**Paulina Latko,
Rafał Kozera,
*Axel Salinier,
Anna Boczkowska**

**Warsaw University of Technology,
Department of Materials Science and Engineering,**
Wołoska 141, 02-507 Warsaw, Poland
E-mail: paulinalatko@interia.pl

***CANOE- Bâtiment Chemstart'Up,**
Pôle 2Allée Le Corbusier, 64170 LACQ - France

Non-Woven Veils Manufactured from Polyamides Doped with Carbon Nanotubes

Abstract
Polymer - based nanocomposite materials with carbon nanotubes (CNT) are novel materials which can hold the potential for airplane applications. One of the fabrication methods appropriate also for large scale is melt-mixing using masterbatch with a high content of CNT and fibre extrusion. Using this, nanocomposite fibres were obtained from polyamide 11 (PA11) with 2, 4 and 6 wt.% of multi-walled carbon nanotubes (MWCT), respectively. The addition of a compatibiliser, trade name MB50-011, was also studied. Fibres obtained were further cut and pressed into non-woven veils. The paper deals with the description of the process from pellets to veils, as well as fibres characterisation. The distribution of MWCT along the fibre length was studied using HRSEM. Also DSC analysis and electrical tests were performed.

Key words: *nanocomposite fibres, veils, carbon nanotubes, polyamide 11, extrusion.*

Introduction

For a long time, polymer-based composites have been willingly applied in the aerospace industry as structural materials. Nevertheless it appears that such materials do not have the sufficient conductivity, especially for lightening strike protection. Furthermore the still growing requirements for composite materials have led to the development of novel structures with higher mechanical properties while increasing their electrical conductivity. One approach towards better mechanical properties is the formation of thermoplastic non-woven two-dimensional veils placed between the layers of reinforcing fibres [1]. Such veils are available on the market, but without any conductive additives. Moreover for veil production usually a chemical compound as a binder is utilised, similarly to polypropylene fabrics made by thermal connection of fibres with the addition of additives and stabilisers [2].

As was mentioned above, novel polymer-based nanocomposites have to posses good mechanical features in tandem with electrical conductivity. These can be achieved by the addition of carbon nanotubes (CNT) to the polymer matrix. Moreover application of a thermoplastic veil doped with CNT can lead to overall weight reduction, which makes them a potential candidate for the replacement of metallic meshes in aircraft used nowadays.

Carbon nanotubes as three dimensional hollow structures can be produced in three forms as single, double or multi-walled (SWCT, DWCT and MWCT, respectively). They can transport electrons along their length practically without any disruptions. Their high electrical conductivity in the range 500 – 10,000 S/cm leads to the fabrication of materials which exhibit a very low electrical percolation threshold [3, 5, 13]. It is usually procured at 1 - 1.5 wt.% of MWCNT, which is much less than for other conductive nanofillers (carbon black or graphite) [3 - 5]. Nevertheless the chemical nature of CNT causes some obstacles during the fabrication process.

Because of the chemical character of CNT, they react with each other and create agglomerates bonded by strong van der Waals interactions, which is entirely unwelcome. They cause an increase in viscosity as well as diminish the properties of final nanocomposites. The satisfactory distribution of CNT within the thermoplastic fibres is still under development and can be implemented according to the various techniques. Mainly there are "in-situ" polymerisation, solution processing and melt mixing methods, within which extruding, melt-, electro- or coagulation spinning are distinguished [6, 7, 9, 13].

As far as the first two being appropriate for lab scale, they may not be applicable on a large scale due to their limitations (e.g. solvent wastes). This is in contrast to the melt-mixing processing methods, which are more convenient for bigger scale due to the environmental benefits and much faster production. Likewise the commercially available Masterbatch is safer due to a lack of dust in comparison to direct dispersion of CNT in the polymer [8. 16].

