

Development of antistatic wire insulator by dispersing electroconductive nanoparticles: from the laboratory material to the prototype

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INTRODUCTION

Spacecraft are subjected to surface charging effects that may engender electrostatic discharge [1], as in the case of solar panel cabling on satellite. Such a phenomenon represents an important hazard for satellite. The formulation of wire insulator is currently being modified to get an antistatic material, enabling to dissipate charges from the insulator surface to the conductor. To this end, the wire insulator, made of a high-performance thermoplastic polymer that is ethylene tetrafluoroethylene (ETFE), is modified by the dispersion of electrically-conductive nanoparticles. Neat ETFE exhibits an electrical resistivity of about 10^{15} ohm.cm, while when it is highly filled with electro-conductive particles, its electrical resistivity is about 10^6 ohm.cm. The challenge here is to find the particle concentration enabling to get a nanocomposite resistivity in the range of 10^{10} to 10^{13} ohm.cm that generally occurs in the electrical percolation threshold. However, to facilitate nanocomposite processing, the targeted range of resistivity should be obtained with the largest particle concentration range as possible. In other words, the electrical percolation has to be the softer as possible. The selected nanoparticles are carbon black (CB) and carbon nanotubes (CNT). To enlarge the percolation threshold of ETFE nanocomposites, different solutions are tested at the laboratory: oxidation of the CB particles, oxidation of CNT particles, mixing of oxidized CNT with non-conductive nanoparticles, mixing CNT with CB, and chemically modifying ETFE matrix and dispersion of CNT. As reference, the simple dispersion of CB and CNT within ETFE matrix is also investigated. The first objective of this work is to identify formulations of ETFE nanocomposites enabling to target antistatic properties and to carefully characterize their structural properties. The second objective of this work is to implement lab formulations of nanocomposite to manufacture a wire prototype and to verify if the electrical and structural properties are retained or not.

NANOCOMPOSITE PROCESSING AND CHARACTERIZATION

The selected ETFE fluoropolymer of this work is characterized by a low melt viscosity for facilitating the dispersion of nanofillers. As electroconductive nanoparticles, carbon black (named opti-CB) and carbon nanotubes (named opti-CNT) are selected. To modify the electrical percolation of ETFE nanocomposites, opti-CB and opti-CNT are oxidized by immersion in a solution of H_2SO_4 (95-98%) and HNO_3 (69%) with volume composition $\text{H}_2\text{SO}_4/\text{HNO}_3$ 3/1 for a given time. Such an acid solution is supposed to damage nanoparticles and hence reduce their electrical conduction. After dilution in distilled water, oxidized opti-CB (alt-opti-CB) and oxidized opti-CNT (alt-opti-CNT) are extracted by centrifugation. After the first centrifugation, the extracted nanopowder is washed in distilled water and centrifugation is then pursued until the pH of the solution reaches 7. After this step, alt-opti-CB and alt-opti-CNT are dried overnight at 80°C in a vacuum oven to remove moisture. As other procedure to modify the conduction of the nanoparticle network, titania (TiO_2) non conductive nanoparticles are mixed with electroconductive nanoparticles. Last, ETFE matrix is chemically modified (mETFE) and mixed with untreated ETFE to tentatively hinder the conduction network of the particles.

To process ETFE-based nanocomposites, a twin-screw micro-extruder reference DSM X'Plore 15cc is utilized at a temperature of 320°C and a screw rotation speed of 10 rpm (during the material injection through the hopper) and then 100 rpm (Fig. 1a). The extrusion duration is set to 6 min, while a nitrogen purging gas is used to avoid oxidation. The extruded strands are cut into 5 mm-long pellets with a pelletizer and shaped into disk of diameter 11 cm and thickness comprised between 1 mm and 2 mm by compression-molding (Fig. 1b). To this end, a 15 tons manual Carver press is utilized with a lab-developed cylindrical mold. ETFE nanocomposites are pressed at 320°C under 1 MPa and cooled down to 160°C at the same stress before extracting the plate from the mold.

