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Morphology and Electrical Properties of Injection-Molded PP Carbon-based Nanocomposites

M. Zaccone[1, a)], I. Armentano[2], L. Torre[2], F. Cesano[3], S. Cravanzola[3], D. Scarano[3] A. Frache[4], M. Monti[1, b)]

[1]Proplast, Strada Comunale Savonesa 9, 15057 Tortona (AL), Italy
[2]Università degli Studi di Perugia, Strada di Pentima 4, 05100 Terni, Italy
[3]Università degli Studi di Torino, Via Pietro Giuria 7, Torino, Italy
[4]Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino, Italy

[a)] marta.zaccone@proplast.it
[b)] marco.monti@proplast.it

Abstract. The aim of this work was to investigate the influence of the process condition on the morphology of PP/MWCNT nanocomposites and its effect on the electrical properties, experimentally developed in this study. Electrical and morphological characterization was performed in order to analyze the multilayered morphology skin-core-skin, validated by a theoretical model.

INTRODUCTION

Carbon-based nanomaterials with different shape and aspect ratio have attracted in recent years considerable attention in several industrial sectors [1, 2], and have been validated as effective fillers for modifying the electrical properties in the polymer matrix, in which they are embedded. Among these fillers, carbon black and expanded graphite are ones of the most used in plastic market for decades, while multi-walled carbon nanotubes (MWCNTs) has been identified in the last years as one of the most promising nanostructures to obtain multifunctional and smart materials [3]. Indeed, because of their high aspect ratio, they have a great tendency to form a conductive network within the polymer matrix, higher than other conductive additives [4].

Many factors can affect the conductivity of the polymer nanocomposites, such as the content and the type of the conducting carbon fillers, the nature of the polymer and finally processing condition [5, 6, 7]. As for the injection molding process, it has been reported that the produced samples show an external layer with a lower electrical conductivity, and this is favored by a low temperature mold [8].

From these considerations, it is clear that the filler dispersion is a key point in determining the conductivity performances of the composite [9, 10, 11, 12, 13].

In this paper, polypropylene (PP) nanocomposites with several content of conductive fillers were developed. Electrical characterization was performed in the two main directions (in-plane and through-thickness directions). The effect of processing condition on the anisotropic electrical percolation threshold and the morphology was deeply investigated and analyzed also by theorizing a conduction model.

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EXPERIMENTAL

Materials and Methods

Multi-walled carbon nanotubes (Nanocyl NC7000, hereinafter referred to as MWCNTs), expanded graphite (Timcal Timrex C-Therm001, hereinafter referred to as EG) and two different kinds of carbon black (Timcal Ensaco 250 G and Timcal Ensaco 350 G, hereinafter referred to as CB-C and CB-S respectively) were used as fillers. Polypropylene (PP) Moplen RP 348 R (LyondellBasell) was selected as polymer matrix. It is a random copolymer, with a MFI of 25 g/10min (230°C – 2.16 kg) and a density of 0.9 g/cm^3. Different contents of fillers were added to PP. All fillers were homogeneously mixed with the polymer in a co-rotating twin-screw extruder. The obtained nanocomposites were injection molded to produce square-shaped samples (100 x 140 x 2.5 mm in sizes).

Direct current (DC) electrical characterization was performed in the two main directions, longitudinal to the flux of the material during the mold filling (in-plane) and in the through-thickness direction (through-thickness). Furthermore, a dedicated setup was developed to measure the influence of the z-coordinate in the electrical properties of a cross sectional area of the specimen. Tests were performed at intervals of 250 µm along the whole sample thickness, from the top to the bottom surfaces. The morphology of the samples has been investigated by means of a Zeiss Evo50 SEM.