In the literature review [7] we found that plenty of nanocomposite fibres have already been produced. It is worth mentioning that probably the most promising approach for obtaining thin nanocomposite fibres is the extrusion process, since the shear forces of screws cause the breakage of agglomerates, resulting in better distribution of the nanofiller [11,14,15]. The shear force applied should be high enough to destroy primary occurring agglomerates and spread the nanotubes

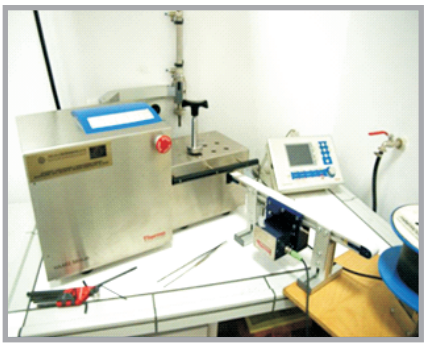

Figure 1. *Equipment used for fibre extrusion and veil fabrication.*

Table 1.

Fibres	Fibre diameter, µm	Extrusion			Pressing	
		T, °C	Screw speed, r.p.m.	Winder speed, r.p.m.	T, °C	t, sec
Neat PA11	33.8 ± 11.5	210	15	200	180	4
PA11 + 2 wt.% MWCT	80.1 ± 4.57	225			210	3
PA11+2 wt.% MWCNT + 2 wt% MB50-011	140 ± 36.9	225			210	3
PA11 + 4wt.% MWCT	126 ± 8.07	250			220	6
PA11 + 6wt.% MWCT	92.3 ± 16.6	270			220	6

throughout the whole network of the polymer [9]. Moreover it has already been reported that probably longer mixing at a low speed is the best to get a material with homogenous CNT distribution [9, 15].

The aim of the studies presented in this paper was the development of a fabrication method of non-woven veils with multi-walled carbon nanotubes. The manufacturing process starts from masterbatch pellets diluted by neat polymer, then fibres extrusion, cutting and pressing fibres into a veil. For further epoxy resin infusion or the Resin Transfer Molding (RTM process), in which veils can be used, the presence of any additional compound in the veil is unacceptable. Hence the method shown is the simplest as possible, without any solvents or other chemical additives and sophisticated tools. It was found that by making one attempt with a compatibiliser, it decreases the properties of filaments. Microscopic observations reveal that the extrusion process leads to the uniform distribution of the nanofiller within the polymer matrix for nanocomposites fibres produced.

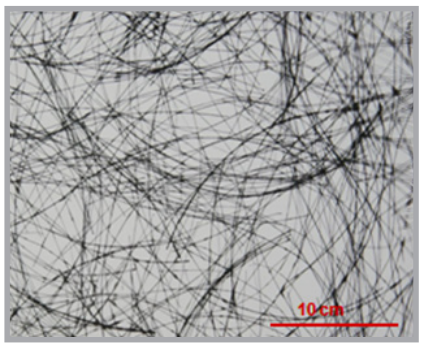

Figure 2. *Non-woven veil made of PA11+ + 6 wt.% MWCT (GSM = 12).*

Experimental

Materials

Masterbatch pellets based on PA11 with 20 wt.% of MWCT (*Graphistrength®C M3-20)* and pellets of neat PA11 (Rilsan® PA11) were supplied by ARKEMA, France. In one attempt the compatibiliser (Dow Corning®MB50-011) commonly used in polyamide processing was applied. It consists of 50 wt.% high molecular weight siloxane dispersed in PA6. Materials were dried in the vacuum oven at 75 °C for 24 h before the further actions.

Nanocomposite fibre fabrication

The Masterbatch containing 20 wt.% MWCT was diluted by neat PA11 using a laboratory twin, co-rotating screws mini–extruder Haake MiniLab (Thermo Scientific, Germany). This instrument has a 7 ml capacity, with a by-pass cycle allowing the mixing of components, and a circular head (d = 0.3 mm) for fibre extrusion. The machine is equipped with a transport belt and winding reel allowing the orientation of nanocomposite fibres after leaving the extruder, as shown in ***Figure 1***.

The masterbatch was diluted in neat PA11 in order to obtain fibres with 2, 4 and 6 wt.% MWCT. In the case of material with 2 wt,% MWCT, compatibiliser MB50-011 was added to investigate the changes in processing. Pellets of the masterbatch and neat PA 11 were blended in the by-pass cycle every 10 min at 100 r.p.m. Afterwards the by-pass cycle was opened to allow the extrusion of fibres. For comparison, fibres from neat PA 11 were also extruded.