The electrical resistivity of the nanocomposite disks is measured based on the ASTM D-257 standard. Volume resistivity is defined as the electrical resistance through a cube of insulating material. When expressed in ohm.centimetres, it would be the electrical resistance through a one centimetre cube of insulating material. Measurements are done at 22°C using an electrometer or picoammeter, voltage source, and a resistivity chamber, as shown in Fig. 1c. Volume resistivity ρ is measured by applying a voltage potential V across opposite sides of the insulator sample and measuring the resultant current I through the sample as shown below:

$$\rho = \left(\frac{22.9}{t_s} \right) \times \left(\frac{V}{I} \right) \quad (1)$$

t_s being the average sample thickness. In particular, the Keithley Model 8009 resistivity chamber contains an electrode located in a shielded box to minimize stray electrostatic pick-up. The minimum sample size to be analysed is 63.5 mm in diameter.

Microstructure observation is conducted with an optical microscope Nikon Eclipse LV100D. To this end, the materials are sectioned into 600 to 1000 nm-thick samples by means of a LEICA UC6 at room temperature. In particular, the samples are cut with a simple glass knife equipped with a water bath (use of Milli-Q water) facilitating the pick-up of the samples. Samples are picked-up with a special loop and are deposited onto a glass microscope slide. The optical microscope images are analyzed by means of the software ImageJ with the following procedure: i) image scaling, ii) grey level thresholding, iii) despeckling, and iv) object quantification. By means of this analysis, the average area of nanoparticle agglomerates is determined. Furthermore, transmission electron microscope (TEM) imaging is conducted to reveal the local dispersion of the nanoparticles from sectioned samples prepared with a cryo-ultramicrotome. In particular, 80 nm-thick specimens are cut at -50°C by means of a diamond knife. Imaging is conducted with a TEM FEI Tecnai 12 Bio Twin equipped with a camera Megaview II at 120 kV. Images are recorded with the bright field mode. Nanocomposite tensile behavior is measured with an electromechanical Instron machine 5967 equipped with an environmental chamber. Testing is done at 22°C and at a crosshead speed of 0.6 mm/min on ASTM D638-10 sample type V. Thermogravimetric (TGA) measurements are conducted to assess the effective nanoparticle content with a TGA2 machine from Mettler Toledo under inert atmosphere with N_2 from 22°C to 800°C at 10°C/min. Alumina crucibles are utilized for the testing. Residual nanoparticles fraction is supposed to be deduced from the residual weight fraction of the samples at 700°C, subtracted by the residual fraction for neat matrices.

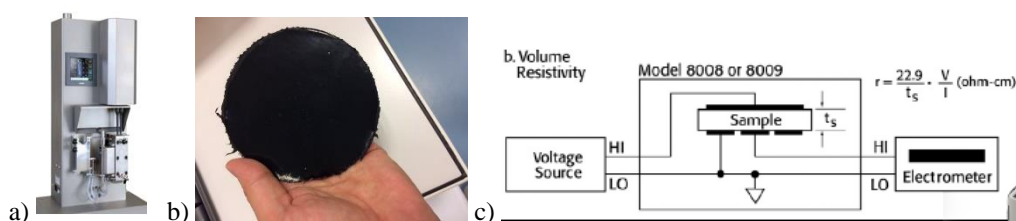


Fig. 1. a) Twin-screw micro-extruder DSM X'Plore 15 cc at LIST for producing nanocomposite batches of about 10 g per formulation, b) disk with diameter 11 cm and thickness of 1-2 mm of nanocomposites processed by compression-molding and c) electrical resistivity measurements with Keithley instruments

Opti-CB and opti-CNT are processed with neat ETFE at different concentrations to investigate the percolation threshold of the two nanocomposites. The obtained electrical resistivities are plotted in Fig. 2a. It can be seen that the percolation threshold is reached at lower nanoparticles concentration for opti-CNT compared to opti-CB (about 1.25 wt% vs. 5.25 wt%). Furthermore, the drop of electrical resistivity is much more marked for opti-CNT than for opti-CB.

