CORRELATION BETWEEN ELECTROMAGNETIC SHIELDING EFFICIENCY AND RESISTIVITY OF THERMOPLASTIC POLYMER NANOCOMPOSITE

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Abstract

This work examines possible correlation between electromagnetic shielding efficiency and resistivity of thermoplastic polymer nanocomposites with carbon nanotubes. Polyoxymethylen was used as basic matrix to which nanoparticles in the weight percentage ratio were added. Multi-walled carbon nanotubes in various percentages by weight ratio were used as filler. The nanocomposite was made by the Arburg injection molding machine. For evaluation of electrical properties electromagnetic shielding effectiveness and resistivity of the final nanocomposite with and without nanofillers was evaluated. These results are compared and discussed. Correlation between electromagnetic shielding efficiency and resistivity of thermoplastic polymer nanocomposite is evaluated and prediction model is introduced in the conclusion.

Keywords: Carbon nanotubes, nanocomposite, electromagnetic interference, injection molding

1. INTRODUCTION

In the past ten years, extensive research and development have been carried out in the field of polymer composite production. On an industrial scale, melt processing has become the method of choice to incorporate many different types of filler. Nowadays, a wide variety of melt compounding technology is available which is applicable to polymer-CNT nanocomposite production [1]. Growing application of these nanocomposites 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. 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 [2].

A carbon nanotube (CNT) is a single sheet of graphite rolled into a cylinder several microns in length and a few nanometers in diameter. Nanotubes can take two forms: single-walled and multi-walled. Single-walled nanotubes consist of one layer of carbon atoms through the thickness of the cylindrical wall. Multi-walled carbon nanotubes, which were the first to be discovered, consist of concentric cylinders around a common central hollow with a constant separation between the layers close to the graphite interlayer spacing (0.34 nm). Each individual cylinder can be characterized by a different helical angle and has a diameter ranging from 2 to 25 nm and a length of several microns [3].

During the 20th century, environmental exposure to man-made electromagnetic fields has been steadily increasing as growing electricity demand, ever-advancing technologies and changes in social behavior. Sources of such emissions could include generation and transmission of electricity, domestic appliances and industrial equipment, telecommunications and broadcasting. If the electromagnetic waves are not isolated effectively, they will cause interference with each other and result in technical errors. Metal is considered to be the best electromagnetic shielding material due its conductivity and permeability, but it is expensive, heavy, and may also have thermal expansion and metal oxidation, or corrosion problems associated with its use [4]. It is necessary to use a higher weight percentage in the polymer matrix, about 30%. In contrast, carbon nanotubes are very low density fillers, have excellent EMI properties and are well dispersed in polymer matrices [5]. In this work are MWCNT used as a filler in Polyoxymethylen (POM) polymer matrix and examined the effect on the nanocomposite using electron microscopy and measurement of electromagnetic interference and resistivity.

2. EXPERIMENAL

2.1. Material

PLASTICYL POM1001 is a conductive masterbatch based on polyoxymethylen loaded with 10 % MWCNTs (NC7000™) from Nanocyl Company. For mixing was used pure polyoxymethylen with trade name Hostaform C9021 from Ticona Company. The masterbatch was used as the parent matrix from which mixed polymer blends. There was chosen 1, 2, 5 % weight ratio of multi wall carbon nanotubes. This percentage of the nanotubes was chosen because of good electrical properties with a small proportion of nanotubes in the matrix. Melting temperature varies around 210 °C. The material was dried before processing at 120 °C for 4 hours. The result of surface resistivity of POM without MWCNTs is 1×10^{13} Ohm.cm. Electromagnetic shielding efficiency of pure matrix POM is zero.

2.2. Method

For injection molding was used standard column-mounted injection machine ARBURG 270S 400-100. 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 245 (°C). Injection rate was 30 (cm^3/s) and size of holding pressure 750 (bar). Holding pressure time for the samples was 20 (s). The mould has cooling channels both on the part of die and part of punch and it was tempered on the temperature 90 (°C) for both sides of injection mould.