Non-woven veil fabrication

In the last step, fibres were compressed into non-woven veils by the hot-pressing method using a laboratory thermo transfer press, Poland (***Figure 1***). For this, long fibres were cut into sections with a length of 70 mm. Then an appropriate amount of fibres were distributed on polytetra-fluoroethylene foil, covered from the top with a second piece of foil and then pressed. Veils are characterised by areal weight -grams of fibres per square meter- the GSM factor. The veils presented have dimensions equal to 300 × 300 mm and an areal weight of 12 g/m^2. ***Table 1*** includes both the fibre extrusion and pressing-parameters for a specific diameter of fibres. In turn, ***Figure 2*** shows an example of a non-woven thermoplastic veil doped with CNT.

Measurement methods

The diameter of extruded fibres was measured at a few points by scanning electron microscopy (SEM Hitachi 3000, Japan) and then the average value was calculated. Samples were firstly sputtered with gold and analysed under low pressure and a voltage of 5 kV.

A scanning transmission electron microscope Hitachi S5500 (Japan) was utilised for CNT distribution observations. A single fibre was stitched to the holder and cut parallel to its axis at a temperature below the glass transition of the material using an Ultramicrotome Leica EM6

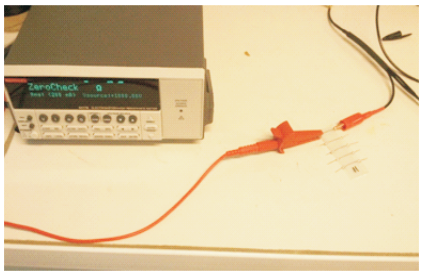

Figure 3. *The set-up for conductivity measurement in CANOE.*

(Germany) equipped with a low temperature chamber and diamond knife. Thanks to this, not only the distribution of MWCT within the polymer matrix was recorded, but also the quality of the fibres in their section.

Samples of about 8 mg were investigated in an aluminum hermetic pan in a nitrogen atmosphere in a run cycle of 1st heating–cooling–2nd heating. (from 0 → 230 °C; scan rate 10 °C/min) using a Differential Scanning Calorimeter Q-1000 (TA Instruments, USA). The changes in glass transition temperature, melting point as well as melting enthalpy were collected. The melting points gained were compared and used for adjusting the extrusion temperature.

A source meter - Keithley 2410 (USA) was utilised to estimate the electrical volume resistivity of fibres using the two electrode set-up (see ***Figure 3***) and silver paint at the fibre end. A voltage of 1000 V was applied and the distance between the electrodes was equal to 20 mm. Five trials were made per two types of fibres produced and the average value of resistance was calculated. The measurements were carried out under the same conditions (temperature and humidity). Fibres were conditioned before measurements at room temperature.