The influence of mixing ETFE with a chemically modified grade of ETFE (mETFE) on the electrical resistivity of ETFE/mETFE/opti-CNT nanocomposite is investigated here. The measured resistivity is plotted in Fig. 2b for ETFE/mETFE/opti-CNT and ETFE/opti-CNT as reference. The new formulations enable to broaden the electrical resistivity drop of the nanocomposite compared to the nanocomposite system ETFE/opti-CNT, which is suitable.

The influence of nanoparticle oxidation time on the electrical resistivity of ETFE/alt-opti-CNT 100/3 ETFE/alt-opti-CB 100/6 nanocomposite is shown in Figs. 3a and 3b. Concerning opti-CB, as soon as they are introduced in the acid solution, the electrical resistivity of ETFE/alt-opti-CB 100/6 is increased by 7 powers of ten indicating an important damaging

(Fig. 3a). It is hence not relevant to pursue the alteration of CB through the use of our protocol. Concerning the alteration of opti-CNT, it can be seen that a damaging threshold occurs just after 10 min of treatment. Indeed, during the first 10 min the electrical resistivity of ETFE/alt-opti-CNT slightly increases from $2.34\text{E}+6$ ohm.cm to $5.51\text{E}+7$ ohm.cm, and then, the electrical resistivity markedly increases to the range comprised between $1\text{E}+13$ ohm.cm and $8\text{E}+13$ ohm.cm (Fig. 3b). This finding implies that the optimal oxidation duration is 10 min to increase the electrical resistivity of the nanocomposite after the percolation threshold (nanoparticle concentration of 3 wt%). More than 10 min engenders too much damage of the nanoparticles.

The measured electrical resistivity of some selected compositions of ETFE/alt-opti-CNT and ETFE/alt-opti-CNT/TiO₂ is plotted in Fig. 4 in comparison with those of ETFE/opti-CNT. It can be noted that oxidation of CNT significantly modify the percolation threshold of the nanocomposite. Indeed, the drop of electrical resistivity is broader than without oxidation. The addition of TiO₂ has only a marked impact for the highest amount of CNT by increasing resistivity by two powers of ten (when comparing ETFE/alt-opti-CNT 100/3 with ETFE/alt-opti-CNT/TiO₂ 100/3/0.5).

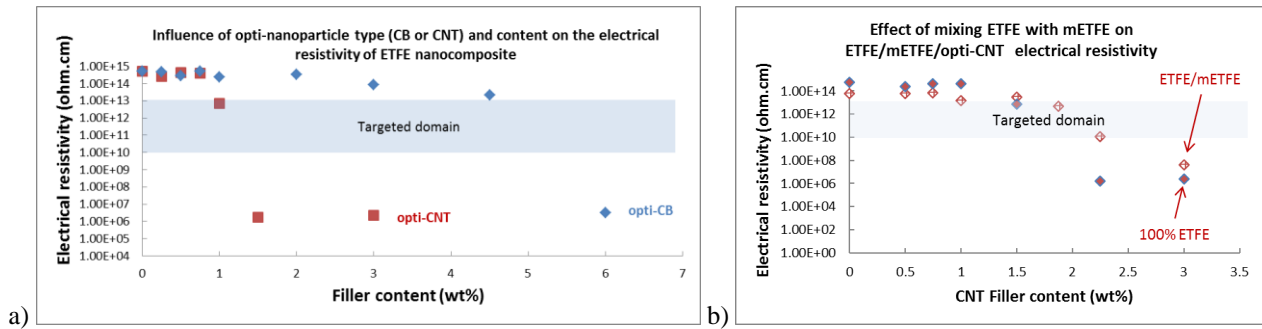


Fig. 2. a) Evolution of the electrical resistivity of ETFE as a function of opti-CB and opti-CNT content and b) evolution of the electrical resistivity of ETFE mixed with a modified ETFE matrix (mETFE) as a function of CNT content