RESULTS AND DISCUSSION

Electrical Properties and Morphology

Figure 1 shows the electrical resistivity as a function of the conductive filler content for the different produced materials: CB-C, CB-S, EG and MWCNTs. In both graphs, through-thickness direction (filled squares) and in-plane direction (empty squares) are represented. First of all, as it is reported in literature [14, 15], it can be observed that the electrical percolation threshold of EG and CB composites can be found at higher content of filler if compared with MWCNTs. However, the most interesting outcome shown in Figure 1 is related to the comparison of the electrical percolation threshold in the through-thickness direction with the in-plane one. This difference is more evident for CB-C composites, where the electrical percolation threshold is in the range of 14-15wt% for the through-thickness direction and 9-10wt% for the in-plane one, and MWCNT composites, where the percolation threshold is in the range of 3wt% for the through-thickness direction and 1-2wt% for the in-plane one. No significant variation in the percolation threshold was observed for CB-S and EG composites, even though in each nanocomposite at the same content of filler, lower values of resistivity were detected in the in-plane direction measurements.

A deeper investigation of the electrical behavior was performed on MWCNT-based nanocomposites, because among all the tested materials, they have the lowest percolation threshold. For this reason, in order to understand the change in the electrical properties in different directions, a thorough study on the influence of the z-coordinate in electrical properties of the cross sectional area was performed. The 2wt% was selected for this analysis, since it is the content at which the gap between the electrical resistivity in the two directions is highest.

Figure 2 shows the depth in which the test has been performed as a function of the surface electrical resistance. The right and left sides of the graph represent the two external surfaces of the injection molded sample, while the whole x-axis represent its thickness.

From this figure, it can be observed that the electrical resistance is not constant in the sample thickness, being higher moving towards the external regions from the center. From the graph, the thickness of the external less-conductive layers can be roughly estimated to be about 500 µm each, with a resulting thickness of the more-conductive region of about 1.5 mm.