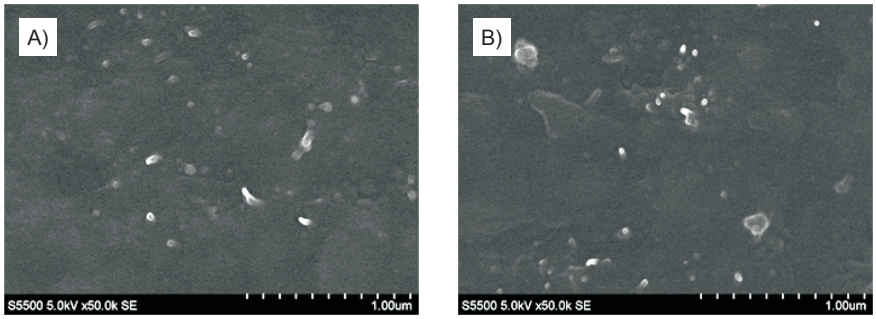

Figure 4. *STEM images of fibres made of PA11 + 2 wt.% MWCT.*

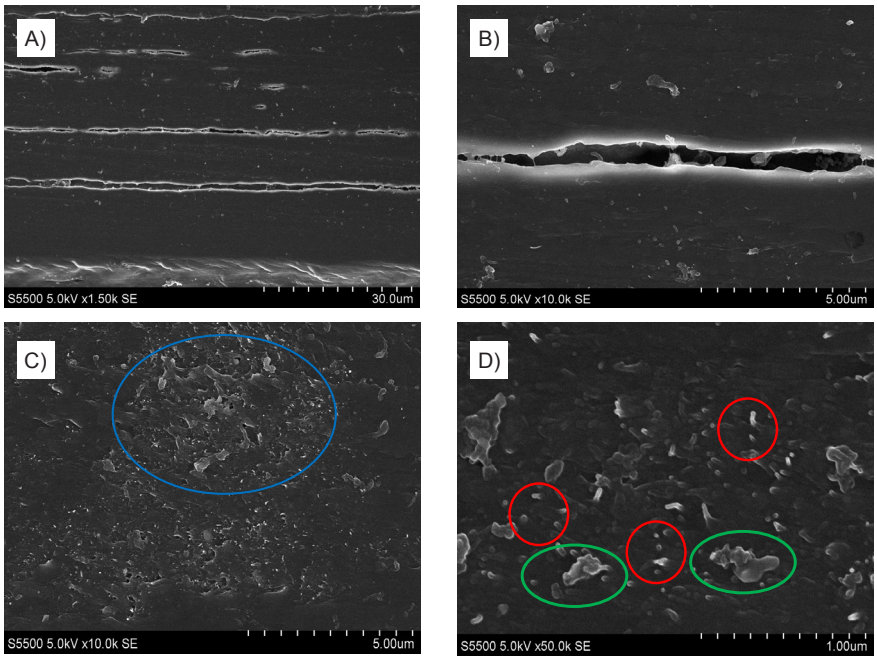

Figure 5. *STEM images of fibres made of PA11 + 2 wt.% MWCT + 2 wt.% MB50-011.*

Results and discussion

The focus of this work was put on the development of a manufacturing process for non-woven veils made of PA11 and MWCT by the pressing method from previously extruded nanocomposite fibres. Besides this the goal was to fabricate fibres and subsequently a veil according to a method which could be transferred to industrial scale. In addition, the achievement of a uniform arrangement of the CNT within the whole polymer matrix - over the entire length of the fibre - was our target. Therefore the extrusion process was chosen as the most appropriate.

Because the addition of MWCT alters the structure of the polymer, leading to a higher melting point (see DSC curves in ***Figure 6*** see page 48), firstly all of the extrusion and pressing parameters were found and then optimised. Owing to this, each fabrication process was continuous and fibres obtained had a smooth surface. ***Table 1*** includes the variations of extrusion conditions and thickness of fibres measured. It should be noted that the diameter of fibres has be as low as possible to get a thin veil in the end. Unfortunately when the MWCT content rises the extrusion process towards thin fibres is tough. In turn, the pressing parameters are chiefly dependent on the fibre diameter. The values enclosed in ***Table 1*** show the time and temperature of pressing resulting in a good quality veil with a lack of visible melted points of polymer fibres.

The microstructure of fibres with 2 wt.% of MWCT was examined in a few sections and any visible agglomerates were found, as is shown in ***Figure 4***. In contrast, for fibres with 4 and 6 wt.%. MWCT, single agglomerates of CNT were found, similar to each Masterbatch with a very high weight fraction of CNT, resulting in agglomerates [14]. It should be noted that all of the fibres tested were extruded under the same velocity of screws to get comparable results of CNT distribution (***Table 1***). Because such a speed could be too low to destroy the agglomerates in the Masterbatch, the mixing step was carried out under ahigher screws velocity (100 r.p.m.). As was mentioned, one attempt was made with the addition of an additive (MB50-011) to see whether it helps with the extrusion process. Indeed the fabrication was easier but the microstructure of the fibre was completely altered. Agglomerates consisting of MWCT and MB50-011 can be clearly seen in ***Figure 5.C*** (blue circles). The red circles in ***Figure 5.D*** refer to single carbon nanotubes; in turn, green circles describe bigger particles, which are more like those on the surface stand for the compatibilizer added. The investigation indicated that the presence of MB50-011 leads to observable cracks and inhomogeneity in the material (***Figure 5.A*** & ***5.B***). It looks like, the additional of a compound works as a hindrance for MWCT and prevents them from moving, thereby facilitating agglomerate formation.

