Conferences

European Congress and Exhibition on Advanced Materials and Processes – EUROMAT 2021

"***Development of multifunctional graphene and carbon nanotube reinforced composites; utilization of advanced thermal properties***", G. Konstantopoulos, P. Maroulas, S. Termine, D. Semitekolos, T. Kosanovic, C. Charitidis

Carbon-based nanomaterials have been proven to be cutting-edge filler materials. The combination of advanced thermal and electrical properties, and their nanodimensions that facilitate the development of defect—free mechanically robust crystal structures, resulting from their strong hexagonal sp2 lattice, allows free electron mobility in plane as well as thermal transport. In particular, carbon nanotubes (CNTs) and graphene, are ideal to add multifunctionality to reinforced composites. In this work, two applications are investigated, i.e., a) functional thermoplastic materials with self-healing properties and application in leisure and every-day life, and b) functional thermoset materials with application on industrial heat management devices with complex architectures, such as heat sinks manufacturing.

The development of these composites covers the need for sustainable, cheap, and re-/up-cyclable composites with advanced thermal functionality. In the first case, Thermoplastic polyurethane (TPU) is reinforced with graphene nanoplatelets (GNPs) and CNTs and self-healing was demonstrated. Due to the high resistance of the polymer matrix, a high portion of electric energy is converted to thermal energy. Local temperature is monitored by using an infrared camera and can reach up to 160oC, and induces local melting and annealing of the TPU matrix. In the case study of a 3D-printed specimens with the TPU masterbatch formulations enriched in GNPs and CNTs, self-healing properties are demonstrated, both in the produced 3D filament and printed parts. Thus, any wear damage will be viable for the nanocomposite and consequently the life cycle will be extended. On the other hand, epoxy-based composites suitable for heat-sink application are also reinforced with GNPs and CNTs to fabricate complex and miniaturized structures. The successful demonstration of enhanced dissipation of heat is realized by achieving composite thermal conductivity equal to 1.4 W/m·K exceeding many of the published state-of-the-art results.

"Hybrid CNTs nanostructures for smart applications", A.F. Trompeta, S. Termine, A. Ntziouni, C.A. Charitidis.

Carbon-based hybrid materials are an important class of artificial materials with potential applications in various fields ranging from energy storage (e.g. harvesting) to recycling applications (e.g. smart debonding). For this reason, both their synthesis process and the assessment of their properties are of high interest. Herein, we present a brief summary of recent developments in the area of functional hybrid materials comprising one-dimensional (1D) carbon allotropes. One of the investigated hybrids are magnesium silicide thermoelectric carbon nanotubes (Mg2Si/CNT) for use as smart flexible n-type thermoelectric materials; these were successfully synthesized through a combined sol-gel and thermal reductive process.

Furthermore, the in-situ growth of CNT-hybrids through chemical vapour deposition process (CVD), was proved to be a facile way to create hybrid materials with unique and interesting properties. In this perspective, the synthesis of hybrid microwave and radiofrequency assisted materials has been investigated, based on metal and ceramic nanoparticles. Synthesis of CNTs on magnetic nanoparticles such as $ZnFe_2O_4$ and Fe_3O_4 was accomplished in a one-step CVD procedure. These hybrids can be used on recycling applications for thermoplastics including carbon fibres, by enabling local heating around the fibre and thus, smart debonding. Also, nanosized silicon carbide has been exploited by utilising the floating catalyst approach, in order to grow SiC/CNT hybrids. The aim for this microwave assisted material is to be incorporated into coatings in a concentration lower than 1 wt. %, in order to provide selective heating on the interphase between the coating and the plastic substrate. By this, smart debonding applications for effective polymers recycling can be achieved.

TNT2021 "Trends in Nanotechnology International Conference"

"Thermoplastic nanocomposites with magnetic nanoparticles for bonding and debonding on demand applications by local induction heating", M. Kanidi, T. Kosanovic, A.F. Trompeta, C.A. Charitidis.

Induction heating is a convenient and flexible method to deliver high-strength magnetic fields to ferromagnetic nanoparticles, which act as susceptors, generating heat in nanocomposite materials by hysteresis. Taking advantage of the induction heating mechanism, nanocomposite materials embedded with MNPs, constitute very promising materials for adhesive joining systems, enabling reversible joining procedures, providing easy-to-disassembly operations by induction disassembly.