Table 1 Injection moulding parameters

Barrel Temperature (°C)					Injection Speed
Zone 5	**Zone 4**	**Zone 3**	**Zone 2**	**Zone 1**	**(cm^3/s)**
245	240	240	235	230	30

Resistivity measurement was carried out according to ČSN EN ISO 3915. On test samples was measured volume resistivity of the device consisting by potentiometric electrodes which comply with the standards, see **Figure 1**. Measuring equipment consisting of power supply, voltmeter and ammeter, see **Figure 2**. As the power supply was used Hadex G855, as a voltmeter was used digital multimeter Agilent 34411A, as ammeter was used digital multimeter Agilent 34401A. The distance between the potentiometric electrodes is 1 (cm). Measurements were carried out at a voltage of U = (V) for all samples. The temperature was 22 (°C) and relative humidity in the room was 55 (%). Measurement was performed always on 10 specimens.

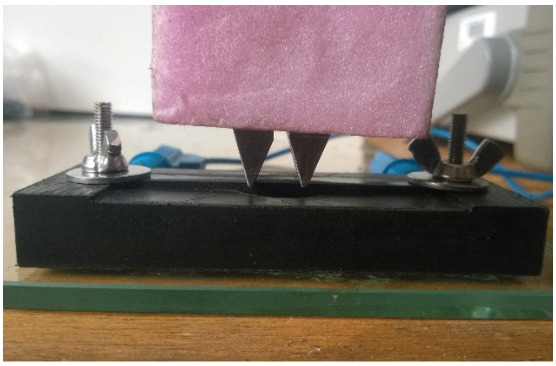

Figure 1 Potentiometric electrodes

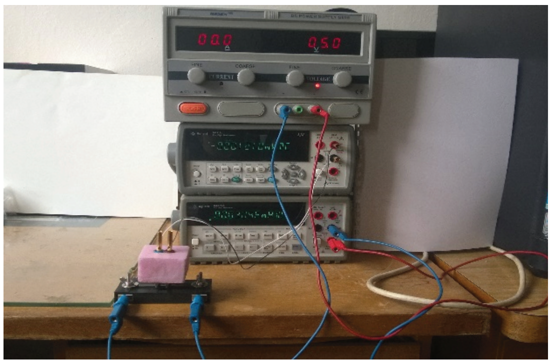

Figure 2 Power supply, voltmetr, ammeter

Electromagnetic interference measurement was carried out according to ASTM D4935-10. This standard works for frequencies from 30 MHz to 1.5 GHz. On test samples was measured electromagnetic interference efficiency on the device consisting of a coaxial sample holder (Electro-Metrics, Inc., Model EM-2107A), see **Figure 3** and measuring equipment Rhode & Schwarz ZNC3 circuit analyzer, which was used to generate and receive the electromagnetic signal, see **Figure 4**. 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.

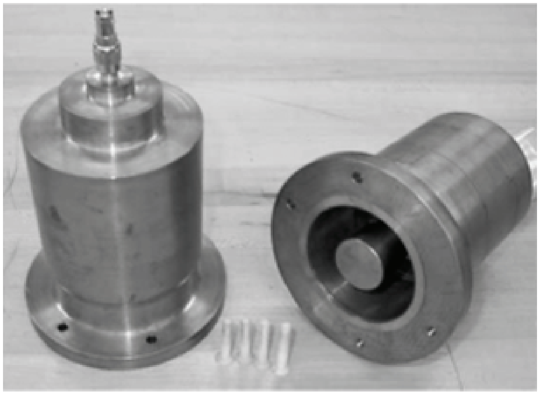

Figure 3 Coaxial sample holder from company Electro-Metrics Inc. model EM-2107A

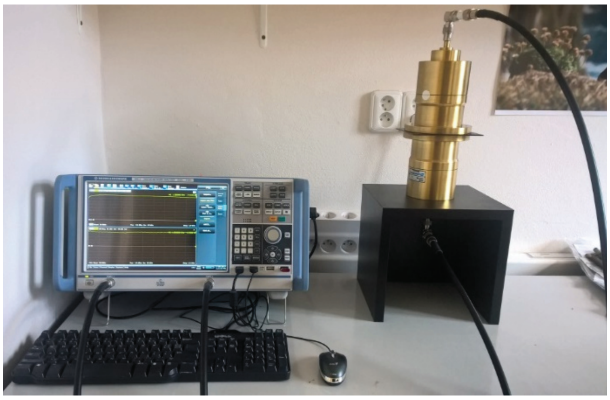

Figure 4 Electromagnetic shielding efficiency meter with Rhode & Schwarz ZNC3 circuit analyzer