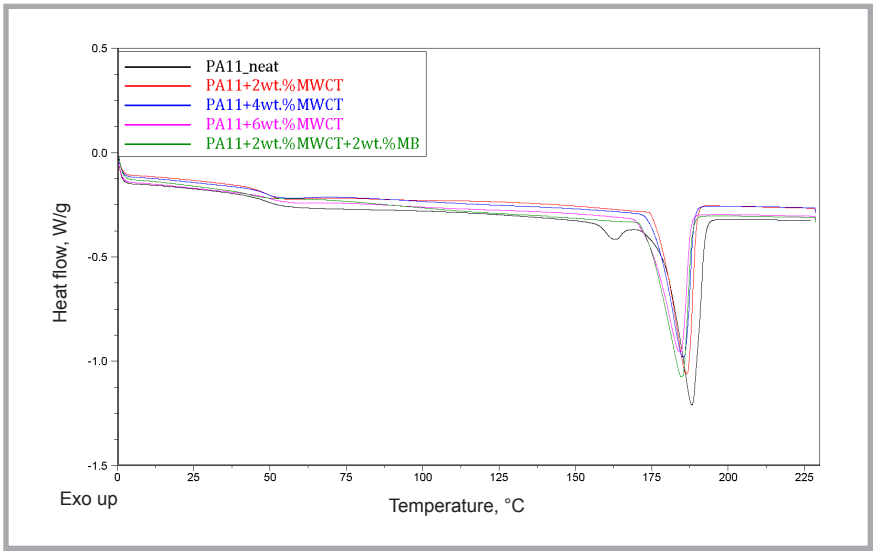

Figure 5. *DSC 1st heating curves of nanocomposite fibres at different MWCT loadings.*

Table 2.

Fibre	T_g, °C	T_m, °C	ΔH, J/g
PA11_neat	48.6	188.2	44.4
PA11+2wt.% MWCT	48.9	186.3	36.1
PA11+4wt.% MWCT	48.5	185.3	33.7
PA11+6wt.% MWCT	50.8	184.2	34.6
PA11+2wt.% MWCT+2wt.% MB	43.7	184.7	39.0

Table 3.

Fibre	Resistivity, Ωm
PA11+2 wt. % MWCNT + 2 wt%. MB50-011	8.22E+03 ± 9.48E+02
PA11+2 wt. % MWCNT	1.18E+09 ± 3.03E+03

DSC analysis was made for nanocomposites fibres, and the results are presented in ***Figure 6*** and ***Table 2***. There is a negligible diminishing in the glass transition temperature for 2, 4 and 6wt.%MWCT in comparison to neat PA11. In contrast, fibres with that addition of a compatibiliser, T_g is significantly lower. Probably the application of a compatibiliser leads to the formation of a more amorphous structure because the mobility of macromolecules is facilitated. During the first heating only small shifts of the melting point towards lower values are visible after the incorporation of MWCT. In the case of neat PA11, the additional peak is observable. Presumably it comes from the distinct character of crystallites being more defective, leading to a lower melting point.

It was also found that the addition of CNTs leads to a decrease in melting enthalpy, which corresponds to the slight decrease in the melting point. Probably it is caused by the different size and quality of spherullites. Due to the presence of CNT, the crystallisation rate can be enhanced and the crystalline phase can be more defective. This will be investigated more deeply in our further studies.

The measurement set-up (CANOE facilities) for volume resistivity measurements of nanocomposite fibres is shown in ***Figure 3***. In this case, an investigation was made to see if the incorporation of MWCT into PA11 matrix and the manufacturing method give conductive fibres (***Table 3***). For comparison, the value of resistivity found in the literature for a PA11 pellet, not fibre, equals 10^{14} Ωm [11]. Obviously the conductive results are below the values expected. The next step should be the heat treatment of fibres to retain the conductivity. Moreover the analysis technique has to be improved to get results within the narrower area.

