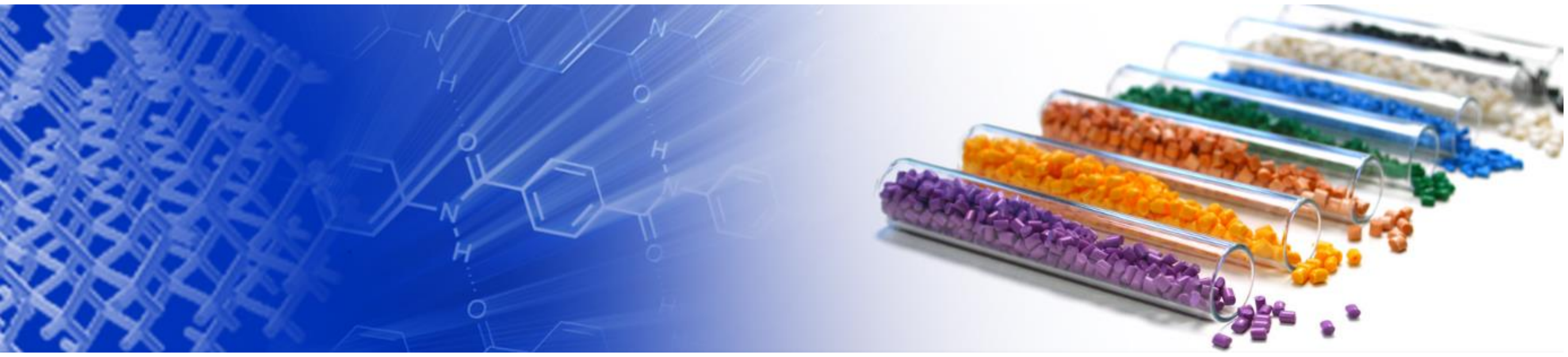


Workshop on nanocomposite polymers for 3D-printing of high-tech structures

Organized in the framework of the

H2020 Graphene3D project

University of Namur, Belgium

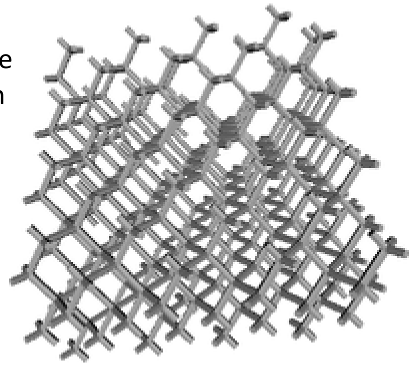
22-23 May 2018

UNIVERSITÉ DE NAMUR

The workshop aims at gathering researchers interested in material-science aspects of additive manufacturing. The focus of the workshop is put on the use of polymers and composite polymers for 3D printing. A special attention is paid to polymers doped with carbon nanostructures for the making of three-dimensional conducting structures. Open to all the interested researchers, the workshop is organized in the framework of the H2020 Graphene-3D project. The project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie-Sklodowska Curie grant agreement N° 734164. The program includes 10 invited talks, 4 oral contributions and a poster session.

Graphene-3D is a joint project on graphene-polymer research based on knowledge sharing in a multidisciplinary international/inter-sectoral consortium of ten partners. The central objective of the project is to design and produce, by additive manufacturing, conducting cellular structures with tailored electromagnetic properties in the GHz and near THz frequency domains. These structures must be light, mechanically robust, and chemically inert.

In addition, they must hold special thermal characteristics. An example of multi-functionality such structure could have is to provide an efficient protection against electromagnetic interference of an electronic device, while making it possible to drain the heat produced by the shielded device.



The cellular structures are manufactured from composite polymers compatible with the 3D printing technology. To become conducting, the polymer is filled with a small fraction of graphene nanoplatlets and other carbon nanostructures. A real challenge of the project is to optimize the formulation and microstructure of the composite according to targeted properties (rheological, mechanical, electrical, thermal …), production cost and environmental footprint. It is important that the characteristics of the composite be robust against fluctuations of the many parameters that enter the production process. In parallel to the important research effort in nanocarbon-polymer composite, computer simulation and experimental measurements are performed to investigate how the geometry of a cellular structure and the characteristics of its constituent material influence its multifunctional performances.

The H2020-MSCA-RISE-2016-734164 Graphene 3D is 48 months research project that facilitates knowledge transfer between height research centres and two SMEs located in Bulgaria, Belgium, Italy, Belarus, Georgia, China and Brazil. Research and innovation staff members strongly benefit from being part of this international and multidisciplinary project consortium. By the end of the year 2020, about 46 researchers will have exchanged 234 secondments funded by the EU for overall 430 researcher months to reach the project objectives.

Two final prototypes are foreseen from this project:

- prototype of robust, multifunctional graphene-based polymer nanocomposite, suitable for 3D printing application;
- prototype of 3D printed cellular structures with tunable properties, fabricated with the graphene-based nanocomposite, having potential for application in power electronics.

At the end of the project, a "Joint Laboratory on graphene-polymer research" will be created by the consortium partners with long-term implication.

