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Electrical Conductivity Enhancement of Hybrid PA6,6 Composite Containing Multiwall Carbon Nanotube and Carbon Black for Shielding Effectiveness Application in textiles

Marzieh Javadi Toghchi^{1,2,3,4}, Christine Campagne^{1,2}, Aurélie Cayla^{1,2}, Pascal Bruniaux^{1,2}, Carmen Loghin³, Irina Cristian³, Ludovic Burgnies^{5,6} and Yan Chen⁴

¹Ecole Nationale Supérieure des Arts et Industries Textiles, GEMTEX, Roubaix, France

²University of Lille, Nord de France, Lille, France

³Faculties of Textile, Leather and Industrial Management, Gheorghe Asachi Technical University, Iasi, Romania

⁴College of Textile and Clothing Engineering, Soochow University, Suzhou, China

⁵Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France

⁶Université du Littoral Côte d'Opale, Rue Ferdinand Buisson, 62228 Calais Cedex, France

Highlights

- A hybrid PA6,6 composite contained multiwall carbon nanotube and carbon black was fabricated for shielding effectiveness application in textiles.
- Melt mixing method was applied to develop the conductive polymer composite.
- Morphology, viscosity and synergism between nanofillers were studied.
- The monofilament of the developed composite was integrated as weft yarn in a woven structure.
- The shielding effectiveness (SE) of the woven fabric with embedded conductive monofilament was evaluated in the frequency between 1 and 10 GHz in a mode-stirred chamber ($SE \geq 10$ dB).

Abstract

Textiles have been highly considered in applications of electromagnetic shielding effectiveness. This is mainly due to an increasing concern of health issues caused by human exposure to radiation.

In the present study, the main objective was to develop a monofilament yarn made of conductive polymer composite (CPC) for electromagnetic shielding application to decline the drawbacks of previous electromagnetic shielding textile products. Thus, CPCs were produced by melt mixing method, using Polyamide 6,6 (PA6,6) as matrix and carbon black (CB) or/and multiwall carbon nanotube (MWCNT) as conductive nanofillers and the synergy effects of CB and MWCNT on electrical conductivity was studied. Consequently, 1.7 wt.% of MWCNT and 3.3 wt.% of CB (1MWCNT:2CB) was applied to generate a PA6,6-based composite at the critical percolation threshold while its electrical conductivity was higher than the PA6,6-based composite contained 20 wt.% of CB and the same as the one contained 3 wt.% of MWCNT.

The developed monofilament is lightweight, corrosion resistant and the manufacturing process is very well established in comparison with metal yarns. These characteristics make it an alternative to produce electromagnetic shielding clothing for personal protection. Thus, the developed monofilament was woven to fabricate an electromagnetic shield fabric and the electromagnetic shielding effectiveness was evaluated in the frequency range 1-10GHz.

In brief, the electrical conductivity was improved using the synergism between nanofillers while the viscosity was in the standard range for monofilament making process by extrusion. Moreover, the shielding effectiveness (SE) of the woven sample made of the developed composite was promising for personal protection (16 dB).

Keywords: Carbon nanofillers, Conductive monofilament, Conductive polymer composite, Electrical conductivity, Electromagnetic shielding effectiveness, Synergy effects.

1. Introduction

Smart textiles (e-textiles) have been developed with new technologies that provide specific added values to the final products. In recent decades, the development of smart textiles has been growing with the aim of applying in industry (e.g. sensors for force and pressure, military applications, or in electromagnetic interference) [1]. Thus, the engineering of innovative materials which are capable to respond to external or internal stimuli is the main objective of smart textile growth. For instance, electrically conductive polymer composites (CPCs) which contain conductive fillers dispersed in a polymer matrix have attracted attention in numerous study fields like electromagnetic shielding [2-3].

Electromagnetic interference shielding can be performed using electrical conductive textiles. Large numbers of commercial electromagnetic shielding textiles have been developed to protect the human body against radiation. A lot of products are made of metallic yarns with high electrical conductivity like copper, silver, nickel and stainless steel for electromagnetic shielding applications [4]. However, poor washability and uncomfotability (e.g. high weight and skin allergy) can be mentioned as the main drawbacks of these products [5-8].

The conductive coating on textiles is also a common way to increase the electrical conductivity of textiles. Some studies have been done on textiles which were coated with metal particles to become electrically conductive and electromagnetic shielded [9]. It has been tried to use electroconductive polymer composites as coating on textile surface to enhance the electrical conductivity [10-12]. For example, polypyrrole was coated on polyethylene terephthalate (PET) fabric to achieve the required electrical conductivity for electromagnetic interference shielding purpose by Kim *et al.* [11]. Although coating is an economical technique to increase the electrical conductivity of textiles, the main drawback is that coating wears away after a short period of use. In recent years, adding conductive nanofillers to the polymer matrix has been developed to enhance the electrical conductivity of the textile products [13-20]. For example, Jagatheesan *et al.* reviewed the theory of electromagnetic interference shielding along with the conductivity of fabrics and composites [19]. They provided details of different electrical conductive textiles for electromagnetic shielding purposes. For example, they stated that 5 wt.% of mixed Ag and MWCNT in polystyrene-based composite showed the shielding effectiveness of 22 dB in the frequency range of 12.4-18 GHz. They suggested that the higher content of nanofillers leads to the higher electrical conductivity on one hand and increases the viscosity of the developed CPC on the other hand.

In another study, the electromagnetic shielding effectiveness of conductive polymer composites with three different carbon nanofillers was discussed by Al-Saleh *et al.* [21]. Multiwall carbon nanotubes (MWCNT), carbon nanofiber (CNF) and high structure carbon black (HS-CB) were applied in their work while the polymer was acrylonitrile-butadiene-styrene (ABS). They studied the electrical volume resistivity and electromagnetic interference shielding effectiveness in X-band frequency range and concluded that MWCNT/ABS composites indicated a high shielding effectiveness. Additionally, they used transmission electron microscopy (TEM) images to investigate the dispersion of the nanofillers and a good level of dispersion for all the nanofillers inside the polymer was revealed.

Moreover, mass production of carbon nanotube (CNT) reinforced polymethyl methacrylate (PMMA) nonwoven nanofiber mats was developed by Weng *et al.* [22]. Their results proved that the electrical properties enhanced in comparison with PMMA nanofibers. Also, they claimed that the developed conductive composite showed reasonable electromagnetic interference shielding effectiveness (SE ~18 dB at 1 GHz with 12 wt.% CNT).

It should be noted that the percolation threshold of conductive polymer composite (CPC) is influenced by the process method, polymer matrix and nanofillers properties [23-24]. For instance, the percolation threshold of CNT composites using different methods, different polymers and CNT properties were described in [25].

In addition, the tensile and electrical properties of carbon filled polyamide (PA6,6) conductive composites were studied by Clingerman *et al.* [26]. They investigated the influences of carbon black (or carbon fiber) concentration on the electrical and mechanical properties of the PA6,6-based composite plate. They applied relatively high carbon black content to achieve a reasonable electrical conductivity for the developed plate (40 wt.%).

Electrical conductive materials can generate and transport free charges which lead to electromagnetic interference shielding effectiveness as mentioned earlier. Thus, it has been tried to define a relationship between electrical conductivity and electromagnetic interference shielding effectiveness in some studies. For instance, the MWCNT within polypropylene random copolymer was prepared by Verma *et al.* [27] and both electrical conductivity and shielding effectiveness were characterized. They indicated that the electrical conductivity, as well as shielding effectiveness, was improved by increasing the quantity of carbon nanofiller. Also, they suggested that the conductivity was not changed meaningfully after percolation threshold despite the fact that shielding effectiveness kept on growing with increasing the filler quantity.

In another study, an equation between electrical conductivity and shielding effectiveness was defined by Han *et al.* [28]. They affirmed that the shielding effectiveness results obtained from the equation were in good agreement with experimental results for polyethylene/MWCNT and polyphenylene sulfide/MWCNT composites. The SE values were 3.6 dB and 13 dB (at 1 GHz) when 5 wt.% and 15 wt.% of MWCNTs were applied in the polyethylene matrix, respectively.

Although the increasing quantity of conductive nanofiller increases the electrical conductivity of the final composite, high quantity of nanofiller causes difficulties in the manufacturing process. It results in deviation during the composite making process due to high viscosity. In addition, the cost of produced CPC increases using high amount of carbon nanofillers. Therefore, it has been suggested to apply the synergy effects of carbon nanofillers to decline the complications of using a high quantity of nanofillers [29–37]. It has been said that the synergy effects of CB and MWCNT (or CNT) considerably increase the electrical conductivity at lower percolation threshold [30,32,35,36].

For instance, MWCNT and CB were introduced as electroconductive nanofillers in polypropylene copolymer and the behavior of percolation threshold was investigated by Zhang *et al.* [30]. They confirmed that the percolation threshold of hybrid nanofillers filled CPC was significantly lower than the percolation threshold of either CB or MWCNT filled CPCs. They stated that the percolation threshold was reduced from 2.4 to 0.21 wt.% while half of the MWCNT was replaced with CB.

Also, the electrical conductivity of epoxy-based composites containing hybrid nanofillers of CNT and CB was studied by Peng Cheng *et al.* [38]. They concluded that adding mixed nanofillers of CB and CNT triggered higher electrical conductivity while CB improved the ductility of the composites.

Furthermore, a mathematic model was proposed to estimate the percolation threshold of hybrid carbon nanofillers in polymer composite (CPC) by Sun *et al.* [39]. According to the proposed model, percolation ensued when all the small volumes were occupied with CB or MWCNT or (MWCNT and CB). The proposed model is applied to calculate the quantity of nanofillers at percolation threshold in extreme state using hybrid nanofillers in composites though the real state of hybrid nanofillers (MWCNT and CB) is not exactly similar to the model. Therefore, the

equation (1) was obtained for the systems containing two types of conductive nanofillers (A and B) where m_A is the weight fractions of nanofiller A and m_B is the weight fraction of nanofiller B in the composition. $\rho_{C,A}$ (or $\rho_{C,B}$) is the corresponding percolation concentration when A (or B) is the only type of filler applied in the composite. It means that the composite is at percolation threshold state when the value of equation (1) is equal to 1.

$$\frac{m_A}{\rho_{C,A}} + \frac{m_B}{\rho_{C,B}} = 1 \text{ (Eq. 1)}$$

As mentioned earlier, composites with carbon nanofillers in their compositions have been used in various applications. For instance, they have been applied as reinforced composites in [40–47]. The effects of surface modification of CNTs and MWCNTs on the properties of the produced composites have been studied in these studies. For example, the surfaces of MWCNTs were modified with acid-and amine-groups and then Polyamide 6,6 (PA6,6)/1wt.% of MWCNT composites were prepared using melt mixing method by Qiu *et al.* [41]. They studied the dispersion of the MWCNTs in PA6,6 matrix and decided that Amine functionalization of MWCNTs improved the dispersion of MWCNTs in PA6,6. However, some compatible solvents with carbon nanofillers (e.g. CNT) are toxic and the applied surfactants negatively affect the electrical conductivity of the carbon nanofillers [12]. Also, reaching the stable suspensions with high concentration of individual nanofiller is limited [47]. Briefly, the aforesaid composites having carbon nanofillers in their compounds were produced for mechanical application which is different from our target application of the produced composites composed of PA6,6 and carbon nanofillers.