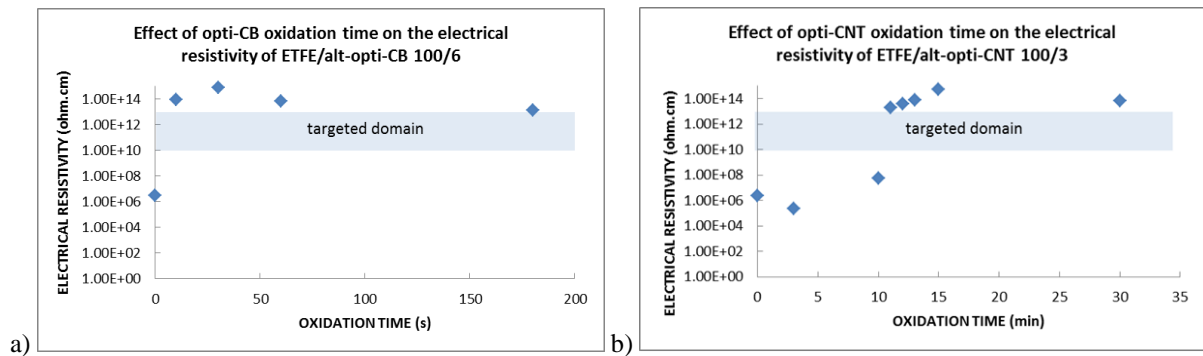


Fig. 3. a) Evolution of the electrical resistivity of ETFE/alt-opti-CB with composition 100/6 as a function of the oxidation time of opti-CB and b) evolution of the electrical resistivity of ETFE/alt-opti-CNT with composition 100/3 as a function of the oxidation time of opti-CNT

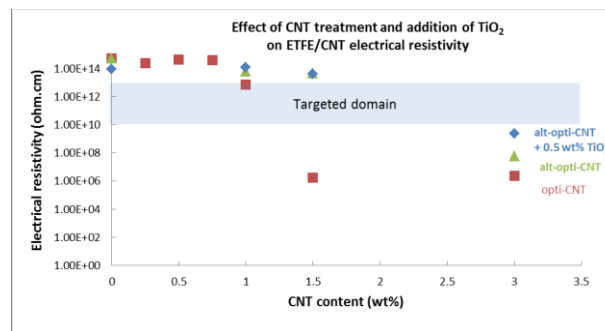


Fig. 4. Evolution of the electrical resistivity of ETFE/opti-CNT/TiO₂ as a function of opti-CNT oxidation state (non oxidized opti-CNT and oxidized alt-opti-CNT for 10 min.), the addition of titania nanoparticles (TiO₂), and opti-CNT content

The methods enabling to significantly modify the percolation threshold are (i) the oxidation of opti-CNT, (ii) mixing oxidized opti-CNT with non conductive nanoparticles, and (iii) the mixing of ETFE with both chemically-modified ETFE and opti-CNT. If at the lab scale the processing of such materials is easy, their scale-up for the manufacturing of wire insulator requires important quantity of raw materials. In particular, at the lab scale, the production of several grams of oxidized CNT is possible, but the production of several hundred grams of oxidized CNT is not possible. So, for the industrial implementation, it is decided to test a simple formulation that is ETFE/opti-CB, and a more complex formulation that is ETFE/mETFE/opti-CNT. Some first tests reveal that ETFE/mETFE/opti-CNT nanocomposite processing by means of industrial scale extruder is extremely complicated due to an important viscosity of the polymer matrix, so only ETFE/opti-CB formulation is finally tested for the scale-up. The formulation ETFE/opti-CB 100/5.5 is hence processed and exhibits an electrical resistivity of $1.32\text{E}+9$ ohm.cm, which is near the targeted antistatic range.