3. RESULT AND DISCUSSION

At composite processing there was presumption that foliation of the multi wall carbon nanotubes is homogenous as it is written in [6-9]. We can see fracture surface of nanocomposite POM with 5% weight of MWCNT after cryogenic freezing and after fracture on **Figure 5**. There is also shown the homogeneous distribution of MWCNT in the thermoplastic polymer matrix POM and only small MWCNT agglomerates of maximum size 1 micrometer. **Figure 5** also confirms that it is a prerequisite for creating a 3D network that has influence on electrical and electromagnetic interference properties.

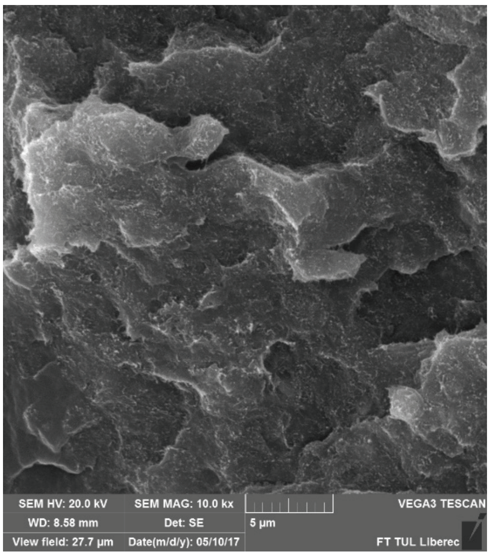

Figure 5 The homogeneous dispersion of MWCNT in POM nanocomposites with 5% weight ratio of MWCNT

On 1, 2, 5 (%) wt. ratio CNT´s in polymer blends made from masterbatch Plasticyl POM1001 was measured volume resistivity. Measurements of volume resistivity show us how good the material is conductor of electric charge. Measurements were performed on 10 samples of each polymer blend. The resulting values of volume resistivity we can see in **Table 2** and **Figure 6**.

Table 2 Volume resistivity of polyoxymethylen

Polyoxymethylen	Neat polymer	1 % wt. of CNT´s	2 % wt. of CNT´s	5 % wt. of CNT´s
Volume resistivity [Ohm.cm]	1 x 10^{13}	4.52 x 10^{2}	6.06	0.65
Standard deviation	1 x 10^{2}	50	2.4	0.2

The resulting samples polymer blend with MWCNT indicates that this nanocomposite is a conductive plastic and that is good conductor of electric charge. These results also indicate that there was a homogeneous dispersion of MWCNTs and the injection moulding had not a great influence on the conductivity of the nanocomposite.

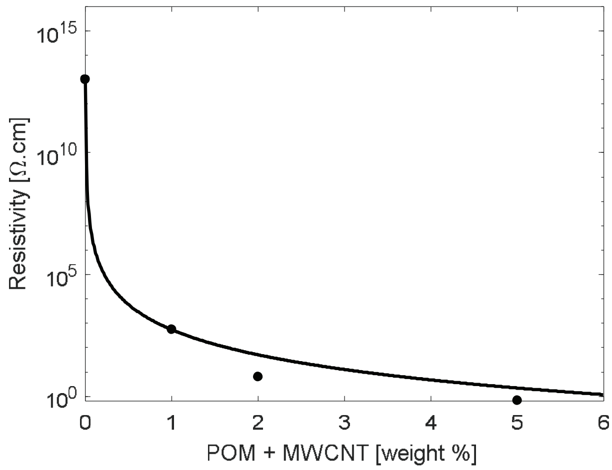

Figure 6 Dependence of electromagnetic shielding efficiency on MWCNT content in PBT

On 1, 2, 5 (%) wt. ratio MWCNT´s in thermoplastic polymer nanocomposites was also measured electromagnetic shielding efficiency from frequency 30 MHz to 1.5 GHz. Measurements show us, how good nanocomposites are for electromagnetic interference applications. 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 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
Polyoxymethylen	4.2	11.39	27.08
Standard deviation	0.34	0.98	1.06

The resulting nanocomposites with 1, 2, 5% ratio of MWCNT indicates that these nanocomposites are a conductive plastics. POM with 5% weight ratio of MWCNT shows very good electromagnetic interference 27 dB for frequency 1.5 GHz. It is 99.9 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 nanocomposites. **Figure 7** shows the dependence of the electromagnetic shielding effect on the 1.5 GHz frequency.