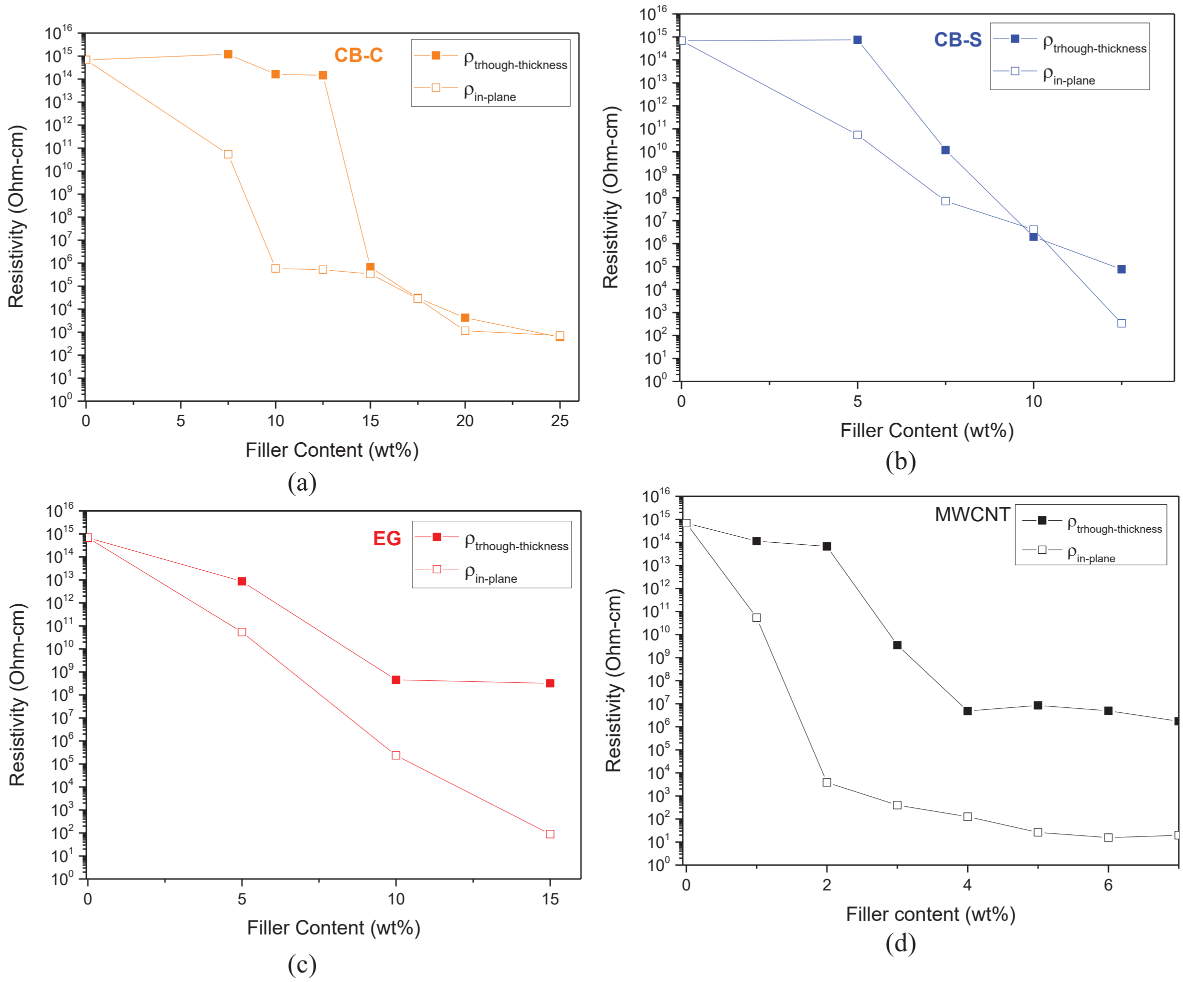


FIGURE 1. DC resistivity versus conductive fillers content in polypropylene: (a) CB-C (orange square), (b) CB-S (blue squares), (c) EG (red squares) and (d) MWCNTs (black squares). In both graphs, through-thickness direction (filled squares) and in-plane direction (empty squares) are represented.

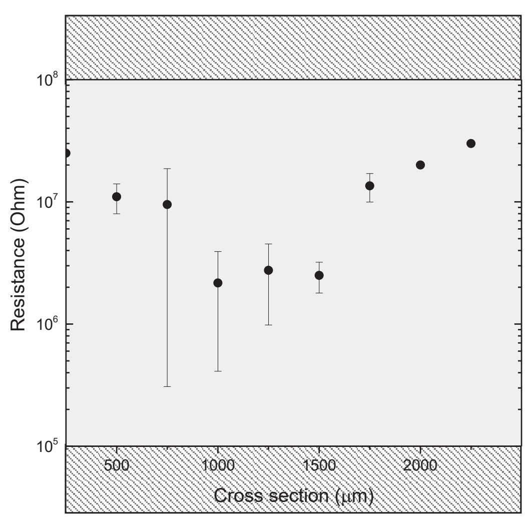
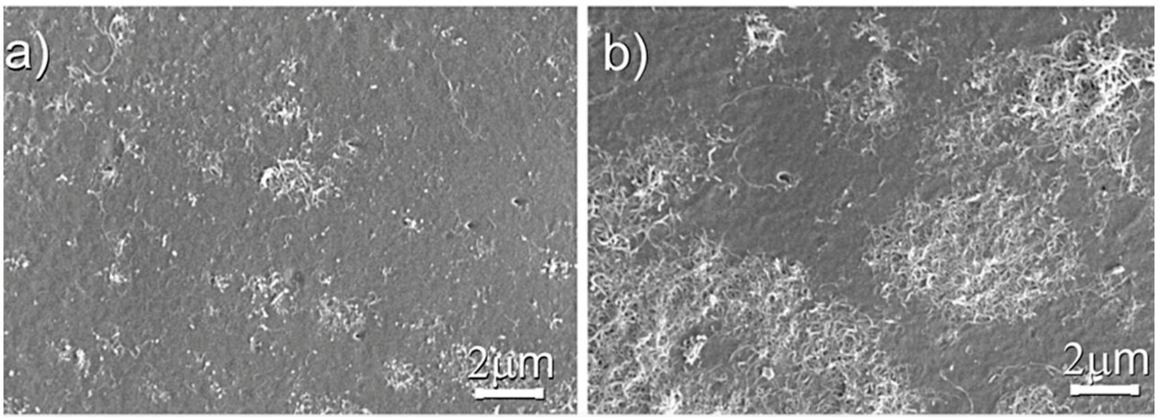


