therefore, functionalization of CNTs is extremely important for their dispersion, stress-transfer, and potential applications in polymer composites [5].

In this work MWCNT are used as filler in polybutylene terephthalate (PBT) polymer matrix and the effect on the nanocomposite is examined using electron microscopy, tensile test and measurement of electromagnetic interference.

2 EXPERIMENT

2.1 Materials

PLASTICYL PBT1501 is a conductive masterbatch based on polybutylene terephthalate loaded with 15% MWCNTs (NC7000™) from Nanocyl Company. For mixing pure polybutylene terephthalate with trade name Celanex 2002-2 from Resinex Company was used. The masterbatch was used as the parent matrix from which mixed polymer blends were created. Following weight ratio of multi wall carbon nanotubes was chosen 1, 2 and 5%. This percentage of the nanotubes was chosen due to satisfactory electrical properties with a relatively small proportion of nanotubes in the matrix. Melting temperature varies around 230°C. The material was dried before processing at 120°C for 4 hours. Surface resistivity of polybutylene terephthalate without MWCNTs is $1x10^{12}$ Ohm.cm. Electromagnetic shielding efficiency of pure matrix PBT is zero on frequency range between 30 MHz and 1.5 GHz.

2.2 Methods

For injection molding the standard column-mounted injection machine ARBURG 270S 400-100 was used. Injection molding technological parameters had to ensure both sample production and also need to avoid degradation of the polymer matrix. It was crucial to set proper plastication and injection moulding parameters (see Table 1) mainly with regard to thermal and shear loading. Aggregate TA3 was used for injection mould tempering. Temperature of melt was 260°C. Injection rate was 30 cm^3/s and size of holding pressure 560 bars. Holding pressure time for the samples was 20 s. Injection mould with central ejector was used for production of testing samples for tensile and impact test which had exchangeable plates according to requirements and individual ISO standards. The mould has cooling channels both on the part of die and part of punch and it was tempered on the temperature 80°C for both sides of injection mould.

Table 1 Injection moulding parameters

Barrel Temperature [°C]					Injection Speed [cm^3/s]
Zone 5	Zone 4	Zone 3	Zone 2	Zone 1	
260	255	250	245	235	30

Measurement of tensile properties of test samples were performed on a multipurpose Hounsfield H10KT tensile machine with the sensor head measuring power up to 10 kN. The measurement procedure was in accordance with standard ČSN EN ISO 527-1, 2. After clamping the sample to the clamping jaws, specimen was tensile loaded. Measurements were taken to the point of test specimen breakage. The loading speed was 50 mm/min.

Electromagnetic interference measurement was carried out according to ASTM D4935-10. This standard works for frequencies from 30 MHz to 1.5 GHz. Electromagnetic interference efficiency of samples was measured on the device consisting of a coaxial sample holder (Electro-Metrics, Inc., Model EM-2107A), see Figure 2 and measuring equipment Rhode & Schwarz ZNC3 circuit analyzer, which was used to generate and receive the electromagnetic signal, see Figure 3. The temperature was 22°C and relative humidity in the room was 55%. The size of the test samples was 150x150x2 mm. Measurement was performed on 10 specimens because of further statistical analysis.

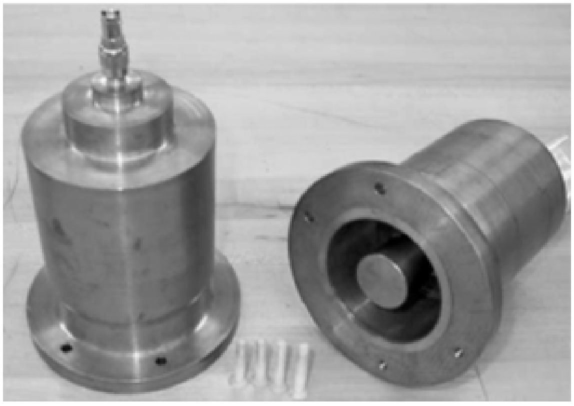

Figure 2 Coaxial sample holder from company Electro-Metrics Inc. model EM-2107A

Figure 3 Electromagnetic shielding efficiency meter with Rhode & Schwarz ZNC3 circuit analyzer

Masterbatch from polybutylene terephthalate with MWCNT in the form of granulates was dried and processed by injection moulding technology to produce testing samples which were evaluated for electromagnetic shielding efficiency and tensile properties. With regard to the fact that nanocomposite melt flow index (MFI) was much lower than MFI of pure PBT, pressure parameters during filling phase and pressure phase for commonly adjusted temperature conditions at injection were quite high: pressure at switch-over was 1000 bars, holding pressure was 560 bars. Adjusted technological parameters for testing samples production were tried out and they were chosen from several testing variants of the technological parameters. Due to the higher viscosity of composite it was necessary to increase the melt temperature from 230°C to 260°C. The structures do not degrade at this temperature. The production parameters were the same for all nanocomposites with different percentage by weight of MWCNT.