Nanocomposite filaments for Additive Manufacturing, reinforced with magnetic nanoparticles (MNPs) were used to investigate the heating capacity, using induction heating technology. Thermoplastic (TP) matrices of polypropylene (PP), polyurethane (TPU), polyamide (PA12) and polyetherketoneketone (PEKK) were compounded with 2.5, 5, 7.5, and 10 % wt. iron oxide nanoparticles (Fe_3O_4). MNPs were introduced to the polymers matrices by a twin-screw extrusion system, following appropriate temperature profiles. After the extrusion, nanocomposite specimens were prepared either by thermo-pressing in specific moulds or by 3D printing. Heating capacity of nanocomposite specimens was examined as a function of time in a radiofrequency (RF) generator with a solenoid inductor coil, varying the working parameters (i.e. maximum power, frequency, time).

All nanocomposite specimens presented an increase of temperature proportional to the concentration of MNPs as a function of exposure time in the magnetic field. Specifically, nanocomposite specimens with higher concentration of MNPs showed more rapid increase of temperature, resulting in melting state in the most of cases/trials. Nanocomposites of PP, TPU, and PA12 with 10% wt. MNPs reached their melting temperature in less than 2 minutes of exposure in a magnetic field of 585 kHz frequency. In the case of PEKK, a lower concentration of MNPs is preferable, since PEKK, as high performance polymer is a more demanding during the extrusion process. Specimens of PEKK with 2 % wt. presented an increase of temperature after 5 minutes of exposure in a magnetic field of 585 kHz frequency. However, the heating capacity was not sufficient to melt the nanocomposite. The working parameters of the RF generator, such as frequency and input power, significantly affect the heating capacity of MNPs. Using a coil with solenoid geometry, higher input power and frequencies promote the rapid increase of temperature of all nanocomposites.

Developing innovative thermoplastic nanocomposites will allow a faster and leaner integration and repair of 3D printed structures, compared to thermoset repair processes, promoting advanced applications in many fields of Nanotechnology.

"Inductive thermal effect on thermoplastic nanocomposites with magnetic nanoparticles for self-healing, bonding and debonding on demand applications", Kanidi, M., Loura, N., Frengkou, A., Kosanovic, T., Trompeta, A. F. & Charitidis, C.

Abstract

Through induction heating method, high-strength magnetic fields can be delivered to ferromagnetic nanoparticles, which act as susceptors, generating heat in nanocomposite materials by hysteresis. Taking advantage of the induction heating mechanism, nano-composite materials with magnetic nanoparticles (MNPs) constitute promising materials for induction-based repair of composites, adhesive joining systems, enabling reversible joining procedures, providing easy-to-disassembly operations. Investigation of the heating capacity of nanocomposite materials were conducted using induction heating technology. Thermoplastic (TP) matrices of polypropylene (PP), thermoplastic polyurethane (TPU), polyamide (PA12) and polyetherketoneketone (PEKK) were compounded with 0–10 % wt. iron oxide based MNPs using a twin-screw extrusion system. Specimens were prepared by 3D printing and injection moulding and their heating capacity was examined as a function of time, frequency and power of RF generator with a solenoid inductor coil. All nanocomposite specimens presented temperature increase proportional to the MNPs concentration as a function of exposure time in magnetic field. Specifically, specimens with higher concentration of MNPs presented more rapid temperature increase, resulting in melting state in the most of trials. The working parameters of the RF generator, such as frequency and input power, significantly affect the heating capacity of specimens. Using a coil with solenoid geometry, higher input power and frequencies promote the rapid increase of temperature of all nanocomposites. Developing innovative TP nanocomposites will allow a faster and leaner integration, triggered healing of TP matrix and bonding/debonding on demand, compared to thermoset repair processes, promoting applications in different fields.

"Reclamation of continuous carbon-fibre from thermoplastic composites by local induction heating", Kanidi, M., Kosanovic, T, Batsouli, D, Athinaios D, Vlachos, D. & Charitidis, C.