Also, monofilament manufacturing of conductive composites for textile applications has been studied in several studies [48-50]. For example, monofilament manufacturing of PLA/CNT for sensor application was studied by Ferreira *et al.* [48]. It should be taken into account that the polymer properties along with the mass concentration of the nanofillers play a significant role in the filament making process.

In the present study, a hybrid conductive monofilament yarn was produced in order to make a wearable electromagnetic shielding textile for personal protection. The advantage of using mixed carbon nanofillers in PA6,6-based composite (common thermoplastic polymer in textile industry) was to achieve higher electrical conductivity. Also, the viscosity complications caused by increasing the content of nanofillers was discussed. The PA6,6 filled carbon nanofillers was generated by melt mixing method to develop a new conductive polymer composite monofilament since CPCs are lightweight, inexpensive, corrosion resistant and the manufacturing process is very well established in comparison to metal yarns. These properties make the developed CPC monofilament suitable for garment making process for personal protection against electromagnetic waves. Accordingly, two developed hybrid monofilaments were applied in the weaving process to produce electromagnetic interference shielding fabrics for personal protection. The electromagnetic shielding effectiveness of compact two-ply woven samples was measured in a stirred-mode chamber in the frequency range 1-10GHz.

2. Experimental

2.1. Materials

For monofilament manufacturing

Polyamide 6,6 (PA6,6) - Torzen™ U4803 NC01 PA6.6 resin (density: 1.14 g/cm³) was used as matrix of the composites in the present work.

Multiwall Carbon Nanotube (MWCNT) - Nanocyl NC7000 series (surface area: 250 - 300 m²/g; density: 1.30–2.00 g/cm³ with an average diameter of 9.5 nm and length: 1.5 μm) was purchased from Nanocyl S.A. (Belgium).

Two different types of carbon black were applied in the present study:

- Carbon Black (CB) - Printex L6 powder series (surface area: 200 m²/g; density: 1.7–1.9 g/cm³ and particle size: 18 nm) which has a spherical cross-section, was purchased from Orion Engineered Carbons Company (Germany).
- Carbon Black (KB*) - Ketjenblack EC-300J series (surface area: 800 m²/g; density: 2.1 g/cm³ and particle size: 39.5 nm) was supplied by Akzo Nobel in Netherlands. Ketjenblack EC-300J has a high effective surface area due to the contribution of internal voids.

Transmission electron microscopy (TEM) images of three applied nanofillers in the present study are illustrated in Figure 1(a, b, c). These nanofillers provide different surface area which leads to dissimilarity in nanofiller dispersion and percolation threshold of the electrical conductivity in conductive polymer composites (CPCs). For example, the pore structure of KB* allows it to perform as high conductive carbon nanofiller in comparison with CB having spherical cross-section.

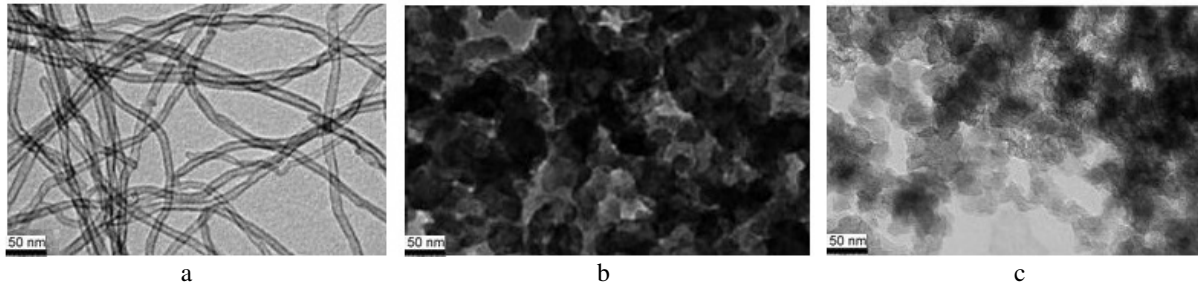


Figure 1- Transmission electron microscopy images of MWCNT (a), CB (b) and KB*(c) applied in the present study

For woven fabric manufacturing

Cotton yarns (N_m 20/2) were applied as weft and warp in the woven structure. (Two-ply cotton yarn is composed of two single strands when metric number (N_m) indicates the number of one thousand meters of yarn per kilogram)

Two developed CPCs made of PA6,6/MWCNT:CB and PA6,6/MWCNT:KB* were introduced as stuffer yarns in weft direction.

2.2. Methods

Monofilament manufacturing

All the pellets with carbon additive were dried at 80°C for 12 hours before extrusion. PA6,6/MWCNT and PA6,6/CB composites were blended by melt mixing method using co-rotating twin-screw extruder ThermoHaake (screw diameter: 16 mm and L (length)/D (diameter): 25) while the rotation speed was fixed to 100 rpm and the temperatures of the extruder were set at 270°C in feeding zone and 280°C, 280°C, 279°C and 278°C in barrels zones, respectively.

First, CPC variants using only one type of nanofillers were produced to study the percolation threshold of the electrical conductivity of CPCs contained CB or MWCNT. Accordingly, the quantity of MWCNT was ranged from 0.5 to 5 wt. % in PA6,6/MWCNT composite and CB was ranged from 5 to 30 wt.% in PA6,6/CB composite. The compositions of all the conductive polymer composites (CPCs) are listed in Table 1.

Table 1- Formulation of the conductive polymer composites (CPCs)

Sample Code	PA66 wt. %	MWCNT wt. %	CB (Printex) wt. %	KB* (Ketjenblack) wt. %
PA	100	-	-	-
PA-MWCNT0.5	99.5	0.5	-	-
PA-MWCNT1	99	1	-	-
PA-MWCNT1.5	98.5	1.5	-	-
PA-MWCNT2	98	2	-	-
PA-MWCNT3	97	3	-	-
PA-MWCNT5	95	5	-	-
PA-CB5	95	-	5	-
PA-CB7.5	92.5	-	7.5	-
PA-CB10	90	-	10	-
PA-CB15	85	-	15	-
PA-CB20	80	-	20	-
PA-CB30	70	-	30	-
PA-MWCNT1.8-CB1.8	96.4	1.8	1.8	-
PA-MWCNT1.7-CB3.3	95	1.7	3.3	-
PA-MWCNT1.3-CB5.2	93.5	1.3	5.2	-
PA-MWCNT2.6-CB2.6	94.8	2.6	2.6	-
PA-MWCNT2.5-CB5	92.5	2.5	5	-
PA-MWCNT2-CB7.8	90.2	2	7.8	-
PA-MWCNT2.6-KB*2.6	94.8	2.6	-	2.6
PA-MWCNT2.5-KB*5	92.5	2.5	-	5
PA-MWCNT2-KB*7.8	90.2	2	-	7.8

As discussed earlier, the synergy effects between CB and MWCNT significantly increase the electrical conductivity of the composite [28]. The main objective was to obtain the higher electrical conductivity using lower quantity of carbon nanofillers in order to increase the electrical conductivity on one hand and to reduce the high viscosity complications in extrusion process on the other hand.

Hence, conductive polymer composites (CPCs) were generated with various ratio of MWCNT:CB at calculated percolation threshold using equation (1). In addition, conductive polymer composites applying greater extent of MWCNT:CB compared to percolation state was produced to study the electrical conductivity performance of the CPCs. Moreover, the three most conductive CPCs with the same ratio of carbon nanofillers were produced while the CB (Printex) was replaced by KB*(Ketjenblack). The compositions of the above-mentioned composites are presented in Table 1.

Fabric manufacturing

Compound woven structure (compact two-ply weave structure with stuffer weft) was designed and produced using ARM AG CH-3507 Biglen weaving loom manufactured in Switzerland. Conductive monofilaments (PA-MWCNT2.5-CB5 or PA-MWCNT2.5-KB*5) was applied as stuffer weft in the middle of the woven structure. The structure consists of two different warp yarn systems and three weft yarn systems. Two weft and two warp yarn systems made two layers with plain structure as the face and back of the final woven fabric while the conductive monofilaments were inserted in the middle of the structure in the weft direction.

This design was chosen since it was required to reach the maximum stuffer yarn density in the middle of structure (stuffer yarns are straight yarns inserted in the middle of compound woven

structure) in order to achieve the desired shielding. Also, it should be mentioned that the conductive monofilament was inserted as stuffer weft in the middle of the woven structure to provide the possibility of introducing common textile yarns on the exterior faces. In fact, various types of textiles yarns with different colors can be applied to external faces since the final application is for personal protection clothing like corset. So, the design and color would be of great importance for the wearer. The designed structure, the developed monofilament and manufactured woven sample are shown in Figure 2 (a, b and c). In addition, Table 2 reports the structural characteristics of the woven samples.