FIGURE 2. Surface resistance versus penetration depth for 2wt% MWCNTs–PP nanocomposite.

In order to explain the obtained results, a morphological characterization was performed by scanning electron microscopy (SEM). Figure 3 reports the micrographs of 2wt%, obtained both in the external layer (a) and in the internal region (b).

The 2wt%-MWCNT nanocomposite morphology is based on internal regions richer of MWCNTs than the external layers. The formation of a conductive network in the internal core leads to a conductive path, which can explain the before discussed electrical properties [16]. Consequently, it is possible to conclude that the skin layers, covering the external regions, are characterized by a low conductivity, while the core region already becomes conductive at low filler content.



(a) (b)

FIGURE 3. SEM images of MWCNT-based PP composites (2wt% MWCNTs) obtained in the external (a) and in the core regions (b) respectively.

Proposed Model for the Electrical Behavior

The results of the electrical characterization (Figures 1 and 2) can be exploited to develop a mathematical model for the through-thickness electrical behavior. The injection-molded component can be modeled as a multilayer system, being the external layers (the skin) less conductive and the internal core more conductive, due to the inhomogeneous distribution of MWCNTs in the two regions. The through-thickness overall electrical resistance can be simulated by a series of resistors corresponding to the four layers in which the cross-sectional area is divided. The in-plane electrical resistance is whilst taken as a parallel of resistors for the same system.

Therefore, the proposed model helps to detect a threshold between the regions with different amount of resistivity. It can be used to identify in the cross-sectional area the skin layers as the less conductive parts and the core region as the more conductive one. The results of the system have been calculated for the 2wt% MWCNT nanocomposite and compared to the resistivity in the through-thickness and in-plane directions, experimentally measured.

The experimentally measured resistivity in the through-thickness direction ($\rho_{through\text{-}thickness}$) is 6.65E+13 Ohm·cm, while the in-plane resistivity ($\rho_{in\text{-}plane}$) is 1.17E+05 Ohm·cm. These values fit in with the results obtained with the proposed theoretical model. In fact, the calculated skin resistivity (ρ_{skin}) is 1.50E+14 Ohm·cm, instead the calculated core resistivity (ρ_{core}) is 1.62E+04 Ohm·cm.

The proposed model allows one to understand the electrical behavior of an injection-molded component, taking into account the skin effect, which is induced by the flow of the molten material inside the mould, during manufacturing.

CONCLUSIONS

The electrical characterization of the produced carbon nanocomposites has shown that the electrical behavior changes when the measurements are performed in different directions. In fact, the electrical percolation threshold is higher for the through-thickness direction than for the in-plane one. This aspect is supported by the morphological characterization, which has highlighted the presence of a percolative conductive network of MWCNTs in the through-thickness area.

Moreover, the electrical resistance in the cross-sectional area increases when moving from the internal area toward the external layers. This can be explained by the skin effect of the external regions, MWCNT-less rich areas.

Indeed, it can be concluded that the injection molding process induces an inhomogeneous distribution of the MWCNTs in the through-thickness direction, which influences the electrical behavior of the injection molded components. This behavior can be predicted and mathematically schematized by the simple phenomenological model proposed in this study.

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