BASIC CHARACTERISTICS OF DIFFERENT NANOCOMPOSITES' FABRICATION METHODS FOR DIRECT INDUSTRIAL IMPLEMENTATION

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1. ABSTRACT

In this work, three vastly different nanocomposites' fabrication methods were utilized, along with three different specimens' fabrication methods, in order to analyse and evaluate their imprint on the morphology and structure of the produced nanocomposites along with their cost efficiency and their ability to be implemented directly in the industry. The main nanocomposite materials' fabrication methods described herein are the solvent, the melting and the extrusion method. Regarding the specimen fabrication, pressing and Fused Filament Fabrication (FFF) 3D printing method, were utilised. The aforementioned methods were used for fabricating a series of different nanocomposites, at various concentrations, including Low Density Polyethylene with Graphene (GnP) and ABS with Zinc Oxide (ZnO) / Graphene Nanoplatelets (GnP) / Titanium Oxide (TiO). It was shown that all these methods, when compared, yielded different internal specimen structuring and more importantly, major differences in homogeneity and nanomaterial's dispersion into the polymer matrix. It was also shown that these methods have drastically different utilization costs, making most of these fabrication techniques unsuitable for implementation in the industry.

2. INTRODUCTION

Polymers nowadays, have been proven suitable materials and matrices for the development of composite materials due to their low cost, ease of production and their good physical, mechanical and electrical properties. In a polymer nanocomposite, the type and size of the filler, the morphology of the filler network, the fabrication methodology, as well as the thermal properties and the conductivity of the polymer matrix have been considered as important variables influencing its final properties [1-2]. Substantial amount of work has been carried out in the field of nanocomposites and their fabrication, using the melt extrusion method approach and Fused Filament Fabrication [3-5] or the sol-gel method approach [6-7]. Comparing the above researches' methodologies and results to current research, it is evident that each method yields different results, not only in internal structure of the nanocomposites but also in the final physical properties of the produced material.

Nanomaterials are nowadays introduced into polymer matrices to improve the overall mechanical, electrical and physical properties of the polymer matrix, cause of their significant surface area due to the nano scale. Different nanofillers are being used to produce nanocomposites, such as metal oxides (Titanium DiOxide, Zinc Oxide etc) or carbon-based fillers (Graphene, Carbon nanotubes). In this work, the methodology for the production of nanocomposites with both metal oxides and carbon-based fillers is presented and evaluated.

It became evident that not all fabrication methods are suitable for synthesizing polymer nanocomposites. Also, not all specimens' fabrication methods yield the same morphological results. While each method introduces different effects on the produced nanocomposites, their industrial implementation is heavily depended on cost, environmental factors and mass production requirements that leads to direct implementation difficulties. This research focuses on analyzing, comparing and evaluating these greatly different nanocomposites fabrication methods from physical properties and morphology to cost efficiency in order to find the best suitable method for industrially mass producing of nanocomposites and nanocomposite parts.

3. METHODOLOGY

Three different fabrication methods were utilized for the creation of nanocomposite materials and three for the specimen fabrication. The methods used are summarized in the Table 1 bellow, including the nanocomposites produced with each methodology.

Fabrication Method	Specimen Fabrication Method	Nano-composites
Solvent	Hot pressing	LDPE / PE / HDPE with GnP
Melting	Hot Molding	LDPE / PE with GnP
Extrusion	3D Printing	ABS with GnP / ZnO / TiO

Table 1.
Fabrication methods used
for each nanocomposite in this work

3.1. Solvent – based fabrication

Solvent method is widely used for processing GnP polymer nanocomposites. In this case, GnP and LDPE are mixed within suitable solvent and antisolvent, which are then evaporated in a controlled way (Figure 1). The solvent and the antisolvent used for LDPE were toluene and ethylene respectively [8], while the evaporation of the residue solvents took place in controlled room temperature. In order to achieve a good dispersion, a magnetic stirrer was implemented kept at a temperature of 250ºC.

Figure 1.
Solvent – based method; Dissolved LDPE
inside toluene solvent with GnP filler

Figure 2.
Hot pressing of the produced nanocomposite
via solvent method into molds

The specimens' fabrication method used along with the aforementioned solvent based method is the hot pressing (Figure 2). In hot pressing, the produced paper-like nanocomposite is hot pressed in aluminum specimen molds under pressure (20-30 MPa). The hot pressing is done at 200ºC.