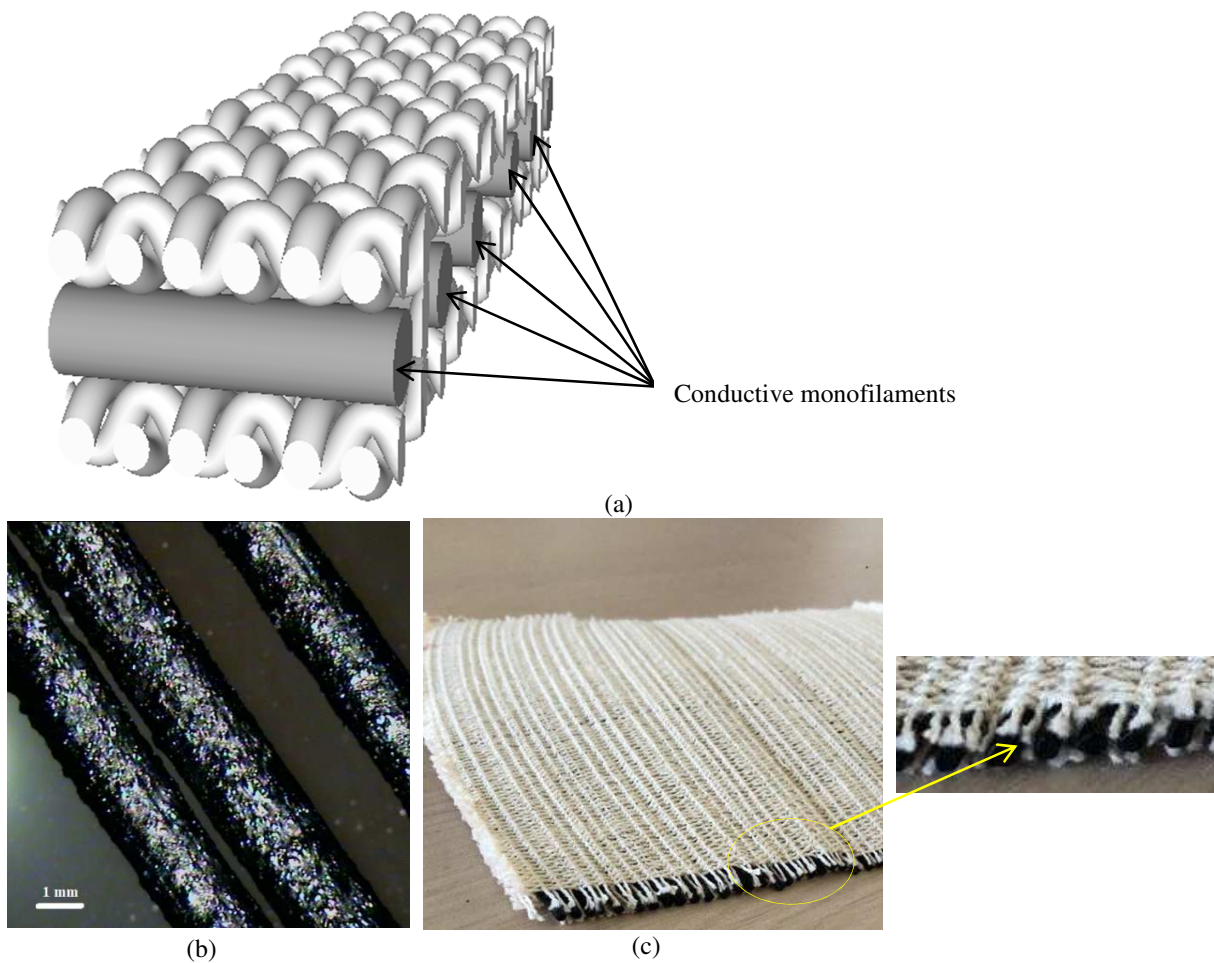


Figure 2- Designed structure (a), conductive monofilament (b) and compact two-ply woven with conductive monofilament as stuffer wefts (c)

Table 2- Structural characteristics of compact two-ply woven samples with stuffer wefts

Fabric characteristics	Thickness (mm)	Arialdensity (g/cm ²)	Material			Yarn diameter (mm)	Yarn density (yarns/cm)
			Warp system	Face	Back		
Sample 1	3.37	0.136	Warp system	Face	Cotton	0.42	15
				Back	Cotton	0.42	15
			Weft system	Face	Cotton	0.42	8
				Stuffer	PA-MWCNT2.5-CB5	1.40	4
				Back	Cotton	0.42	8
Sample 2	3.66	0.155	Warp system	Face	Cotton	0.42	15
				Back	Cotton	0.42	15
			Weft system	Face	Cotton	0.42	8
				Stuffer	PA-MWCNT2.5-KB*5	1.40	4
				Back	Cotton	0.42	8

2.3. Characterization

Characterization of the developed monofilament

Electrical conductivity

As mentioned previously, the electrically conductive materials can produce and conduct free charges which lead to electromagnetic shielding effectiveness. Therefore, the electrical conductivity of all the monofilaments was measured by means of Keithley SMU 2461 source meter by applying a given DC voltage and then measuring the current passing through the monofilament. The voltage applied between two points spaced by $L = 1$ cm was varied from -0.5 to 5 V with an automatic increment of 0.5 V. The (I/V) curve was plotted for each sample and the electrical resistance R was inferred as the inverse slope of the curve. Then, equation (2) was applied to calculate the electrical conductivity.

$$\sigma = \frac{L}{S \times R} \text{ (Eq. 2)}$$

Where σ shows the electrical conductivity (S/m) and S is the cross-section area of the monofilament (m²). The cross-section area was calculated with the mean value of the rod diameter measurement (regarded as circular) for the monofilament. First, the electrical conductivity of PA6,6/MWCNT and PA6,6/CB was measured and plotted as a function of the filler concentration. Then, the percolation threshold generating an electrical conductivity (σ_{th}) for PA6,6-based composite filled with MWCNT as well as the one filled with CB was determined from the curve of electrical conductivity versus filler concentration. Finally, composites with higher electrical conductivity compared to σ_{th} were considered as conductive composites. Moreover, the electrical conductivity of the developed CPCs filled with (MWCNT:CB) or (MWCNT:KB*) was calculated. The preparing process of the composites contained MWCNT and CB (or KB*) was discussed earlier.

Morphology analysis

Dispersion of nanofiller inside the polymer along with its concentration plays a significant role in electrical conductivity of the composite.

Therefore, the qualitative dispersion of MWCNT, CB and (MWCNT:CB) inside PA6,6 was observed for six samples using transmission electron microscopy (TEM).

For this purpose, all the samples were embedded into epoxy resin and ultramicrotome along the longitudinal direction using a diamond knife on a Leica ultra-cut UCT microtome, at Cryo temperature (-120°C) to give a section with a nominal thickness of 70 nm. Then, sections were transferred to Cu grids of 400 meshes. Bright-field TEM images of composites were obtained at 200kV under low dose condition with FEI TECNAI G2 20 electron microscope, using a Gatan CCD camera and Gatan digital micrograph software.

Melt flow index (MFI)

The filament making process is strongly influenced by the viscosity of the composite. So, the MFI value of the composite should be in the standard range for melt mixing process by means of extrusion.

As mentioned previously, increasing of carbon nanofiller inside the conductive polymer composites (CPC) is the main cause of difficulties in filament making process as a result of high viscosity. As a result, low values of MFI approve that the extrusion process of thermoplastic polymers meets complications. Therefore, the viscosity of all the composites was determined by melt flow index (MFI) test, performed at 280 °C with 2.16 kg load (ISO 1133-1), using ThermoHaake apparatus. (All the composite pellets were dried at 80°C for 12 hours before MFI test.)

Mechanical properties

A tensile test was performed for two developed monofilaments using Tinius Olsen H5KT Benchtop tensile tester (ISO 2062) at 20-25°C, 65 RH%. The sample length for the tensile test was fixed at 100 mm and the speed of traction was 50 mm/min. The tensile test was implemented for 5 specimens of each woven sample (sample 1 and sample 2) and the mean values were calculated. Mechanical properties of the electroconductive monofilaments are reported in Table 3.

Table 3- Mechanical properties of the monofilaments applied in the weaving process

Mechanical properties	PA-MWCNT2.5-CB5	PA-MWCNT2.5-KB*5
Maximum Force (N)	159.6	112.1
Elongation at Maximum Force (Δl , mm)	29.9	13
Stress at Maximum Force (MPa)	103.5	72.8
Strain at Maximum Force ($\Delta l/l_0$)	0.3	0.13
Elastic Modulus or E (GPa)	2.78	2.08
Modulus of Rigidity or G (GPa)	1.39	1.04
Tenacity (cN/Tex)	8	5.6

Electromagnetic Shielding effectiveness evaluation of compact two-ply woven structures with conductive monofilaments as stuffer wefts

As mentioned previously, the main objective of the present study was to develop a monofilament yarn of conductive polymer composite (CPC) to produce wearable electromagnetic shielding clothing for personal protection. Therefore, the two developed electrical conductive monofilaments (PA-MWCNT2.5-CB5 and PA-MWCNT2.5-KB*5) were chosen due to their

electrical conductivity and viscosity in order to manufacture electromagnetic shielding woven samples (sample 1 and sample 2).

The electromagnetic shielding effectiveness can be outlined as the ratio of the energy impinging on a side of the shield to the transmitted energy out the other side. Absorption and reflection occur when an electromagnetic wave passes through a shield and the remaining energy is the energy that emerges out from the shield.

An anechoic chamber with a cut-out portion has been employed by some researchers to evaluate the shielding effectiveness of the planar materials such as fabrics [51–55]. However, such electromagnetic measurements are dependent on the wave polarization and a post-calculation should be required to evaluate the shielding effectiveness in a realistic electromagnetic environment. Here, an electromagnetic reverberation chamber (mode-stirred chamber) was employed to evaluate the shielding effectiveness of the samples. Such an apparatus allows evaluating the shielding effectiveness of the fabric in a realistic electromagnetic environment where the wave polarization cannot be controlled. A simple sketch of the mode-stirred chamber used for shielding effectiveness measurement based on IEC61000-4-21 standard is represented in Figure 3 [56]. The experimental set-up includes an emitting antenna and a mode-stirrer producing the external ambient electromagnetic energy around a closed region formed by a metallic box. On one side of the box only a window (size 15x15 cm²) allows to couple a receiving antenna to the ambient electromagnetic energy. The sample under test was introduced in front of the window and the transmitted power to the receiving antenna was measured P_S . The transmitted power was previously measured without sample as a reference P_{REF} as well.

Actually, thanks to the stirrer all the wave polarizations were considered for the measurement. The transmitted power $P_S(\theta)$ and $P_{REF}(\theta)$ was measured by the receiving antenna when the stirrer was rotated from $\theta=0$ to $\theta=360$ degrees (one complete turn) by steps of 4 degrees, and the mean value of P_S and P_{REF} integrated over all the angle θ was considered to calculate the shielding effectiveness by means of equation (3).

$$SE(\text{dB}) = 10 \log_{10} \left(\frac{P_{REF}}{P_S} \right) \quad (\text{Eq. 3})$$

A two-layered sample was introduced in front of the window for electromagnetic shielding effectiveness evaluation. It means that two pieces (15x15cm²) of a woven sample were positioned perpendicular to each other in order to have electrical conductive monofilaments in both vertical and horizontal directions. The shielding effectiveness SE (dB) was measured and recorded at each frequency between 1 and 10 GHz.

Table 4 shows that there is a significant difference across the groups in terms of the electromagnetic shielding effectiveness for general and professional use [57]. It should be noted that the final application of woven samples is to protect body against electromagnetic waves existing in the living environment (for general use).