Before the scale-up of ETFE/opti-CB 100/5.5, it is of high importance to identify its structural properties to verify if the later are retained or not after the scale-up. First, the dispersion state of the nanoparticle is analyzed by image analysis from optical microscopy imaging (Fig. 5a). Indeed, the opti-CB particles forming micron-scale agglomerates, it is easy to treat the image (Fig. 5b) and assess the area distribution of the agglomerates (Fig. 5c and 5d). The average agglomerate size is $289.7\text{ }\mu\text{m}^2$, most of the agglomerate areas being below $400\text{ }\mu\text{m}^2$. The presence of agglomerate is inherent of the melt-processing methodology by extrusion that cannot totally breaks all the initial agglomerates of opti-CB particles. As complementary structural characterization, transmission electron microscope (TEM) imaging is conducted on the same material (Fig. 6). At this scale, the local organization of the opti-CB nanoparticles into aggregates is observed [2]. It is explained that carbon black always coalesces into aggregates due to the important Van der Waals interactions. These aggregates are irreversible and can interact with other aggregates to form agglomerates (as noted by optical microscopy in Fig. 5a). In our case, TEM imaging highlights a spherical to ellipsoidal organization of the opti-CB aggregates [2]. Last, the tensile behavior of ETFE/opti-CB 100/5.5 is measured and compared to that of neat ETFE (Table 1). If the elastic modulus and the tensile strength at break of ETFE are no or little influenced by the addition of opti-CB, the elongation at break is significantly reduced passing from 431 % to 248 %, which remains acceptable for the targeted application.

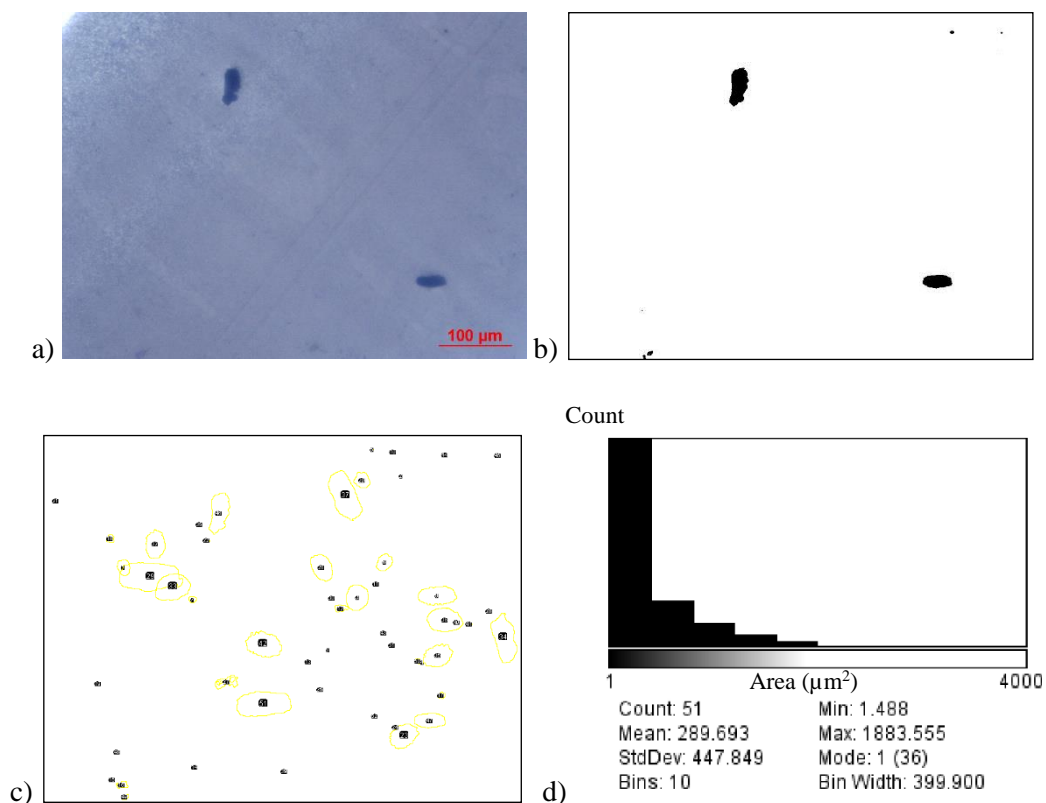


Fig. 5. a) Agglomeration observation in ETFE/opti-CB 100/5.5 by optical microscopy, b) grey level thresholding to reveal the agglomerates, c) stacking of all the particles originated from 45 images, and d) agglomerate area distribution from the 45 images