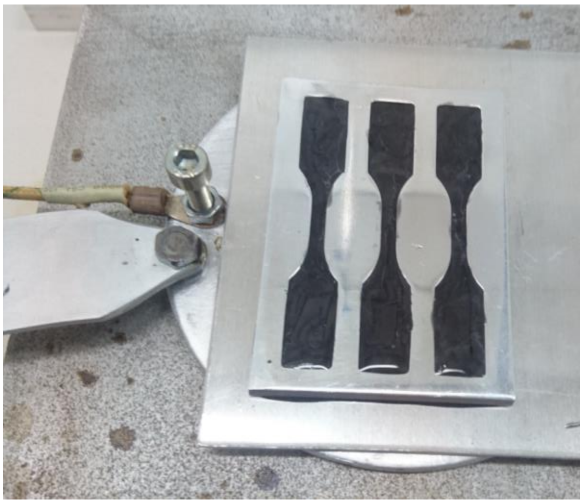

Figure 3.
Melting – based fabrication; Melting LDPE
with GnP in hot molds

3.2. Melting – based fabrication

Melting method, which is simpler for fabricating polymer nanocomposites consisting of low molecular weight polymer matrices and thermoplastics. Limiting factor in this case is the solubility of the polymers and the cost for obtaining large quantities of nanocomposites. This method involves melting of the polymer to its viscous form, followed by mechanical mixing of the filler within the polymer matrix. This technique is less efficient, in timely and costly manner, than the solvent one or the melt extrusion, due to the high viscosity of the polymer. A uniform dispersion is achieved in this way. The resulting nanocomposite from the aforementioned procedure, is poured into heated aluminum molds in atmospheric pressure that shape the nanocomposite into the desired specimen (Figure 3).

3.3. Filament Extrusion

For this research, nanocomposite filaments were fabricated by means of extrusion melting at different concentrations of ZnO, TiO and GnP. Filament extrusion was made with a single-screw Noztech Pro extruder (Figure 4), at a temperature range of 200oC to 230oC, depending on the selected filler concentration. Materials were fed into the extrusion system as a homogeneous powder mixture. Parts of the nanocomposite filaments were initially analyzed before being used for 3D printing. The 3D printer used in all cases was a MakerBot replicator 2x (Figure 5), commercially available desktop 3D printer.

3.4. Morphological and structural characterization

Regarding the morphological characterization, SEM characterization was performed using a (FE-SEM) Nova NanoSEM 630 (FEI Company, SUA), equipped with an EDX detector (EDAX TEAM™, SUA) FEI Nova NanoSEM 630 field emission microscope, in order to investigate and understand the formation and the structuring of the obtained nanocomposite materials. All samples were characterized in the high vacuum mode without any conductive coating.

Regarding the internal structural characterization and homogeneity, Raman analysis was done using a Witec alpha 300S/Witec/2008 Witec Gmbh Germany with Nd-YAG – 532 nm laser, confocal Raman microscopy (high-resolution confocal Raman imaging, AFM and SNOM). For the recording of the Raman spectra, a 532 nm laser was used, with a power of 10 mW at the sample. A 20x objective and a 25 μm slit aperture were used to obtain more detailed spectra, while a total acquisition time of 10 seconds (1 second exposure x 10 exposures) was chosen for each Raman spectrum.