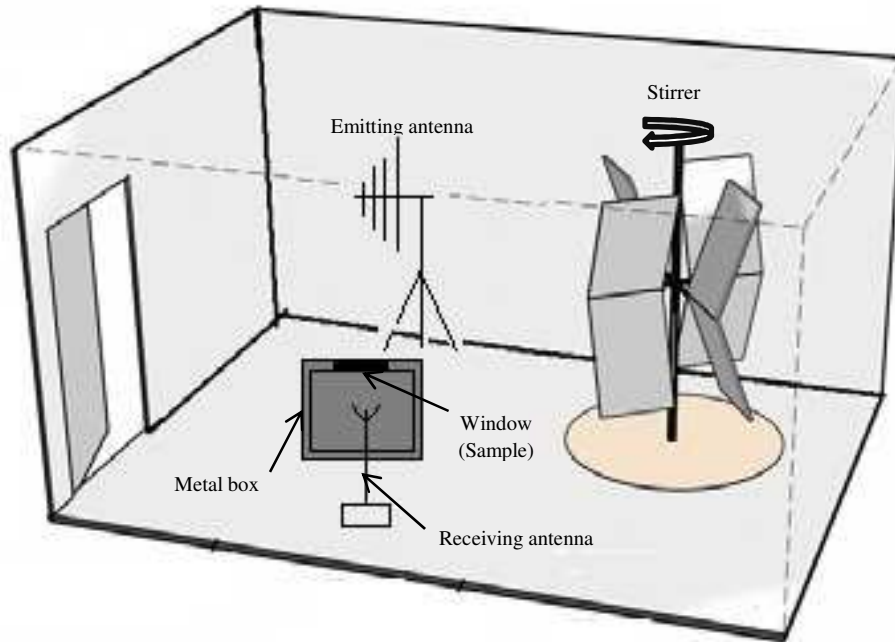


Figure 3- Schematic of the mode-stirred chamber for shielding effectiveness evaluation

Table 4- Performance specifications of electromagnetic shielding textiles [57]

Grade	5	4	3	2	1
	Excellent	Very good	Good	Moderate	Fair
Percentage of electromagnetic shielding (ES)	$SE > 99.9\%$	$99.9\% \geq SE > 99\%$	$99\% \geq SE > 90\%$	$90\% \geq SE > 80\%$	$80\% \geq SE > 70\%$
Shielding effectiveness (SE) in general use	$SE > 30\text{dB}$	$30\text{dB} \geq SE > 20\text{dB}$	$20\text{dB} \geq SE > 10\text{dB}$	$10\text{dB} \geq SE > 7\text{dB}$	$7\text{dB} \geq SE > 5\text{dB}$
Shielding effectiveness (SE) in professional use	$SE > 60\text{dB}$	$60\text{dB} \geq SE > 50\text{dB}$	$50\text{dB} \geq SE > 40\text{dB}$	$40\text{dB} \geq SE > 30\text{dB}$	$30\text{dB} \geq SE > 20\text{dB}$

3. Result and Discussion

Electrical conductivity of monofilament composites contained MWCNT or CB

The objective of the present work was to obtain high electrical conductivity using low content of conductive nanofillers in the composite. The function of the produced composite was to develop a hybrid monofilament yarn for electromagnetic shielding effectiveness textile application. Therefore, the viscosity of the composite should be taken into account since high viscosity causes complications during the melt mixing (extrusion) process.

PA6,6/MWCNT composites were produced with different content of MWCNT and the electrical conductivity curve is represented in Figure 4 (the blue curve). The percolation threshold of electrical conductivity of PA6,6 composite filled with MWCNT was determined on electrical conductivity curve. It is noted that the quantity of MWCNT should be higher than its amount at percolation threshold to generate an electroconductive composite. The conductive network was developed by increasing the content of MWCNT in CPC which led to higher electrical conductivity. The mass concentration of MWCNT in the polymer matrix (PA6,6) was 2 wt.% at percolation threshold. Obviously, the conductivity was increased using more quantity of

MWCNT in polymer substrate while all the developed CPCs after percolation are considered electrically conductive. As a result, PA-MWCNT2, PA-MWCNT3 and PA-MWCNT5 were revealed as electrical conductive composites.

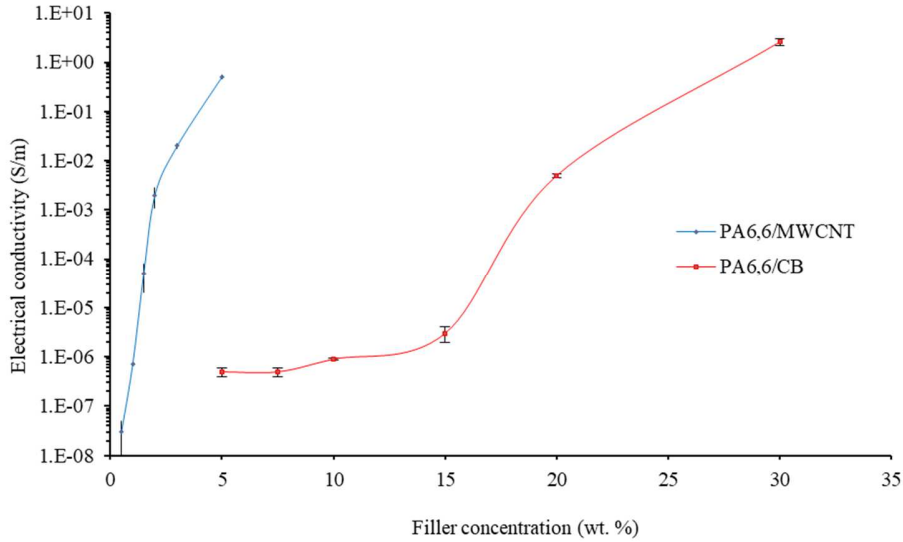


Figure 4- Electrical conductivity of PA6,6 composites filled with MWCNT or CB

Also, the electrical conductivity of PA6,6/MWCNT was plotted versus MWCNT weight percentage (wt.%) in Figure 5 according to the classical percolation power law given in equation (4) [58-59]. Where σ_0 is scaling factor, ρ_c is the percolation threshold of electrical conductivity, σ is the conductivity of the CPC and ρ is the nanofiller content of the produced CPC. It can be seen that the critical component was 0.8 when ρ_c was 2 wt. %.

$$\sigma = \sigma_0(\rho - \rho_c)^t, \text{ for } \rho > \rho_c \text{ (Eq. 4)}$$

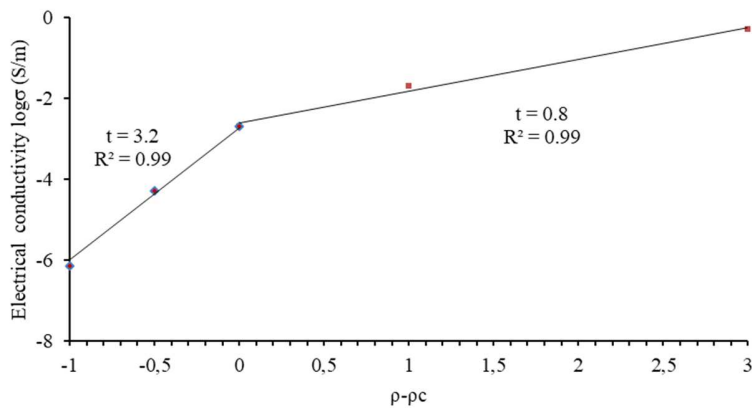


Figure 5- Electrical conductivity of fitting curve with $\rho_c = 2$ wt. % using power law equation for PA6,6/MWCNT composite

Similarly, PA6,6/CB composite was produced using different quantity of CB. The percolation threshold of electrical conductivity for PA6,6/CB was determined on the electrical conductivity curve represented in Figure 4 (the red curve). The amount of CB was 15 wt.% at percolation threshold and the electrical conductivity of the CPC was meaningfully increased after percolation threshold. Consequently, PA-CB15, PA-CB20 and PA-CB30 were considered as conductive composites though the concentration of CB was considerably high to generate an electroconductive composite. Furthermore, the electrical conductivity of PA6,6/CB was plotted versus CB weight percentage (wt.%). This curve is depicted in Figure 6 while the critical component was 0.4 and ρ_c was 15 wt.%.

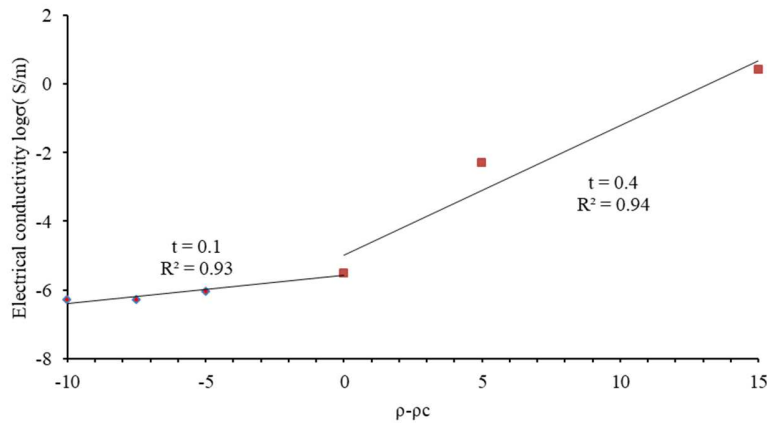


Figure 6- Electrical conductivity of fitting curve with $\rho_c = 15$ wt. % using power law equation for PA6,6/CB composite

In addition, the dispersion of MWCNT was observed using TEM images for two samples before (PA-MWCNT1.5) and after (PA-MWCNT5) percolation threshold in Figure 7 (a and b). The MWCNTs in PA-MWCNT1.5 composite was not well dispersed as MWCNTs agglomerated in some regions. Also, the mass concentration of MWCNT was not sufficient for PA-MWCNT1.5 and as a result, PA-MWCNT1.5 was not electrically conductive.

The TEM image of PA6,6/MWCNT while the quantity of MWCNT was increased to 5 wt.% (PA-MWCNT5) is shown in Figure 7(b). It was suggested that MWCNTs were homogeneously dispersed in PA-MWCNT5 which established the electrical conductivity.