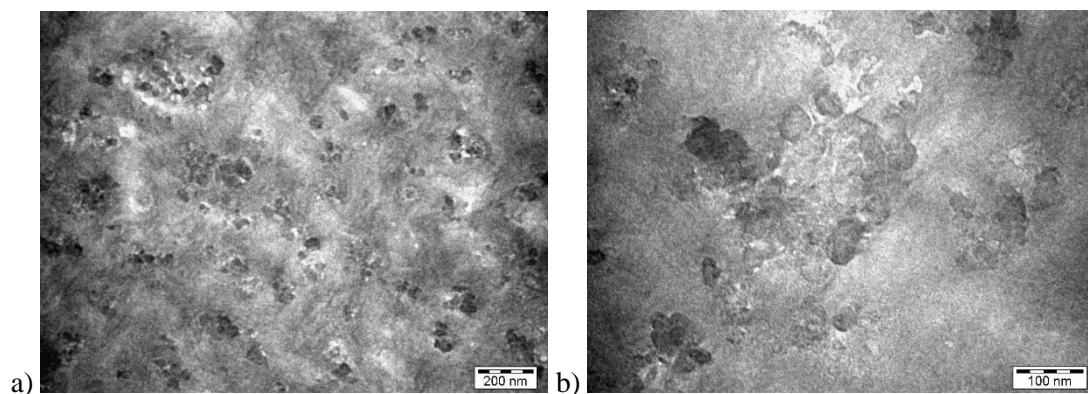


Fig. 6. TEM investigation of ETFE/opti-CB 100/5.5 aggregates at a) a low magnification, and b) a high magnification

Table 1. Averaged tensile characteristics of ETFE and ETFE/opti-CB 100/5.5 at 22°C and 0.025 mm/s

Material	Young modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
ETFE (100)	941±190	33±3	431±7
ETFE/opti-CB (100/5.5)	1120±20	28±1	248±30

MASTERBATCH PROCESSING AND CHARACTERIZATION

The first step of the scale-up of the nanocomposite developed at the lab is the production of a masterbatch that is ETFE with the highest content in opti-CB as possible. In principle, the dispersion state of the nanoparticles has to be the highest as possible to facilitate further processing (dilution to the desired opti-CB concentration). To this end, a mini-extruder reference Thermo Scientific Haake PTW 16/40 with a motor Rheodrive 7 is used (Fig. 7a). The processing conditions are reported in Table 2. The strands are cooled by means of a water bath (Fig. 7b) before being pelletized into pellets (Fig 7c). To verify the influence of the processing tool changing from the micro-extruder DSM to the mini-extruder Thermo Scientific, a similar masterbatch formulation is prepared with the DSM extruder (see Table 2 for the processing conditions). After extrusion, the materials are molded into disks by compression molding. It is found that the masterbatches produced with the two extruders have the same electrical resistivity of around 1E+5 ohm.cm (Table 2), highlighting a similar particle dispersion state despite totally different processing tools. This result can be due to the fact that a similar specific mechanical energy (SME) is used with the two instruments (Table 2). It is also important to verify that the two masterbatches have the same nanoparticles concentration, which is done by TGA. Similar content are obtained with the two extruders, enabling to validate that the nanocomposite structural properties are not significantly changed between the materials developed with the micro-extruder and the materials developed with the mini-extruder.



Fig. 7. Mini-extruder Thermo Scientific Haake PTW 16/40 with a motor Rheodrive 7 used at LIST to process nanocomposite masterbatches of 10 kg per formulation, a) gravimetric feeder (left) for nanopowder and volumetric feeder (right) for the polymer pellets, b) water bath to cool the extruded strands, and c) pelletizer and packing

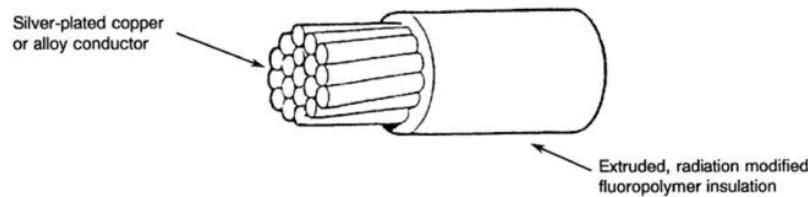
Table 2. Comparison between the processing of ETFE/opti-CB nanocomposite masterbatches processed with the micro-extruder and the mini-extruder