At composite processing there was presumption that foliation of the multi wall carbon nanotubes is homogenous as shown in [6, 7]. We can see fracture on surface of nanocomposite PBT with 5% weight of MWCNT after cryogenic freezing and after fracture in Figure 4. There is also shown the homogeneous distribution of MWCNT in the thermoplastic polymer matrix PBT and only small MWCNT agglomerates of maximum size 1 micrometer. Figure 4 also confirms that it is a prerequisite for creating a 3D network that has influence on mechanical, electrical and electromagnetic interference properties.

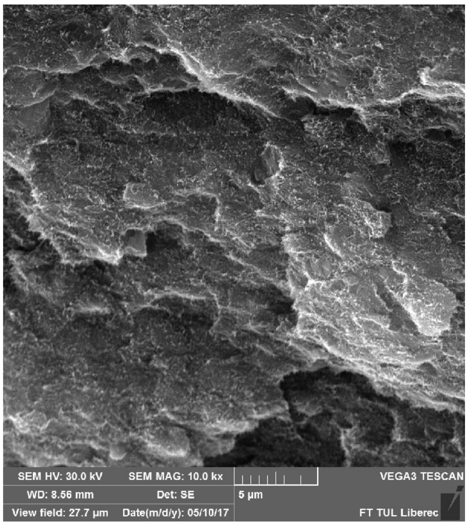

Figure 4 The homogeneous dispersion of MWCNT in PBT nanocomposites with 5% weight ratio of MWCNT

3 RESULT AND DISCUSSION

On 1, 2 and 5 wt.% ratio MWCNT´s in thermoplastic polymer nanocomposites made from masterbatch Plasticyl PBT1501 electromagnetic shielding efficiency was measured. Measurements show us, how appropriate nanocomposites are for electromagnetic interference applications. Table 2 shows the determination of the percentage of electromagnetic shielding effectiveness as written in [8]. Measurements were performed on 10 samples of each nanocomposite with different percentage ratio of MWCNT. The resulting values of electromagnetic shielding efficiency, we can see in Table 3.

Table 2 Determination of percent shielding efficiency

Degree of effectiveness	Electromagnetic shielding efficiency SE	Percentage of shielding effectiveness ES
5 - Excellent	SE>30 dB	ES>99.9%
4 - Very good	30 dB≥SE>20 dB	99.9%≥ES>99.0%
3 - Good	20 dB≥SE>10 dB	99.0%≥ES>90.0%
2 - Moderate	10 dB≥SE>7 dB	90.0%≥ES>80.0%
1 - Poor	7 dB≥SE>5 dB	80.0%≥ES>70.0%

Table 3 Determination of percent shielding efficiency

Electromagnetic shielding efficiency SE [dB] for frequency 1.5 GHz			
	1 wt.% of MWCNT	2 wt.% of MWCNT	5 wt.% of MWCNT
PBT	4.29	6.23	15.5
Standard deviation	0.99	0.68	0.69

The resulting nanocomposites with 1, 2 and 5% ratio of MWCNT indicates that these nanocomposites are conductive plastics. PBT with 5% weight ratio of MWCNT shows good electromagnetic interference - 15 dB for frequency 1.5 GHz. It is 90-99 percentage of shielding effectiveness. These results also indicate that there was a homogeneous dispersion of MWCNTs (as shown Figure 4) and the injection moulding had not a great influence on the electric and electromagnetic properties of the nano-composites. The dependence of the electromagnetic shielding efficiency on the content of the conductive component above the percolation threshold (>1% by weight MWCNT) can be approximated by means of power function [9].

$$SE = SE_P \, CNT^X \quad (1)$$

where SE_P is a shielding efficiency of 1% weight ratio of MWCNT in polymer matrix, *CNT* is % weight ratio of MWCNT in the thermoplastic polymer matrix and parameter *X* is dependent on the type of thermoplastic polymer matrix.

Figure 5 shows the dependence of the electro-magnetic shielding effect on the 1.5 GHz frequency with the expressed dependence and the interlaced power function.

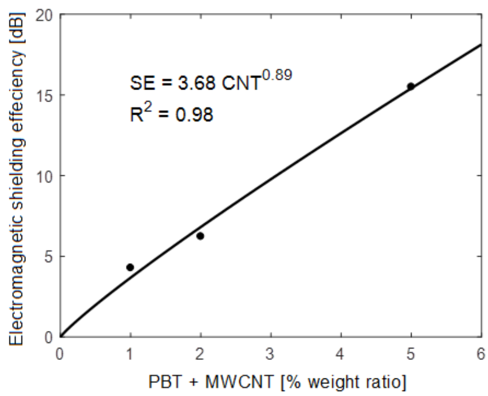

Figure 5 Dependence of electromagnetic shielding efficiency on MWCNT content in PBT interleaved by power function with its expression

The resulting regression models were obtained using the least squares method. Coefficient of determination (denoted as R^2) indicates a high correlation of the measured results.