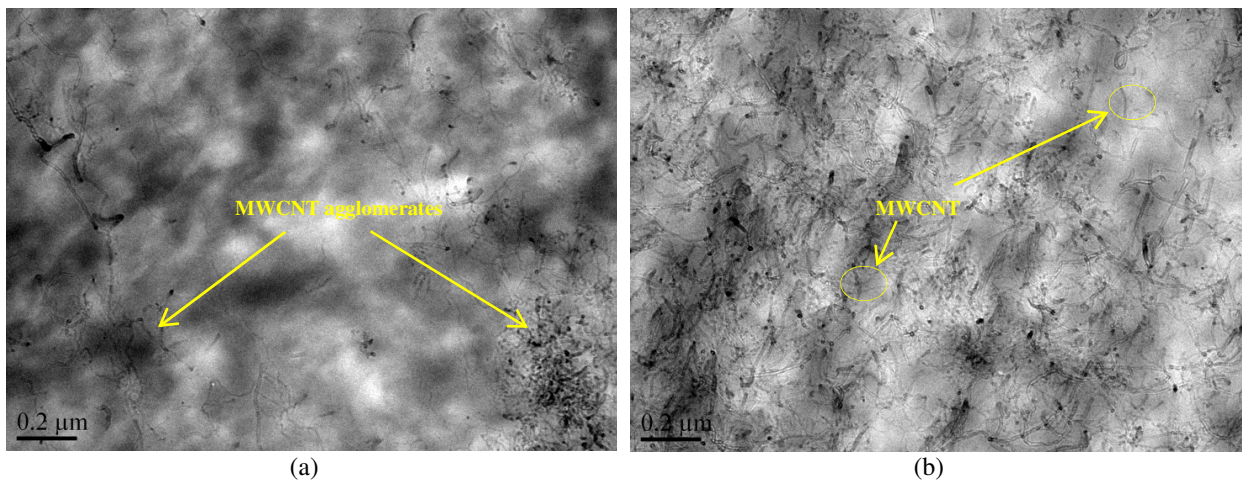


Figure 7-Transmission electron microscopy images of PA-MWCNT1.5 (a) and PA-MWCNT5 (b)

Also, the TEM images of PA-CB10 and PA-CB20 are represented in Figure 8 (a and b) to investigate the performance of CB nanofillers at two different concentrations of CB. It was suggested that CBs were agglomerated in some regions of PA-CB10 while CBs were homogeneously dispersed in PA-CB20.

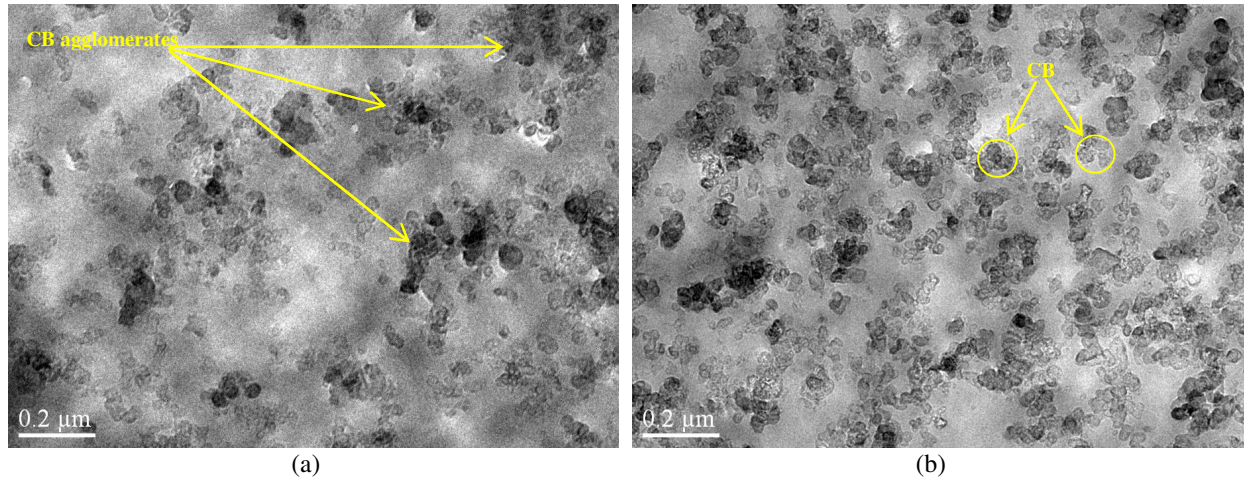


Figure 8- Transmission electron microscopy images of PA-CB10 (a) and PA-CB20 (b)

In general, the CPC having MWCNT has a quite low percolation threshold compared to the one with CB in its composition. This is certainly because of the higher surface area of MWCNT compared to CB which cooperates in electrical conductivity enhancement. Also, it should be noted that the MWCNT dispersion was satisfactory in the polymer matrix and the electrical conductivity was established in the polymer using less amount of MWCNT compared to CB.

Electrical conductivity of monofilament composites contained MWCNT and CB (MWCNT:CB)

As declared in aforementioned section, the higher electrical conductivity was attained while the amount of conductive nanofiller was increased. The thermoplastic polymers are not generally electrically conductive and using conductive nanofillers is the well-known technique to enhance the electrical conductivity of the composites. However, the high quantity of conductive nanofiller increases the viscosity and the cost of the final product.

Therefore, the best alternative was to increase the electrical conductivity while the amount of carbon nanofillers kept low applying the constructive effects of synergy between MWCNT and CB. For this purpose, different composites were produced with three different ratio between MWCNT and CB. Three CPCs were generated at percolation threshold and three other composites were produced while the greater amount of carbon nanofillers (50% greater) compared to the mass concentrations of nanofillers at percolation threshold was applied. It is noted that the critical percolation threshold of conductivity was calculated using the equation (1) provided in [34]. After that, the electrical conductivity of all the composites was determined and shown in Figure 9.

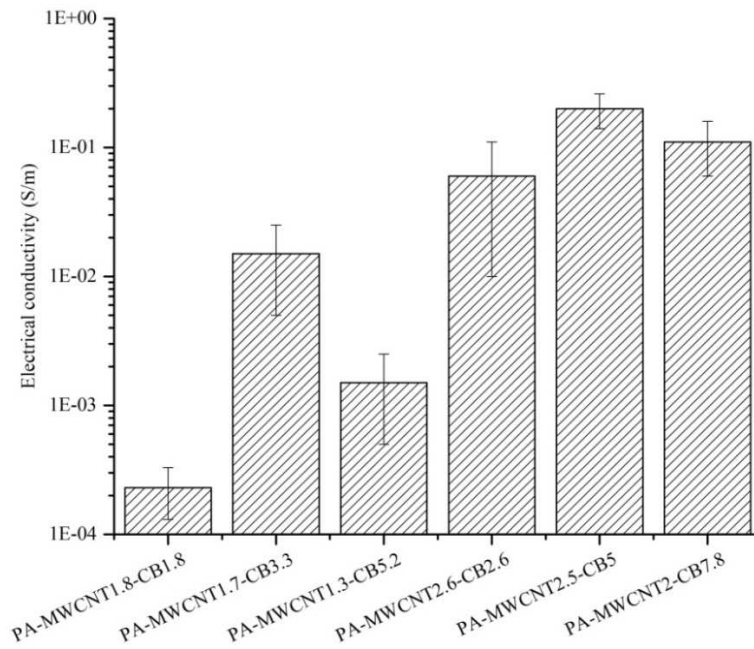


Figure 9 - Electrical conductivity versus nanofiller concentration (MWCNT:CB)

The results confirmed a significant growth in electrical conductivity due to the positive effects of synergism between MWCNT and CB.

Furthermore, three composites were produced using the same mass concentration of nanofillers while the CB was substituted with KB* (PA-MWCNT2.6-KB*2.6, PA-MWCNT2.5-KB*5 and PA-MWCNT2-KB*7.8).

Figure 10 illustrates the electrical conductivity of six generated composites contained MWCNT:KB* or MWCNT:CB. The higher electrical conductivity was observed for the composites with KB* compared to the ones with CB while other parameters kept constant (unchanged). The idea was to confirm the influence of the surface area of conductive additive on electrical conductivity due to the fact that KB* surface area is four times greater than CB.

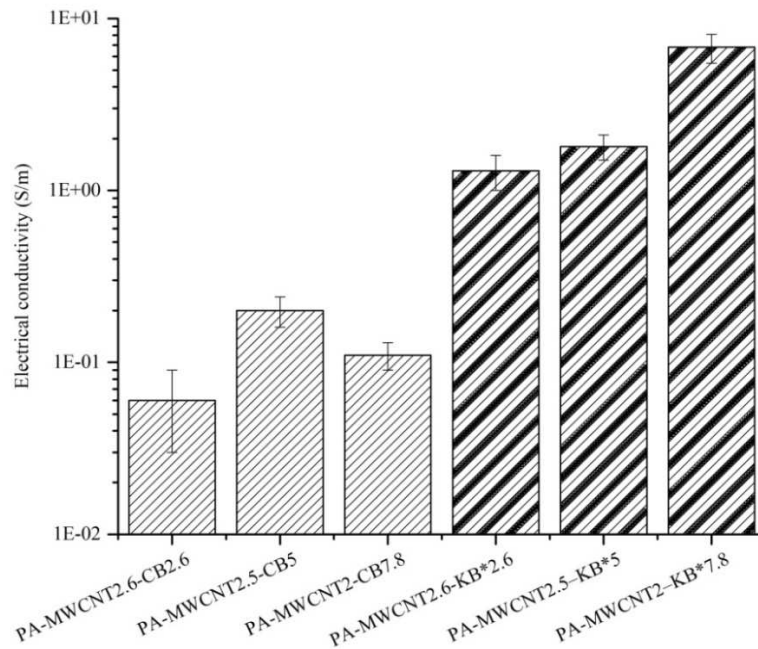


Figure 10- Electrical conductivity versus nanofillers concentration (MWCNT:CB or MWCNT:KB*)

The results stated that the conductivity of the composite with KB* was higher than the one contained CB. It is speculated to be due to a higher surface area of KB* which has a great impact on the electrical conductivity of the developed CPCs.

As discussed earlier, the conductivity of CPCs is influenced by dispersion and concentration of carbon nanofillers in the polymer matrix. Thus, the dispersion of carbon nanofillers in PA6,6 was observed for two samples (PA-MWCNT1.7-CB3.3) and (PA-MWCNT2.5-CB5) using TEM which is illustrated in Figure 11 (a and b).