Processing tool	Twin-screw micro-extruder DSM X'Plore 15 cc	Twin-screw mini-extruder, Thermo Scientific Haake PTW 16/40 with a motor Rheodrive 7
Localization	Cleanroom with operator protected against nanoparticles (coverall, gloves, boot-cover, respirator, mask....) and air filtration to retain nanoparticles, special cleaning procedures	
Temperature	320°C	320°C-340°C

Residence time (min)	2	-
Feeding	Manual feeding of polymer pellets mixed with the nanopowder by means of a piston feeder	Gravimetric feeder for the polymer pellets and volumetric feeder for the nanopowder
Cooling of the material	ambient air	water bath
Pelletizing procedure	Manual cutting of the extruded strands	Use of the extruder pelletizer in continuous
Rounds per minute (min ⁻¹)	10 (during powder and pellet introduction) and 100	100
Torque (N.m)	5000-8000	60-90
Specific mechanical energy (Wh/kg)	290-465	318-480
Shaping	Disk of diameter 11 cm and thickness 1 to 2 mm processed by compression molding	
Electrical resistivity at room temperature from compression molded plate (ohm.cm)	3.30E5	1.09E5
Particles effective content by thermogravimetric analysis	Similar content	

WIRE PROTOTYPE PROCESSING AND CHARACTERIZATION

The implementation of the ETFE/opti-CB nanocomposite masterbatches to manufacture wire prototype is conducted at AXON company. As represented in Fig. 8, the variant 4 of ESCC3901/012 type ETFE-based wire is manufactured from the nanocomposite masterbatches, based on a typical crosshead extrusion process for wire and cable manufacturing as represented in Fig. 9a. The production of wire with ETFE nanocomposite insulator has been successful, as represented in Fig. 9b showing a spool of finished wire prototype (wire with a diameter of 0.99 mm).



Variant No.	Shielded	Un-Shielded	No. of Cores	ISO 2635 Wire Code	Stranding No. of Strands × Diameter (mm)	Conductor Characteristics			Shield Strand Ø (mm)	Core Max Ø (mm)	Finished Wire or Cable Characteristics	
						Max Ø (mm)	Nom Section (mm ²)	Max Ohmic Resistance (Ω/km)			Max Ø (mm)	Max Weight (kg/km)
01		X	1	-	7×0.1 (1)	0.3	0.06	385.1	-	-	0.64	0.98
02		X	1	-	7×0.12 (1)	0.38	0.08	244	-	-	0.7	1.35
03		X	1	001	19×0.1 (1)	0.53	0.15	149	-	-	0.86	2.11
04		X	1	002	19×0.12 (1)	0.66	0.25	106.2	-	-	0.99	2.97

Fig. 8. ESCC3901/012 type ETFE-based wire variant table extract-variant 4 is highlighted

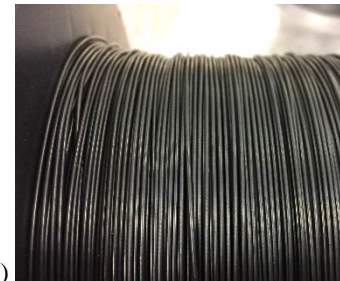
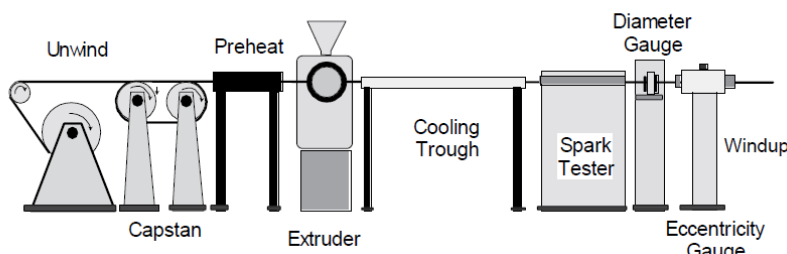