Abstract

Induction heating is a convenient and flexible method to deliver high-strength magnetic fields to ferromagnetic nanoparticles, which act as susceptors, generating heat in nanocomposite materials by hysteresis. Taking advantage of the induction heating mechanism, composite materials reinforced with carbon fibers (CF) functionalized with magnetic nanoparticles (MNPs) constitute promising materials for composite systems, enabling reclamation of CFs in recycling, providing easy-to-disassembly operations by induction disassembly. Polypropylene matrix was reinforced with different fractions of CF bundles functionalized with iron oxide (Fe3O4) MNPs. Using induction heating technology, heating capacity of composite specimens was initially investigated as a function of time in a radiofrequency (RF) generator with a solenoid inductor coil, varying the working parameters (i.e., power, frequency). All nancomposite specimens presented temperature increase proportional to the content of functionalized CFs, thus the content of MNPs. Specimens with higher CF fraction of functionalized CFs bundles reach the melting temperature of PP in less than 10 minutes, enabling reclamation of CFs by the end of induction heating. Heating capacity of specimens is significantly affected by the working parameters of the RF generator, such as frequency and input power. The rapid increase of temperature is promoted by higher input power and frequencies for all nanocomposites using a coil with solenoid geometry. Taking advantage of the fast and lean CF reclamation that is offered by induction heating technology, advanced applications in many

fields of Nanotechnology are promoted by the development of innovative thermoplastic based CFRP nanocomposites suitable for recycling procedures.

"Development of nanocomposites with self-healing properties for use in additive manufacturing technologies", Niki Loura, Aikaterini-Flora Trompeta Georgios Konstantopoulos, Dionisis Semitekolos, Stefania Termine, Panagiotis Klonos, Apostolos Kyritsis, Costas A. Charitidis

Abstract

The development of carbon nanomaterials and their incorporation into polymer matrices for the production of filaments of fixed cross-section with final application in three-dimensional (3D) printing was studied. The scope of the present research is to investigate the effect of carbon nanomaterials on the thermal and electrical conductivity of nanocomposite filaments and to evaluate their self-healing capability. The synthesis of nanomaterials focused on the production of carbon nanotubes (CNTs) and graphene derivatives. In particular, two types of carbon nanotubes were produced via chemical vapor deposition, as well as graphene by chemical and electrochemical processes, which were subsequently characterized. Emphasis was placed on up-scaling the production of the materials in order to use them in melt-extrusion process as a method of mixing and filament production. Recycled thermoplastic polyurethane (TPU) and polyamide 12 (PA12) were selected as polymeric matrices. For all of the polymer nanocomposites, samples were prepared at additive contents of 1 - 5 - 10 - 15% w/w. The aim of the melt-extrusion process was to produce filaments of a constant diameter, material capable of being a raw material for Fused Deposition Modeling (FDM). A PRUSA home-made 3D printer was used to fabricate a pair of circular specimens, which were then studied for their thermal and electrical conductivity. In regard to the thermal conductivity, the nanocomposites with 10% and 15% wt. content of CNTs derivatives showed the twice value compared to the reference pure samples. To evaluate the electrical conductivity, in addition to the two-wire method, the analysis of Dielectric Relaxation Spectroscopy (DRS) was performed. It was revealed that the highest electrical conductivity value was exhibited by the PA12 printed nanocomposite with 15% w/w CNTs. The self-healing ability was identified in commercial TPU-based and PA12-based fibers with 10% w/w CNTs. By the experimental method applied and through SEM analysis, was revealed the ability of the material to be able to heal internal microcracks up to 20 μm thickness under the application of potential difference.

SMARTFAN SICS 2021 CONFERENCE

Smart and intelligent composite structures for innovative industrial applications

Development of nanocomposites with self-healing property for use in additive manufacturing technologies

Niki Loura[a], Aikaterini-Flora Trompeta[a], Georgios Konstantopoulos[a], Dionisis Semitekolos[a], Stefania Termine[a], Panagiotis Klonos[b], Apostolos Kyritsis[b], Costas A. Charitidis[a,*]

[a]Research Lab of Advanced, Composite, Nano-Materials and Nanotechnology (R-NanoLab), School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou, GR-15780, Greece

[b]Dielectrics Group, Physics Department, School of Applied Mathematical and Physics Science, National Technical University of Athens, 9 Heroon Polytechniou, GR-15780, Greece

*Corresponding author: charitidis@chemeng.ntua.gr

Abstract

This research aims to the development of carbon nanomaterials and their incorporation into polymer matrices for the production of filaments of fixed cross-section with final application in three-dimensional (3D) printing. The synthesis of nanomaterials focused on the production of carbon nanotubes (CNTs) and graphene derivatives and as polymeric matrices were selected recycled polyamide 12 (rPA12) and recycled thermoplastic polyurethane (rTPU). The whole synthesis process was aimed at developing self-healing behavior by analyzing the electrical and thermal conductivity of the materials.