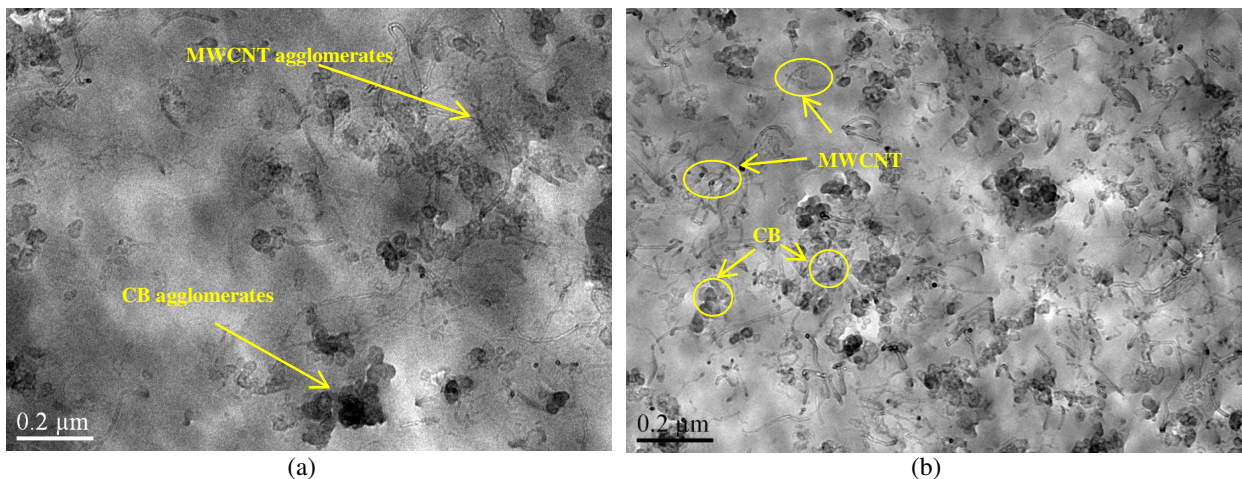


Figure 11- Transmission electron microscopy images of PA-MWCNT1.7-CB3.3 (a) and PA-MWCNT2.5-CB5 (b)

The dispersion of carbon nanofillers was absolutely satisfying for sample PA-MWCNT2.5-CB5 as it can be observed in Figure 11(b). It affirms that nanofillers mutually act like connections between one another thanks to synergy effects between CB and MWCNT.

In fact, carbon nanofillers in PA-MWCNT2.5-CB5 were well dispersed compared to the composite contained one kind of carbon nanofillers. It occurred due to the fact that one of nanofiller particles (e.g. CB) played a connection role between the other nanofiller particles (e.g. MWCNT) and it led to uniform dispersion of nanofillers inside the composite. To conclude, the nanofillers were homogeneously dispersed in PA-MWCNT2.5-CB5. Therefore, PA-MWCNT2.5-CB5 revealed the highest conductivity among all PA6,6-base composites filled with CB, MWCNT or MWCNT:CB.

Melt flow index experiment

It should be taken into account that the main peculiarity in high electrical conductive composite making process is viscosity. So, the viscosity of composites was defined by MFI test. The MFI values for all the composites (listed in Table 1) were measured since MFI has a major impact on determining spinnability conditions and the possibility of melt spinning. The very low value of MFI indicates the high viscosity of the composite and probable difficulties in the extrusion process.

The MFI value was decreased by increasing the quantity of nanofillers shown in Figure 12. The same MFI trend was observed for both PA6,6/MWCNT and PA6,6/CB composites although the viscosity was significantly increased using the smaller amount of MWCNT compared to CB.

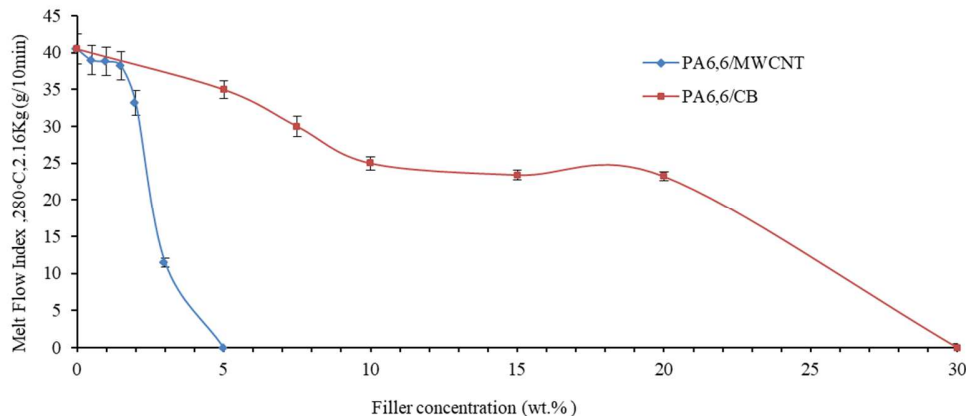


Figure 12- Melt flow index values for PA6,6/MWCNT and PA6,6/CB composites

The results confirmed that nanofillers cause viscosity complications in extrusion process although the electrical conductivity is increased. For example, PA-MWCNT5 and PA-CB30 cannot be considered to apply in yarn making process by melt mixing method due to the high viscosity. Also, the higher surface area of MWCNT compared to CB led to MFI value reduction using less amount of MWCNT. It should be considered that MFI value plays a crucial role in spinnability of polymer composites using melt mixing method. Thus, the composition should be optimized in terms of electrical conductivity and viscosity.

The synergy between MWCNT and CB was applied to obtain the high electrical conductivity in the composite. The results showed that the electrical conductivity was relatively high compared to the composite contained one kind of nanofillers. The MFI values for all the composites contained MWCNT:CB is represented in Figure 13.

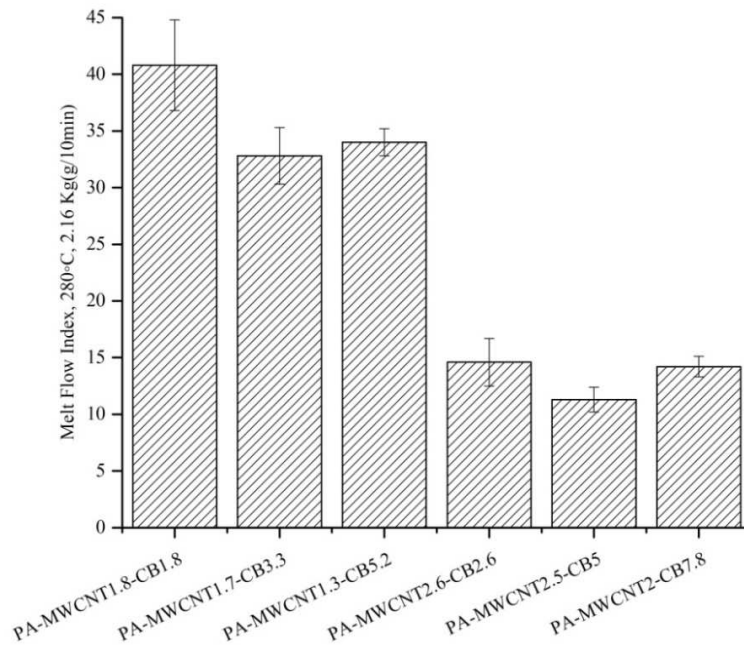


Figure 13- Melt flow index values for PA6,6/MWCNT:CB composites

The results were compared to MFI values of the composites contained one kind of nanofillers (MWCNT or CB) in their compositions. It was concluded that badly behaved of viscosity was diminished given that the synergy effects between carbon nanofillers. Furthermore, the MFI values of the composites contained MWCNT:CB or MWCNT:KB* were presented in Figure 14.

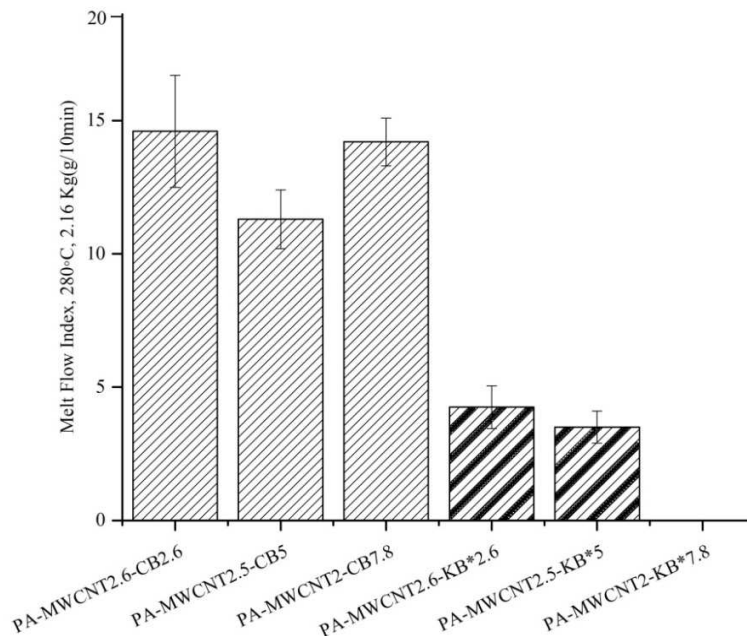


Figure 14- Melt flow index values for PA6, 6/MWCNT:CB and PA6,6/MWCNT:KB* composites

It was observed that the MFI of PA-MWCNT2-KB*7.8 was zero though this composite reached the highest electrical conductivity among all the produced CPCs. To conclude, the high viscosity of the composite with high content of KB* (PA-MWCNT2-KB*7.8) made it incompatible with melt mixing process even though its electrical conductivity was comparatively appropriate compared to the one contained the same content of CB and MWCNT.

Electromagnetic Shielding effectiveness evaluation of compact two-ply woven samples using conductive monofilaments as stuffer wefts

Two compact two-ply samples were manufactured with conductive monofilaments PA-MWCNT2.5-CB5 for sample 1 and PA-MWCNT2.5-KB*5 for sample 2 as stuffer weft yarn in the middle of the structure. The electromagnetic shielding effectiveness of woven samples was measured in the frequency band 1-10 GHz in a mode-stirred chamber. The shielding effectiveness of these samples (sample 1 and sample 2) and the average curves of the electromagnetic shielding effectiveness are represented in Figure 15. It should be noted that the scattered SE data can be explained by the limited number of measurements. The stirrer was rotated by steps of 4 degrees and SE was calculated by the average of 90 measurements. In order to reduce the data scattering, the step intervals have to be reduced which results in a greater number of measurements. However, the average value is considered as SE value at each frequency and it is not meaningfully influenced by increasing the number of measurements.

It should be noted that these two monofilaments were chosen for fabric weaving due to their electrical conductivity and viscosity which make them appropriate for yarn making process by melt mixing method.