Fig. 9. a) Scheme of a typical crosshead extrusion process for wire and cable manufacturing [3], and b) spool of finished wire prototype (wire diameter 0.99 mm)

The electrical resistivity of the wire insulator is measured by a special method. Wires specimens of 1 meter in length are immersed in a salted water bath (NaCl 5%) at room temperature (Fig. 10). The first electrode of the Milli- and TeraOhmmeter (Milli-TO 3) is connected to the wire conductor and the second electrode to the conductive salted water

bath. A voltage of 500V is applied to the first electrode and the resistance value after 60 s is recorded. The volume resistivity in “ohm.cm” is then obtained by the following formula (based on ASTM D257):

$$\rho = \frac{2\pi LR}{\ln\left(\frac{D_{isol}}{D_{cond}}\right)} \quad (2)$$

where R is the measured resistance (ohm), L is the immersed wire length (cm), Disol is the diameter of the finished wire (cm), and Dcond is the diameter of the wire central conductor (cm). The electrical resistivity of the wire prototype is measured by means of this method and compared to the conventional method applied from the extracted insulator that is reprocessed by compression molding into disk (Table 3). Unfortunately, the manufactured wire insulator exhibits an electrical resistivity higher than the targeted antistatic range, while after extraction and reprocessing, the insulator exhibits an electrical resistivity lower than the targeted antistatic range. Despite the simple formulation tested for the scale-up, it seems that the processing conditions drastically influence the final electrical resistivity of the wire insulator, and have to be further tuned to reach an antistatic behaviour.

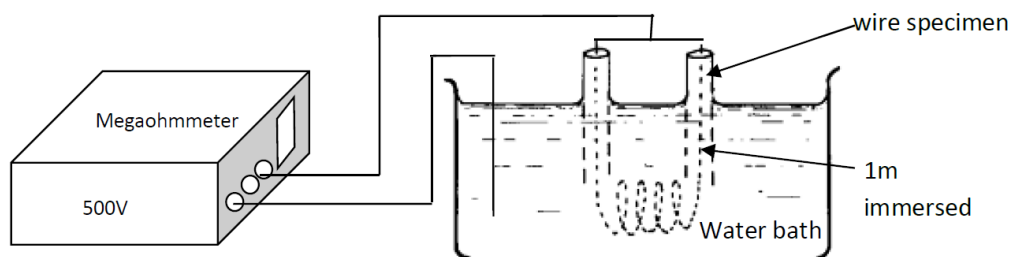


Fig. 10. Water-electrode-bath system for volume resistivity measurements on unshielded wires

Table 3. Electrical resistivity of the new wire prototype

Material	Electrical resistivity (ohm.cm)
Wire prototype with insulator made of ETFE/opti-CB	5.71E+16
Disk processed from the wire insulator made of ETFE/opti-CB	1.15E+6

CONCLUSIONS

At the laboratory scale, the electrical percolation threshold of ETFE nanocomposites can be tailored by different methodologies including (i) oxidation of the electrically-conductive nanoparticles, (ii) the mixing between oxidized electrically conductive nanoparticles and non-conductive nanoparticles, and (iii) the mixing of ETFE with chemically modified ETFE and electrically-conductive nanoparticles. Therefore, potential antistatic formulations of nanocomposites could be identified. However, the scale-up of these methodologies to produce wire prototype requires large quantity of highly concentrated masterbatches, and hence, important quantities of raw materials, which is not possible in the case of oxidized nanoparticles developed at the Lab. Accordingly, it is decided to process a masterbatch based on a simple nanocomposite formulation consisting in ETFE filled with carbon black nanoparticles. The application of this masterbatch for the manufacturing a prototype wire with ETFE nanocomposite insulator is successful, but the electrical resistivity of the insulator is not to date in the antistatic range. The wire manufacturing processing conditions have to be further tuned and optimized to finally reach the targeted antistatic behaviour. To reach this final objective, LIST and AXON have advanced structural characterization tools for an in-depth understanding of the electrical resistivity – structural properties relationships.

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