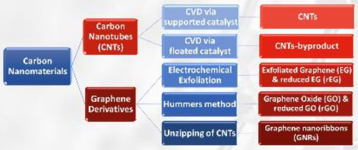
Introduction

Additive manufacturing (AM) techniques fabricate a wide range of structures from 3D model data. Its most recognizable form is the 3D printing process known as Fused filament fabrication (FFF) that uses a continuous filament of a thermoplastic material. Melt extrusion is an eco-friendly filament production process that can reduce the manufacturing cost, especially when it uses recyclable plastics.

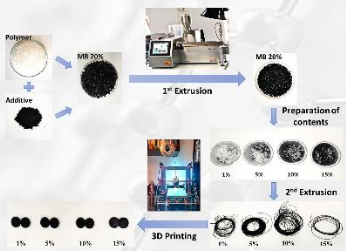
Thermoplastic polyurethane (TPU) and polyamide 12 (PA12) are strong, abrasion resistant polymers that have the potential for the inclusion of carbon nanostructured additives to extend their utility in multi-functional 3D printed composites. More specifically, it is desirable to develop smart composite systems with built-in capacities to detect and characterize mechanical damage as well as the ability to self-heal. Particularly, polymer/carbon nanotube or graphene nanocomposites, produced by melt extrusion with final application the 3D printing, have been studied due to their rapid healing efficiency.

Experimental Methods & Materials

The different types of nanomaterials that were produced are referred briefly, as well as their experimental method of production. Emphasis was placed on up-scaling the production of the materials in order to use them afterwards in melt-extrusion process.

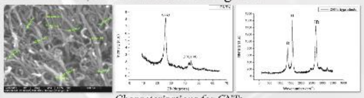


Below it is demonstrated the schematic extrusion and 3D printing process of the nanocomposites.

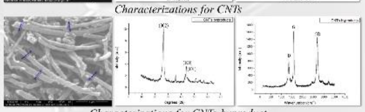


Results & Discussion

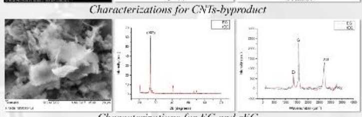
Prior to the production of the nanocomposites, the nanomaterials were characterized by SEM, EDX, XRD and RAMAN, as shown below at Figures.



Characterizations for CNTs

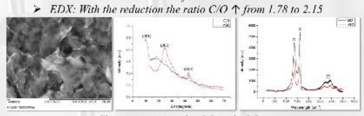


Characterizations for CNTs-byproduct



Characterizations for EG and rEG

➢ *EDX: With the reduction the ratio C/O ↑ from 1.78 to 2.15*



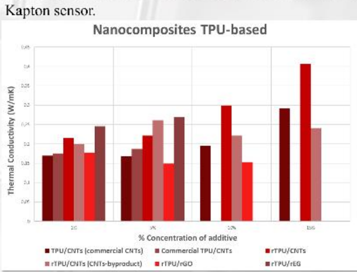
Characterizations for GO and rGO

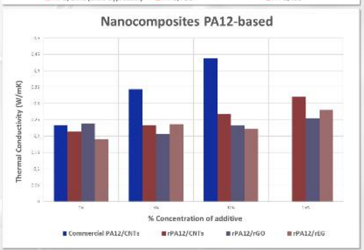
➢ *EDX: With the reduction the ratio C/O ↑ from 1.31 to 1.98*

Following the characterization of the nanomaterials, the nanocomposites were produced by melt extrusion and after 3D printed in a pair of circular specimens.