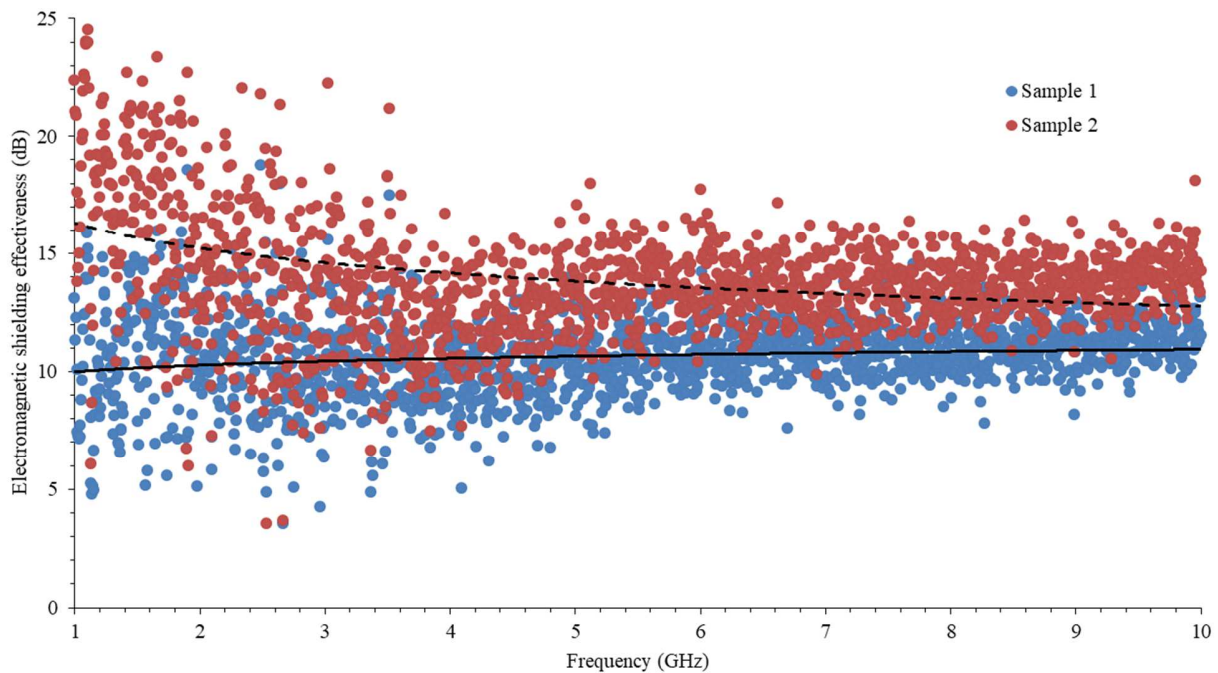


Figure 15- Electromagnetic shielding effectiveness of compact two-ply woven samples with conductive monofilaments as stuffer wefts in the frequency band 1-10 GHz

The average value of electromagnetic shielding effectiveness for the sample woven with PA-MWCNT2.5-KB*5 monofilament as stuffer weft yarn (sample 2) was 16 dB at 1 GHz while it slightly decreased to 13dB at 10 GHz. The electromagnetic shielding effectiveness was around

15.5 dB between 1.8 GHz and 2.4 GHz and it was 14 dB at 5.8 GHz when 1.8 GHz corresponds to the frequency for mobile applications and 2.4 GHz and 5.8 GHz correspond to the ISM bands in Europe [60].

Moreover, the average value of electromagnetic shielding effectiveness of the woven sample with PA-MWCNT2.5-CB5 monofilament as middle weft yarn (sample 1) was higher than 10 dB in the frequency range 1-10 GHz. It was suggested that sample 2 (contained PA-MWCNT2.5-KB*5 monofilament as middle weft) showed higher protection compared to the one weaved with PA-MWCNT2.5-CB5 monofilament. The reason for that is correlated to the tenfold greater conductivity measured for PA-MWCNT2.5-KB*5 in comparison with that of PA-MWCNT2.5-CB5.

In conclusion, woven samples using the developed monofilaments are introduced as good candidates to apply for personal protection clothing against electromagnetic waves in our living environments as mentioned in Table 4.

4. Conclusion

In the present study, a set of conductive polymer composites (CPC) were developed using PA6,6 and the combination of carbon black (CB or KB*) and multiwall carbon nanotube (MWCNT) by melt mixing method. The measured electrical conductivity of the developed monofilament was in agreement with the synergy effects between carbon nanofillers.

It was noted that the nanofillers concentration has to be optimized due to the electrical conductivity and viscosity in order to make an appropriate composite for textile application. In terms of viscosity, the MFI value of the most conductive monofilament contained PA6,6, MWCNT and CB was 11.5 g/10min (at 280°C, 2.16 Kg load) which is tolerable in melt mixing method. In brief, the synergy effects of CB and MWCNT increased the electrical conductivity while the viscosity was controllable.

Moreover, two conductive monofilaments (PA-MWCNT2.5-CB5 and PA-MWCNT2.5-KB*5) were applied in weaving process in order to make electromagnetic shield fabrics for wearable personal protection and the electromagnetic shielding effectiveness was evaluated in the frequency range 1-10 GHz.

To conclude, the synergy effects between carbon black and multi wall carbon nanotube had a constructive influence on nanofiller dispersion in the composite. As a result, the electrical conductivity was improved while the viscosity was in acceptable range for extrusion. Also, the electromagnetic shielding effectiveness of the woven sample using the developed conductive monofilament as stuffer weft in the middle of the structure was promising for personal protection clothing ($SE \geq 10$ dB).

In our further work, the diameter and flexibility of the developed monofilament will be improved in order to design various comfortable electromagnetic shield fabrics for personal protection.

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References

- [1] L.M. Castano, A.B. Flatau, Smart fabric sensors and e-textile technologies: a review, *Smart Mater. Struct.* 23 (2014) 053001. doi:10.1088/0964-1726/23/5/053001.
- [2] H. Pang, L. Xu, D. Yan, Z. Li, Progress in polymer science conductive polymer composites with segregated

- structures, *Prog. Polym. Sci.* 39 (2014) 1908–1933. doi:10.1016/j.progpolymsci.2014.07.007.
- [3] A. Kolanowska, D. Janas, A.P. Herman, R.G. Jędrzyak, T. Giżewski, S. Boncel, From blackness to invisibility – Carbon nanotubes role in the attenuation of and shielding from radio waves for stealth technology, *Carbon N. Y.* 126 (2018) 31–52. doi:10.1016/j.carbon.2017.09.078.
- [4] H.G. Ortlek, O.G. Saracoglu, O. Saritas, S. Bilgin, Electromagnetic shielding characteristics of woven fabrics made of hybrid yarns containing metal wire, *Fibers Polym.* (2012). doi:10.1007/s12221-012-0063-6.
- [5] S. Maity, K. Singha, P. Debnath, M. Singha, Textiles in electromagnetic radiation protection, *J. Saf. Eng.* 2 (2013) 11–19. doi:10.5923/j.safety.20130202.01.
- [6] K. Takazawa, N. Ishikawa, H. Miyagawa, T. Yamamoto, A. Hariya, Sh. Dohi, Metal allergy to stainless steel wire after coronary artery bypass grafting, *Journal of Artificial Organs*, 6 (2003), 71-72.
- [7] G. N. Flint, A metallurgical approach to metal contact dermatitis, *Metallurgy and Contact Dermatitis*, 39(1998) , 213–221.
- [8] W.R. Schriver, R.H. Shereff, J. Domnitz, E. Swintak, S.Sivjan, Allergic response to stainless steel wire, *Oral Surgery, Oral Medicine, Oral Pathology*, 42-5(1976), 578-581. [https://doi.org/10.1016/0030-4220\(76\)90207-3](https://doi.org/10.1016/0030-4220(76)90207-3).
- [9] Y. Lu, S. Jiang, Y. Huang, Ultrasonic-assisted electroless deposition of Ag on PET fabric with low silver content for EMI shielding, *Surf. Coatings Technol.* (2010). doi:10.1016/j.surfcoat.2010.02.061.
- [10] D. Negru, C. Buda, Electrical conductivity of woven fabrics coated with carbon black particles, *Fibres Text. East. Eur.* 1 (2012) 53–56.
- [11] M.S. Kim, H.K. Kim, S.W. Byun, S.H. Jeong, Y.K. Hong, J.S. Joo, K.T. Song, J.K. Kim, C.J. Lee, J.Y. Lee, PET fabric/polypyrrole composite with high electrical conductivity for EMI shielding, *Synth. Met.* (2002). doi:10.1016/S0379-6779(01)00562-8.
- [12] B. Weng, F. Xu, K. Lozano, Development of hierarchical structured carbon nanotube-nylon nanofiber mats, *J. Appl. Polym. Sci.* 132 (2015) 3–9. doi:10.1002/app.42535.
- [13] D.J. Thomas, Ultrafine graphitised MWCNT nanostructured yarn for the manufacture of electrically conductive fabric, (2017) 1–4.
- [14] G.H. Motlagh, A.N. Hrymak, M.R.Thomson, Improved Through-Plane Electrical Conductivity in a Carbon-Filled Thermoplastic via Foaming, *Polym. Eng. Sci.* 48 (2008) 687–696. doi:10.1002/pen.21001.
- [15] M.B.Jakubinek, M. B. Johnson, M. A. White, C. Jayasinghe, G. Le, W. Cho, M. J.Schulz, V. Shanove, Thermal and electrical conductivity of array-spun multi-walled carbon nanotube yarns, *Carbon N. Y.* 50 (2012) 244–248. <https://doi.org/10.1016/j.carbon.2011.08.041>.
- [16] S.A. Hashemi, S.M. Mousavi, M. Arjmand, N. Yan, U. Sundararaj, Electrified single-walled carbon nanotube/epoxy composite via vacuum shock technique: Effect of alignment on electrical conductivity and electromagnetic interference shielding, *Polym. Compos.* 39 (2018) E1139–E1148. doi:10.1002/pc.24632.
- [17] L. Wang, H. Liang, P. Song, Y. Han, J. Gu, J. Gu, Z. Guo, Electromagnetic interference shielding MWCNT - Fe₃O₄Ag /epoxy nanocomposites with satisfactory thermal conductivity and high thermal stability, *Carbon* 141 (2019) 506-514. <https://doi.org/10.1016/j.carbon.2018.10.003>.
- [18] X. Ma, B. Shen, L. Zhang, Y. Liu, W. Zhai, W. Zheng, Porous super hydrophobic polymer/carbon composites for lightweight and self-cleaning EMI shielding application, *Compo Science and Technology.* 158 (2018) 86-93. <https://doi.org/10.1016/j.compscitech.2018.02.006>.
- [19] K. Jagatheesan, A. Ramasamy, A. Das, A. Basu, Electromagnetic shielding behavior of conductive filler composites and conductive fabrics ??? A review, *Indian J. Fibre Text. Res.* 39 (2014).
- [20] W.L. Song, M.S. Cao, M.M. Lu, S. Bi, C.Y. Wang, J. Liu, J. Yuan, L.Z. Fan, Flexible graphene/polymer composite films in sandwich structures for effective electromagnetic interference shielding, *Carbon N. Y.* (2014). doi:10.1016/j.carbon.2013.08.043.
- [21] M.H. Al-Saleh, W.H. Saadeh, U. Sundararaj, EMI shielding effectiveness of carbon-based nanostructured polymeric materials: A comparative study, *Carbon N. Y.* (2013). doi:10.1016/j.carbon.2013.04.008.
- [22] B. Weng, F. Xu, A. Salinas, K. Lozano, Mass production of carbon nanotube reinforced poly(methyl methacrylate) nonwoven nanofiber mats, *Carbon N. Y.* 75 (2014) 217–226. doi:10.1016/j.carbon.2014.03.056.
- [23] F. Du, J.E. Fischer, K.I. Winey, Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites, *Phys. Rev. B - Condens. Matter Mater. Phys.* 72 (2005) 1–4. doi:10.1103/PhysRevB.72.121404.
- [24] Y.L. Huang, S.M. Yuen, C.C.M. Ma, C.Y. Chuang, K.C. Yu, C.C. Teng, H.W. Tien, Y.C. Chiu, S.Y. Wu, S.H. Liao, F.B. Weng, Morphological, electrical, electromagnetic interference (EMI) shielding, and tribological properties of functionalized multi-walled carbon nanotube/poly methyl methacrylate (PMMA)

