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## **Additive Manufacturing of Polypropylene Composites with Enhanced Mechanical and Electrical Properties**

### **Abstract**

This PhD work is focused on the production, through Fused Deposition Modeling (FDM) technology, of polymer matrix composites having polypropylene (PP) as the matrix and reinforced with different types of fillers, either of inorganic or carbonaceous origin. The effect of amount, dispersion and kind of filler was investigated with the aim to obtain advanced materials showing improved mechanical and electrical properties to be used in different applications fields with particular focus on electronic one.

Polypropylene ranks among the most widely used plastic materials due to its excellent mechanical properties, low cost, excellent chemical resistance, and ease of manufacturing composites having it as a matrix. However, this material is particularly challenging to be processed by FDM due to its high degree of crystallinity and very low adhesion with the main materials used as substrates of the printing plane. These factors can often lead to inconveniences during the printing process, such as part detachment from the print bed.

Firstly, various formulations based on commercial polypropylene in form of pellets with the addition of short carbon fibers (CF) or carbon nanotubes (CNTs) in different amounts were used to produce filaments to feed the FDM printer. Then, the FDM process parameters such as printing speed, nozzle and bed temperature and material used as substrate of the building platform, were optimized in order to make possible the print of all the developed formulations.

The processed materials were characterized in terms of chemical, thermal, physical, morphological, mechanical, and electrical properties. The characterization by means of DSC, FTIR and XRD analyses allowed to identify the matrix as a blend of polypropylene and polyethylene reinforced with talc particles. Moreover, the influence that the addition of the various fillers had on composite properties was systematically investigated. CNTs-reinforced composite showed higher values of enthalpy of fusion, indicating an increase in the degree of crystallinity with respect to the matrix; conversely, the addition of CF led to a decrease of melting enthalpy. The addition of the fillers allowed to obtain an improvement in terms of mechanical properties, as shown in Figure 1. This was more significant with the addition of CF, as both elastic modulus and tensile strength were significantly increased, while the CNTs-reinforced composites exhibited a slight increase of the elastic modulus.

Considering the increasing interest of scientific and industrial communities for advanced materials for electronic applications, a particular focus has been made on the characterization of the of the CNTs-reinforced composites in term of electrical conductivity. It is worth noting that initial formulations containing carbon nanotubes (in a range from 0.7 to 2.25 % wt.) exhibited electrically

conductive behavior when produced through compression molding. Nevertheless, after filament extrusion step all the formulations suffered a significant decrease of conductivity, and eventually all the CNTs-reinforced composites produced by FDM showed electrically insulating behavior. For this reason, the dispersion state of the carbon nanotubes within the matrix was investigated through microscopic and rheological analyses, arriving at the conclusion that the different process cycles led to the agglomeration of the nanotubes, which was responsible for the decrease of electrical conductivity.

Since the composites exhibited electrical insulating behavior after FDM process, the resulting samples were processed through laser writing treatment. This technology consists of applying a laser beam along selective paths on the surface of composites loaded with conductive fillers but presenting an insulating behavior. The passage of the laser beam leads to the pyrolysis of the matrix, which results in an increase in the local concentration of conductive particles and thus in the formation of conductive pathways. A preliminary study was carried out to verify the effects of the process parameters, namely the laser scanning speed and the applied power, over the values of linear electrical resistance. The disposition of the CNTs along the conductive track obtained by laser writing is shown in Figure 2.

An alternative approach that has been routed to obtain FDM conductive materials is based on the production of composites containing hybrid fillers. A design of experiment was formulated to develop polypropylene-matrix composites containing up to three fillers, namely carbon nanotubes, conductive carbon black and short glass fibers, respectively, with the aim of obtaining materials with high mechanical and electrical properties, which were evaluated both in filaments and FDM specimens. Materials with significantly improved mechanical properties and extremely low values of electrical resistance were thus produced through FDM process.

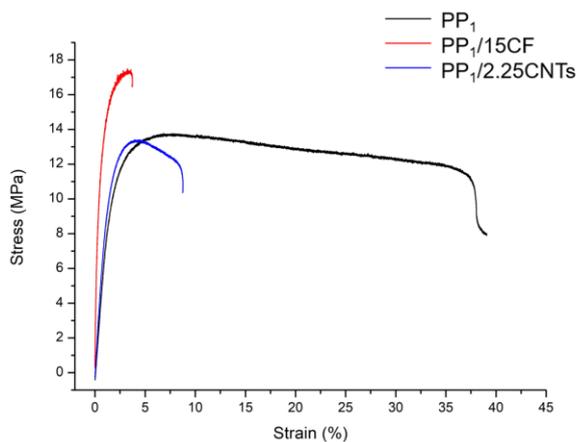


Figure 1. Tensile test curves referred to PP and its composites produced by FDM

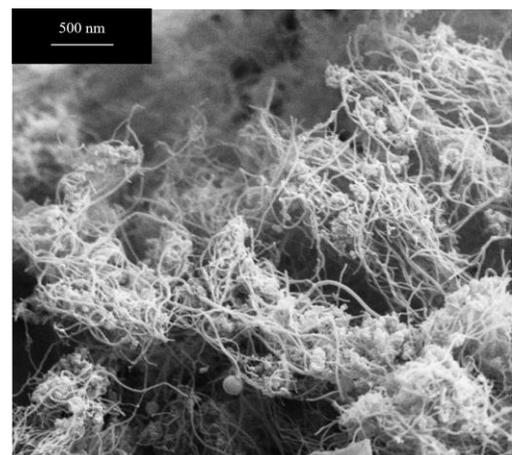


Figure 2. Carbon nanotubes located along laser tracks