Conclusions

Non-woven veils with 2, 4 and 6 wt.% of MWCT were fabricated by the hot-pressing method from previously extruded fibres based on PA11 according to the method developed without any additives. All of the processing conditions were found and optimised towards good quality fibres and veils without any discontinuities or melting points, respectively. Studies indicated that the extrusion process can lead to destroying the agglomerates, thus a uniform dispersion of CNT on the fibre sections was observed. In contrast to our expectations, investigations with a chemical compatibilizer in an industrial application led to a significant decrease in the quality of fibres manufactured.

Despite the fact that approach for fabrication of fibres and veils doped with CNT presented was undertaken only on laboratory equipment, it could be used in industry not only for PA11 but for other thermoplastic polymers. To recap, this technique is convincing but further efforts should be made to examining the electrical and mechanical properties of veils in detail because of their further application as a interlayer in laminate materials for the aerospace industry.

Acknowledgment

Financial support from statutory funds (FME WUT 504P/0007/001) is gratefully acknowledged.

References

1. Hogg PJ. Toughening of thermosetting composites with thermoplastic fibers. *Materials Science and Engineering* 2005; A 412: 97–103.
2. Aslanzadeh S, Haghighat Kish M. Photodegradation of polypropylene thermal bonded non-woven fabric. *Polymer Degradation and Stability* 2005; 90: 461-470.
3. Grossiord N, Loos J, Regev O, Koning CE. Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites. *Chem. Mater.* 2006; 18, 5: 1089–99.
4. Song. YS, Youn JR. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. *Carbon* 2005; 43: 1378–1385.
5. Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composite Science Technology* 2009; 69, 10: 1486–98.
6. Spitalsky Z, Tasis D, Papagelis K, Galiotis C. Carbon nanotube-polymer composites: Chemistry, processing,

mechanical and electrical properties. *Progress in Polymer Science* 2010; 35: 357-401.
7. Gil Min B, Chae HG, Minus ML, Kumar S. Polymer/carbon nanotube composite fibers - An overview. *Functional Composites of Carbon Nanotubes and Applications* 2009: 43-73.
8. Prashantha K, Soulestin J, Lacrampe MF, Krawczak P, Dupin G, Claes M. Masterbatch- based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties. *Composite Science and Technology* 2009; 69: 1756-1763.
9. Pötschke P, Bhattacharyya AR, Janke A. Carbon nanotube-filled polycarbonate composites produced by melt mixing and their use in blends with polyethylene. *Carbon* 2004; 42: 965–969.
10. Carponcin D, Dantras E, Aridon G, Levallois F, Cadiergues L, Lacabanne C. Evolution of dispersion of carbon nanotubes in Polyamide 11 matrix composites as determined by DC conductivity. *Composites Science and Technology* 2012; 72: 515–520.
11. Warlimont M. *Springer Handbook of Condensed Matter and Material*. Data Springer Berlin, 2005, p. 501.
12. Mago G, Kalyon DM, Fisher FT. Nanocomposites of Polyamide-11 and Carbon Nanostructures: Development of Microstructure and Ultimate Properties Following Solution Processing. *Polymer Physiscs* 2011; 49: 1311-1321.
13. Moniruzzaman M, Winey KI. Polymer Nanocomposites Containing Carbon Nanotubes. *Macromolecules* 2006; 39: 5194-5205.
14. Pötschke P, Bhattacharyya AR, Janke A. Melt mixing of polycarbonate with multiwalled carbon nanotubes: microscopic studies on the state of dispersion. *European Polymer Journal* 2004; 40: 137–148.
15. Villmow T, Pötschke P, Pegel S, Häussler L, Kretzschmar B. Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. *Polymer* 2008; 49: 3500–3509.
16. Logakis E, Pollatos E, Pandis Ch, Peoglos V, Zuburtikudis I, Delides CG, Vatalis A, Gjoka M, Syskakis E, Viras K, Pissis P. Structure–property relationships in isotactic polypropylene/multi-walled carbon nanotubes nanocomposites. *Composites Science and Technology* 2010; 70: 328–335.

Received 20.08.2012 Reviewed 14.02.2013