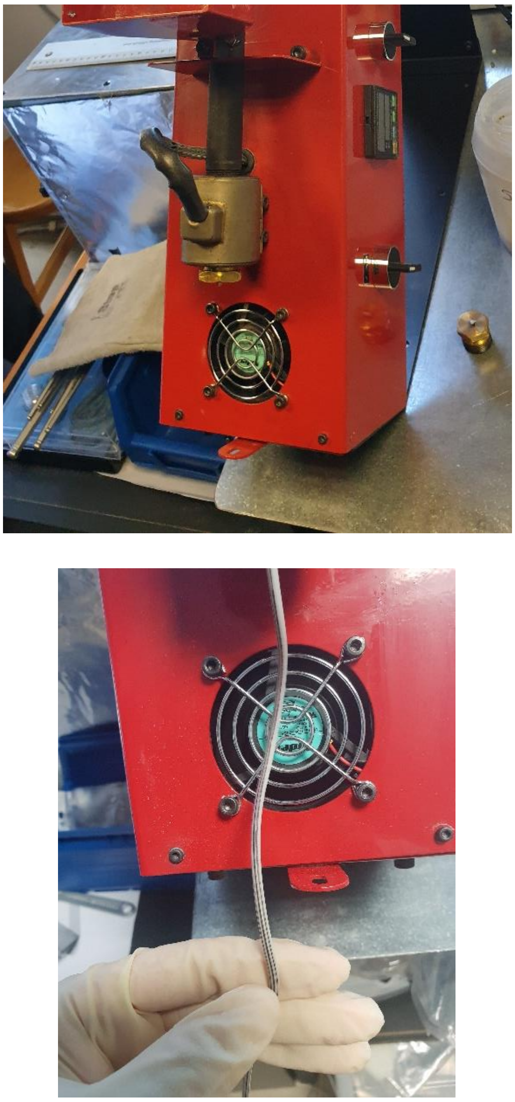

Figure 4.
Filament fabrication via

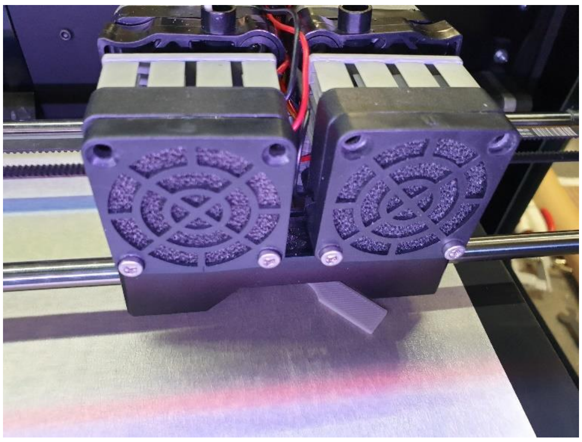

Figure 5.
3D printing specimens in a commercially available printer; MakerBot replicator 2x

4. RESULTS

4.1. Internal structure and homogeneity

SEM characterization of samples was performed in order to observe the formation and structuring of the composite material. Nanocomposite materials fabricated by two of the three aforementioned techniques, the solvent and the melt extrusion were found to consist of a quite inhomogeneous bulk formed by different polymerization domains as well as regions with concentrated nano filler material. This effect was not present on the nanocomposites fabricated by melt extrusion and specimens by FFF.

4.2. Cost analysis and suitability

Materials' fabrication cost has a major role regarding industrial implementation. Each of the aforementioned fabrication methods has a fixed production cost which is analysed further bellow. Note that in this chapter, only the main production costs are considered. Each method's cost can be seen summarized in the following Table 2.

Fabrication Method	Cost for producing 150gr nanocomposite	Applicability on a variety of polymers	Fabrication Time
Solvent	161,25€	No (requires low molecular weight polymers or high dissolving temperatures i.e. 250°C)	24+ hours
Melting	<1,00€	No (requires low viscosity polymers)	~2 hours
Extrusion	<4,00€	Yes	~20 minutes

Table 2.
Fabrication methods' cost

The solvent fabrication method requires a solvent and an antisolvent. In most of the cases studied, these solvents are Toluene / Xylene and Ethylene [8]. For the solvent method, it was required for the production of 150gr nanocomposite the amount of 1.5L solvent and 1L antisolvent. For that amount of polymer its critical that there's sufficient amount of solvent due to polymer swelling and solvent saturation. Having obtained the aforementioned solvent and antisolvent from Sigma Aldrich, costs 135,00€ for the 2L bottle of Toluene (without delivery costs) and 120,00€ for the 2L bottle of Ethylene. Note that the cost of these solvents depends on the purity offered. To summarize, this method costs 161,25€ for the production of 150gr of nanocomposite, without taking into account other smaller application costs.

Regarding the melting method, the only main cost of the application is the mold manufacturing and maintenance including the mechanical stirrer. Depending on the specimens' size and complexity, the production cost is calculated to be less than 1,00€ per 150gr of polymer knowing that aluminum molds can produce thousands of specimens before wearing down.

The melt extrusion method follows the same principle. The main cost of this method derives from the purchase and maintenance cost of the extruder machine. The extruder machine used (Noztek pro) has a cost label of 1.087,00€ and an additional maintenance cost of 20€. Maintenance is critical; at least one time every 1000gr of nanocomposite production or mandatory maintenance before switching the feeding material to a different nanocomposite mixture. Concluding, this method has an overall fabrication cost of less than 4,00€ for 150gr of nanocomposite production.

Concluding the above, it is shown that the solvent method is extremely costly and cannot be adapted to industrial needs. Especially for the production of large amounts of nanocomposites. Major implementation factor is also the manufacturing time. Making the solvent method not only expensive, but also slow production method. On the contrary, melting and extrusion methods, are currently implemented in the polymer industries due to their low cost and fast production ratio but not yet on the nano scale level.

5. DISCUSSION

This research focused on evaluating the suitability of available nanocomposite fabrication methods; solvent, melt and melt extrusion. It was shown that the best suitable method that yields the best mechanical and morphological properties on the fabricated nanocomposites and is cost efficient for direct implementation in the industry is the melt extrusion. It was also found that the specimens fabrication method that is more efficient and introduces less faults in the internal structuring (i.e. bubbles) is the Fused Filament Fabrication.

It was also shown that the cost of the aforementioned methods, which is an impactful factor for the polymer industry, is different for each case scenario, while specifically the cost of incorporating the solvent method is prohibitive.

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