Measurements of tensile test were performed on 10 specimens for 1, 2 and 5% weight ratio of carbon nanotubes and pure PBT. The resulting values of Young's modulus we can see in Table 4.

Table 4 Young's modulus of pure PBT and PBT with MWCNT

Young's modulus [MPa] - ISO 527-1,2				
PBT	**Neat polymer**	**1 wt.% of MWCNT**	**2 wt.% of MWCNT**	**5 wt.% of MWCNT**
[MPa]	2753.3	3267.5	3535.2	3922.6

The Young's modulus of PBT without carbon nanotubes as fillers is 2753.3 MPa with 5 wt.% ratio MWCNT´s is 3922.6 MPa. From results, an increase in young modulus more than 1200 MPa can be seen. Ductility as also reduced, resulting in increased hardness and brittleness of the final composite. Due to the continually decreasing cost of a CNT application of these fillers to improve the mechanical properties seems to be profitable in future.

4 CONCLUSION

The progression of composites with thermoplastic and carbon nanotubes is a constantly evolving process that will be influenced by expanding number of application possibilities, using not only excellent electrical properties of such composites. These properties and application potentials will be influenced not only by the type and form of nanotubes, their percentage weight ratio, but also the type and kind of the polymer matrix. Picture from SEM and results indicate that there is a homogeneous dispersion of MWCNTs and the injection moulding had not a great influence on the mechanical and electromagnetic properties of the nanocomposites. The test results show an increase in the mechanical properties of young modulus. Due to the decreasing cost of CNT's probably in the future these nanofillers will be used to improve the mechanical properties of composites. Measurements of electromagnetic shielding efficiency show than the PBT nanocomposite with 5% weight ratio have good electromagnetic interference 15 dB for frequency 1.5 GHz which means 90-99 percentage of shielding effectiveness. These properties enable wide use of this nanocomposite, such as applications requiring superior electrostatic discharge (ESD) properties, electrically conductive parts (EC), electrical and electronics (E&E) and electromagnetic interference (EMI) parts. Influence of change of processing parameter will be examined in the near future.

ACKNOWLEDGEMENT: The report has been prepared under the terms of solution of SGS 21 122.

5 REFERENCES

1. Duleba B.: Uhlíkové nanotrubice - materiál budoucnosti (Carbon nanotubes - the material of the future). Košice: Transfer inovacií (Transfer of Innovations) 21, 2011 (in Slovak)
2. Lew C.Y., Dewaghe C., Claes M.: Injection moulding of polymer-carbon nanotube composites, Polymer-Carbon Nanotube Composites, Cambridge: Woodhead Publishing, 2011, doi: 10.1533/9780857091390.1.155
3. Bai J.B, Allaoui A.: Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of nanocomposites-experimental investigation, Composites Part A: Appl. Sci. Manuf. 34(8), 2003, pp. 689-694, doi: 10.1016/S1359-835X(03)00140-4
4. Kasaliwal G.R., Villmow T., Pegel S., et. al.: Influence of material and processing parameters on carbon nanotube dispersion in polymer melts, Polymer-Carbon Nanotube Composites, Cambridge: Woodhead Publishing, 2011, doi: 10.1533/9780857091390.1.92
5. Dai L, Sun J.: Mechanical Properties of Carbon Nanotubes-Polymer Composites, Carbon Nanotubes, London: InTech, 2016, doi: 10.5772/62635
6. Pötschke P., Pegel S., Claes M., et al.: A novel strategy to incorporate carbon nanotubes into thermoplastic matrices, Macromolecular Rapid Communication 29(3), 2008, pp. 244-251, doi: 10.1002/marc.200700637
7. Lenfeld P., et. al.: Evaluation of plastication and injection molding influence on the morphology of polyamide with carbon nanotubes, In: Proceedings of The 28th International Conference of Polymer Processing Society (PPS-28), Pattaya, Thailand, 2012, pp 134-138
8. Safarova V., Militky J.: Multifunctional metal composite textile shields against electromagnetic radiation-effect of various parameters on electromagnetic shielding effectiveness, Polymer Composites 38(2), 2017, pp. 309-323, doi: 10.1002/pc.23588
9. Clingerman M., King J., Schulz K.: Evaluation of electrical conductivity models for conductive polymer composites, Journal of Applied Polymer Science 83(6), 2002, pp. 1341-1356, doi: 10.1002/app.10014