- composites, *Compos. Sci. Technol.* (2009). doi:10.1016/j.compscitech.2009.05.006.
- [25] Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, Carbon nanotube-polymer composites: Chemistry, processing, mechanical and electrical properties, *Prog. Polym. Sci.* 35 (2010) 357–401. doi:10.1016/j.progpolymsci.2009.09.003.
- [26] M.L. Clingerman, E.H. Weber, K.H. Schulz, J.A. King, Tensile, thermal, and electrical properties of carbon filled Nylon 6,6 conductive resins, Department of Chem Engineering, Michigan Technological University 262–263.
- [27] P. Verma, P. Saini, R.S. Malik, V. Choudhary, Excellent electromagnetic interference shielding and mechanical properties of high loading carbon-nanotubes/polymer composites designed using melt recirculation equipped twin-screw extruder, *Carbon N. Y.* 89 (2015) 308–317. doi:10.1016/j.carbon.2015.03.063.
- [28] M.S. Han, Y.K. Lee, H.S. Lee, C.H. Yun, W.N. Kim, Electrical, morphological and rheological properties of carbon nanotube composites with polyethylene and poly(phenylene sulfide) by melt mixing, *Chem. Eng. Sci.* (2009). doi:10.1016/j.ces.2009.02.026.
- [29] Z.A. Ghaleb, M. Mariatti, Z.M. Ariff, Synergy effects of graphene and multiwalled carbon nanotubes hybrid system on properties of epoxy composites, (2017). doi:10.1177/0731684417692055.
- [30] S.M. Zhang, L. Lin, H. Deng, X. Gao, E. Bilotti, T. Peijs, Q. Zhang, Q. Fu, Synergistic effect in conductive networks constructed with carbon nanofillers in different dimensions, *Express Polym. Lett.* 6 (2012) 159–168. doi:10.3144/expresspolymlett.2012.17.
- [31] H. Ismail, A.F. Ramly, N. Othman, The Effect of Carbon Black/Multiwall Carbon Nanotube Hybrid Fillers on the Properties of Natural Rubber Composites, *Polym. Plast. Technol. Eng.* 50 (2011) 660–666. doi:10.1080/03602559.2010.551380.
- [32] A. Dorigato, M. Brugnara, A. Pegoretti, Synergistic effects of carbon black and carbon nanotubes on the electrical resistivity of poly(butylene-terephthalate) composites, *Adv. Polym. Technol.* (2017) 1–11. doi:10.1002/adv.21833.
- [33] A. Motaghi, A. Hrymak, G.H. Motlagh, Electrical conductivity and percolation threshold of hybrid carbon/polymer composites, *J. Appl. Polym. Sci.* 132 (2015) 1–9. doi:10.1002/app.41744.
- [34] I. Kranauskaitė, J. Macutkevič, A. Borisova, A. Martone, M. Zarrelli, A. Selskis, A. Aniskevich, J. Banys, Enhancing electrical conductivity of multiwalled carbon nanotube/epoxy composites by graphene nanoplatelets, *Lith. J. Phys.* 57 (2017) 232–242. doi:10.3952/physics.v57i4.3602.
- [35] M. Sadari, M.S. Alhaik, A review on polymeric nanocomposites: effect of hybridization and synergy on electrical properties, *Carbon-Based Polymer Nanocomposites for Environmental and Energy Applications* (2018) 113-146, <https://doi.org/10.1016/B978-0-12-813574-7.00005-8>.
- [36] H. Zhang, G. Zhang, M. Tang, L. Zhou, X. Fan, X. Shi, J. Qin, Synergistic effect of carbon nanotube and graphene nanoplatelets on the mechanical, electrical and electromagnetic interference shielding properties of polymer composites and polymer composite foams, *Chemical Engineering Journal*, 353 (2018) 381-393.
- [37] Z. F. Sun, P.G. Ren, Z.W. Zhang, F. Ren, Synergistic effects of conductive carbon nanofillers based on the ultrahigh-molecular-weight polyethylene with uniform and segregated structures, *Journal of Applied Polymer Science* (2018). <https://doi.org/10.1002/app.47317>.
- [38] P. Cheng, Ma, H. Zhang, S.Q. Wang, Y.K. Wong, B.Z. Tang, S.H. Hong, K.-W. Paik, J.-K. Kim, Electrical conducting behavior of hybrid composites containing carbon nanotubes and carbon black, 2007 Int. Conf. Electron. Mater. Packag. (2007) 1–4. doi:10.1109/EMAP.2007.4510279.
- [39] Y. Sun, H. Da Bao, Z.X. Guo, J. Yu, Modeling of the electrical percolation of mixed carbon fillers in polymer-based composites, *Macromolecules.* 42 (2009) 459–463. doi:10.1021/ma8023188.
- [40] W. De Zhang, L. Shen, I.Y. Phang, T. Liu, Carbon nanotubes reinforced nylon-6 composite prepared by simple melt-compounding, *Macromolecules.* 37 (2004) 256–259. doi:10.1021/ma035594f.
- [41] L. Qiu, Y. Chen, Y. Yang, L. Xu, X. Liu, A Study of surface modifications of carbon nanotubes on the properties of Polyamide 66 / Multiwalled Carbon Nanotube Composites, *Journal of Nanomaterials* (2013), 1-8, <http://dx.doi.org/10.1155/2013/252417>.
- [42] O. Breuer, U. Sundararaj, Big returns from small fibers: A review of polymer/carbon nanotube composites, *Polym. Compos.* 25 (2004) 630–645. doi:10.1002/pc.20058.
- [43] I.Y. Phang, J. Ma, L. Shen, T. Liu, W. Zhang, Crystallization and melting behavior of multi-walled carbon nanotube-reinforced nylon-6 composites, 79 (2006) 71–79. doi:10.1002/pi.1920.
- [44] S.W. Kim, T. Kim, Y.S. Kim, S. H. Choi, H. Lim, S.J. Yang, Ch. R. Park, Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers, *Carbon* 50(2012)3–33. <https://doi.org/10.1016/j.carbon.2011.08.011>.

- [45] P. Cheng, Ma, N. A. Siddiquia, GadMarom, Jang-KyoKim, Dispersion and functionalization of carbon nanotubes for polymer-based composites: A review, *Compos. Part A Appl. Sci. Manuf.* 41 (2010) 1345–1367. <https://www.sciencedirect.com/science/article/pii/S1359835X10002009>.
- [46] R. Rastogi, R. Kaushal, S.K. Tripathi, A.L. Sharma, I. Kaur, L.M. Bharadwaj, Comparative study of carbon nanotube dispersion using surfactants, *J. Colloid Interface Sci.* 328 (2008) 421–428. doi:10.1016/j.jcis.2008.09.015.
- [47] H. Wang, Dispersing carbon nanotubes using surfactants, *Curr. Opin. Colloid Interface Sci.* 14 (2009) 364–371. doi:10.1016/j.cocis.2009.06.004.
- [48] A. Ferreira, F. Ferreira and M.C. Paiva, Textile sensor applications with composite monofilaments of Polymer /carbon nanotubes, *Advances in Science and Technology*, 80 (2013) 65 doi:10.4028/www.scientific.net/AST.80.65
- [49] M. T. Byrne and Y. K. Gunko, Recent advances in research on carbon nanotube-polymer composites, *Advanced Materials*, 22 (2010), 1672-1688. doi/10.1002/adma.200901545.
- [50] K. Liu, Y. Sun, X. Lin, R. Zhou, J. Wang, S. Fan and K. Jiang, Scratch-resistant, highly conductive High-strength carbon nanotube-based composite yarns, *American Chemical Society*, 4(10), (2010), 5827-5843; doi/abs/10.1021/nn1017318.
- [51] J.M. Janukiewicz, Methods for evaluating the shielding effectiveness of textiles, *Fibres & Textiles in Eastern Europe*, vol. 14, no. 5 (2006) 18–22.
- [52] C. Morari, I. Bălan, Methods for determining shielding effectiveness of materials, *Electrotehnică, electronică, automatică*, vol. 63,2 (2015) 126-136.
- [53] R. Perumalraj, B.S. Dasaradan, Electromagnetic shielding effectiveness of copper core yarn knitted fabrics, *Indian J. Fibre Text. Res.* (2009).
- [54] A. Niembro-martin, E. Pistono, P. Lemaître-auger, T. Vuong, G. Eymin, P. Tourtollet, Efficient setup for the measurement of transmission- coefficients with a single-room anechoic chamber, *IEEE* (2014) 3–5.
- [55] S. Geetha, K.K.S. Kumar, D. C. Trivedi Chepuri R. K. Rao, M. Vijayan, EMI Shielding: Methods and materials—a review, *J. Appl. Polym. Sci.* 112 (2009) 2073–2086.
- [56] Electromagnetic compatibility (EMC) – Part 4-21: Testing and measurement techniques – Reverberation chamber test methods, *International Standard IEC 61000-4-21* (2011).
- [57] FTTS-FA-003: Test method of specified requirements of electromagnetic shielding textiles., Taiwan, 2003.
- [58] A.S. Hoang, Electrical conductivity and electromagnetic interference shielding characteristics of multiwalled carbon nanotube filled polyurethane composite films, *Adv. Nat. Sci. Nanosci. Nanotechnol.* 2 (2011) 025007. doi:10.1088/2043-6262/2/2/025007.
- [59] J. Xu, M. Wong, C.P. Wong, Super high dielectric constant carbon black-filled polymer composites as integral capacitor dielectrics, 2004 Proceedings. 54th Electron. Components Technol. Conf. (IEEE Cat. No.04CH37546). 1 (2004) 536–541. doi:10.1109/ECTC.2004.1319391.
- [60] The European table of frequency allocations and applications in the frequency range 8.3 KHz to 3000 GHz (ECA Table), European conference of postal and telecommunication administration (CEPT), (2015).