❖ **Thermal conductivity measurements:**

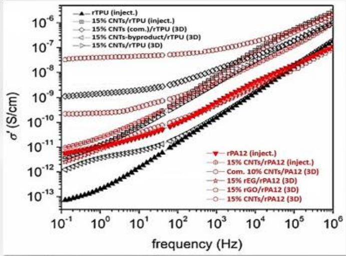
The thermal conductivity of the 3D printed samples was measured on the Hot Disk TPS 500 instrument with a Kapton sensor.





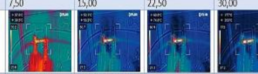
❖ **Electrical conductivity measurements:**

The electrical conductivity of the 3D printed specimens was measured using the DRS method. In order to distinguish the effect of 3D printing on the electrically conductive behavior of the specimens, some high concentration at additives specimens were fabricated for comparison with injection moulding.

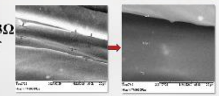


❖ **Self-healing capability:**

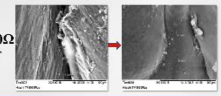
The ohmic behavior of the filaments was evaluated by the Joule effect. Specifically, it was examined their response to changes in applied voltage with temperature increase. The following commercial nanocomposites were shown to exhibit self-healing behavior: ***10% CNTs-PA12 and 10% CNTs-TPU.***

Applied Voltage (V)	7,50	15,00	22,50	30,00
Image IR				
Mean Temperature (°C)	37,60 ± 2,00	53,10 ± 2,00	69,80 ± 2,00	177,00 ± 10,00
Max Temperature (°C)	39,50 ± 3,00	56,20 ± 3,00	74,80 ± 7,00	253,00 ± 15,00
Current (A)	0,01 ± 0,01	0,03 ± 0,01	0,04 ± 0,01	0,06 ± 0,01

10% CNTs-PA12:
- Ohm's law: **R=526.3Ω**
- Complete healing of internal cracks **up to 7 μm.**



10% CNTs-TPU:
- Ohm's law: **R=101.0Ω**
- Complete healing of internal cracks **up to 20 μm.**



Conclusions

❖ Large-scale synthesis of nanomaterials was achieved through recalibration and optimization of the synthesis process.

❖ By utilizing recycled products and by-products, it was possible to produce various printable concentrations of reinforced filaments up to 15% additive content.

❖ The thermal conductivity of the 3D printed specimens increased with % of additive, and also doubled at 15% concentration of CNTs.

❖ The electrical conductivity was not dependent on the 3D printing process. On the contrary, its strong correlation with the dispersion and nature of the nanomaterials is concluded.

❖ The Joule effect was exploited and the self-healing was induced when the additive corresponded to 10% by weight for CNTs.

Acknowledgements

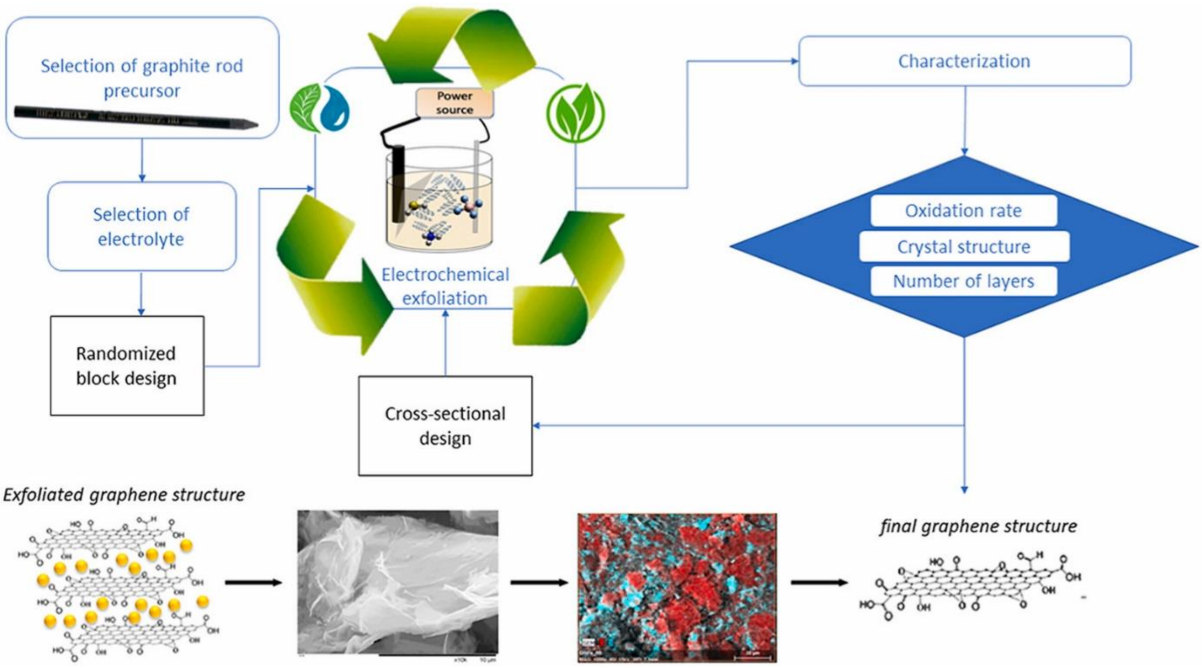
This study was funded by the Horizon 2020 European Research Program, "**Repair3D**: Recycling and Repurposing of Plastic Waste for Advanced 3D Printing Applications" with contract number **No. 814588**.