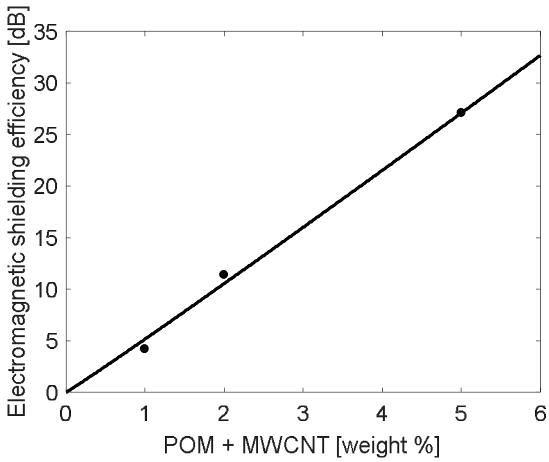

Figure 7 Dependence of electromagnetic shielding efficiency on MWCNT content in PBT

Correlation between electric conductivity and shielding effectiveness

The electromagnetic interference shielding efficiency needs to use special devices. Simpler are measurements of surface or volume resistivity. It is known from theory that at sufficiently high frequencies it is possible to measure characteristics of electrical part of electromagnetic field only and therefore it should be mathematical relation between total shielding effectiveness SE [dB] and fabric resistivity or conductivity.

Based on extensive experiments it was found out that there is a statistical dependence between SE and electrical resistivity of samples. We can observe two areas: area below percolation threshold and area above percolation threshold (for sufficiently high content of conductive component). The most suitable (for nanocomposites) is prediction based on volume resistivity by this mode [4, 10]:

$$SE = K_1 \cdot \ln(\rho_V) + K_2 \tag{1}$$

where SE is electromagnetic shielding efficiency [dB], K1 and K2 are constants dependent on frequency and polymer material. The prediction ability of this linear model is restricted to the higher content of conductive component above conductivity percolation threshold. **Figure 8** shown dependence of SE on natural logarithm of volume resistivity with the expressed dependence and the interlaced power function. The resulting regression models were obtained using the least squares method. Pearson's correlation coefficient of 0.89 indicates a high correlation of the measured results.

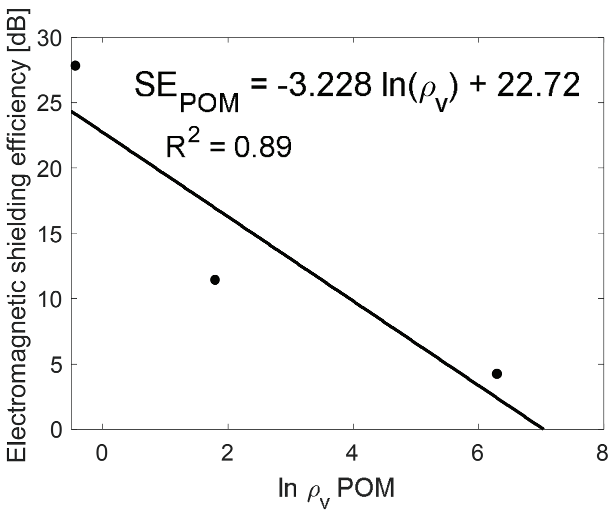

Figure 8 The dependence of SE on natural logarithm of volume resistivity for POM nanocomposite with MWCNT interleaved by a power function with its expression

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 nanocomposites. 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 electrical and electromagnetic properties of the nanocomposites. Measurements of electromagnetic shielding efficiency show that the POM nanocomposite with 5 % weight ratio have good electromagnetic interference 27 dB for frequency 1.5 GHz and it is 99.9 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. It was confirmed that using the regression model SE_{POM}=-3.228 ln(ρ_V) + 22.72, it is possible to predict electromagnetic shielding efficiency for POM nanocomposite with a wall thickness of 2 mm based on knowledge of the electrical properties of nanocomposites above percolation threshold. Influence of change of processing parameter will be examined in the near future.

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