Publications

"A systematic study of electrolyte effect on exfoliation efficiency and green synthesis of graphene oxide", Georgios Konstantopoulos, Eleni Fotou, Afroditi Ntziouni, Konstantinos Kordatos, Costas A.Charitidis, https://doi.org/10.1016/j.ceramint.2021.08.122

Abstract

A systematic study on the effect of the electrochemical exfoliation of graphite was conducted to provide new insights on the structure and material properties. Graphene-like structures are produced at scale currently using the wet chemical approaches, which is usually followed by an additional reduction step. The electrochemical exfoliation constitutes a promising alternative method for green, fast, and safe industrial exploitation, due to its low cost, mild conditions, basic equipment requirement and eco-friendlier electrolytes. Additionally, crystal structure of graphene related materials demonstrates less defective sights due to the high speed of exfoliation. A thorough investigation was conducted on critical parameters of the electrochemical process. The parameters of concentration, voltage, temperature and sonication assistance were studied using the randomized block design approach for various electrolytes. After the evaluation and screening of the materials with several characterization techniques, three optimization routes were selected, which included a modified Hummers' method, exfoliation based on the surface energy of pure DMF, and violent pH neutralization. The production of graphene oxide nanoplatelets was achieved, with high oxidation rates, high crystallinity and limited imperfections. The materials were consisted of less than 10 layers and up to 5 layers as demonstrated by the low crystallite size, which was also demonstrated for GO that underwent post-treatment optimization. Higher yields were achieved with electrolytes known for their strong oxidative effect, while the hydrogen peroxide electrolyte and the ionic liquid demonstrated lower exfoliation rates.



"Research and Development in Carbon Fibers and Advanced High-Performance Composites Supply Chain in Europe: A Roadmap for Challenges and the Industrial Uptake", Elias P Koumoulos, Aikaterini-Flora Trompeta, Raquel-Miriam Santos, Marta Martins, Cláudio Monterio dos Santos, Vanessa Iglesias, Robert Böhm, Guan Gong, Agustin Chiminelli, Ignaas Verpoest, Paul Kiekens, Costas A Charitidis, https://doi.org/10.3390/jcs3030086

Abstract

Structural materials, typically based on metal, have been gradually substituted by high-performance composites based on carbon fibers, embedded in a polymer matrix, due to their potential to provide lighter, stronger, and more durable solutions. In the last decades, the composites industry has witnessed a sustained growth, especially due to diffusion of these materials in key markets, such as the construction, wind energy, aeronautics, and automobile sectors. Carbon fibers are, by far, the most widely used fiber in high-performance applications. This important technology has huge potential for the future and it is expected to have a significant impact in the manufacturing industry within Europe and, therefore, coordination and strategic roadmapping actions are required. To lead a further drive to develop the potential of composites into new sectors, it is important to establish strategic roadmapping actions, including the development of business and cost models, supply chains implementation, and development, suitability for high volume markets and addressing technology management. Europe already has a vibrant and competitive composites industry that is supported by several research centers, but for its positioning in a forefront position in this technology, further challenges are still required to be addressed.