Program - Tuesday 22 May 2018

08:30 Registration

09:15 Welcome

09:30 *2D and 3D structured nanocomposites containing carbon and magnetic nanoparticles for the efficient control of electromagnetic signals*
Yann Danlée and Raj Jaiswar, Ecole polytechnique de Louvain, Université Catholique de Louvain, Louvain-La-Neuve, Belgium

10:15 *Carbon based photonics crystals and electromagnetic tunable absorbers*
Polina Kuzhir, Institute for Nuclear Problem, Belarusian State University, Minsk, Belarus

11:00 Break

11:15 *Effect of graphene quality on its high-frequency electromagnetic properties*
Alesia Paddubskaya, Institute for Nuclear Problem, Belarusian State University, Minsk, Belarus

11:30 *Anisotropic composite materials based on carbon nanotubes for electromagnetic applications*
Alexander V. Okotrub, Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

12:30 Lunch

02:00 *The multiple roles of ionic liquids applied to polymer/2D-materials nanocomposites*
Ricardo Donato, Graphene and Nanomaterial Research Center, Sao Paulo, Brazil

02:45 *PLA/Graphene/MWCNT composites with improved electrical and thermal properties for 3D printing applications*
Evgeni Ivanov, NanoTechLab, Sofia, Bulgaria

03:30 *A state of art for 3D printing materials - Characterization of Black Magic produced by Graphene 3D Lab*
Marcello Casa, Narrando SRL, Salerno, Italy

03:45 Break

04:00 *Synergy effects in polymer composites with different nanocarbons*
Juras Banys, Department of Radiophysics, Vilnius University, Vilnus, Lithuania

05:00 Poster session

Program - Wednesday 23 May 2018

08:30 Welcome

09:00 *SLS 3D printing of flexible polymer materials*
Hesheng Xia, Sichuan University, China

09:45 *Electrically conductive filaments based on PLA reinforced with carbon nanoparticles for 3D printing applications*
Giovanni Spinelli, Department of Information, Electrical Engineering and Applied Mathematics, University of Salerno, Italy

10:00 *Nanocomposites for DLP 3D printing, from materials' engineering to materials' science*
Ignazio Roppolo, Department of Applied Science and Technology, Politecnico di Torino, Italy

10:45 Break

11:00 *Obtaining UV curable PDMS by hydrosilylation reaction*
Natia Jalagonia, Sokhumi Ilia Vekua Institute of Physics and Technology, Tbilisi, Georgia

11:45 *Rheology of polylactic acid composites filled with multi-walled carbon nanotubes and graphene nanoplates for 3D printing application*
Sonia S. Tabakova, Institute of Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria

12:15 *Rheology and processing of polymer nanocomposites with graphene and other 2D materials*
Ricardo J.E. Andrade, Graphene and Nanomaterial Research Center, Sao Paulo, Brazil

12:30 Closing

Abstracts
for
TALKS

2D AND 3D STRUCTURED NANOCOMPOSITES CONTAINING CARBON AND MAGNETIC NANOPARTICLES FOR THE EFFICIENT CONTROL OF ELECTROMAGNETIC SIGNALS

Christian Bailly(1), Isabelle Huynen(2), Yann Danlée(1)(2) and Rajkumar R. Jaiswar(2)

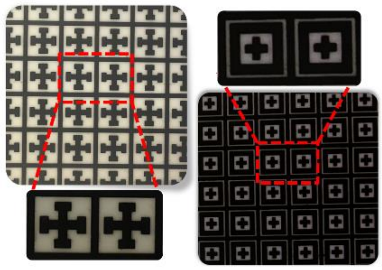
(1) Institute of Condensed Matter and Nanosciences, Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium

(2) Institute of Information and Communication Technologies, Electronics and Applied Mathematics, Place du Levant 3, 1348 Louvain-la-Neuve, Belgium

Classical electromagnetic interference (EMI) shielding is based on EM reflectors, but these devices do not solve the fundamental interference issue since the signal is simply reflected back to the environment without significant loss. We present novel ways to control the microwave propagation by absorption, polarisation or wave transmission thanks to the combined use and structuring of conductive and magnetic nanoparticles in a dispersing medium.

Nowadays, the dispersion of nanofillers in a polymer matrix is well managed, and the output electrical properties of the nanocomposites cover a wide range of conductivity depending on the percentage of carbon nanotubes (CNT), graphene nanoplatelets (GNP) or nanowires (NW)[1]. Those extremely conductive particles provide a high absorption index over a wide spectrum. The addition of a ferromagnetic component via magnetic nanowires or grafted magnetic nanoparticles (MNP) on nanocarbon[2] further pushes the absorption/thickness ratio close to the ultimate Rozanov's limit.

The structure of the absorber plays a significant role in the wave propagation control. A stack of thin composite layers in gradient of conductivity and/or magnetic permeability enhances broadband absorption[3]. The organisation of the fillers in a nanocomposite sheet opens avenues towards specific behaviour like polariser-absorber, twist polariser, frequency selective surface (FSS) etc. Many methods of nanofiller alignment have been experimented: the unidirectional alignment by stretching/squeezing, airbrushing of CNT striplines and printing of CNT ink on a polymer substrate. As an example, a homemade water-based solution of CNT or GNP has been prepared for impression of precise patterns (see picture). This conductive ink is used to draw resonant motifs and create a very efficient microwave filter reflecting or absorbing one narrow frequency band[4]. The resulting multilayers based on printed nanoparticles offer then a wide panel of EM properties.



References:

1. J.-M. Thomassin et al. "Polymer/carbon based composites as electromagnetic interference (EMI) shielding materials" Materials Science and Engineering: R: Reports 74.7 (2013): 211-232.

2. F. Mederos-Henry et al. "Decoration of nanocarbon solids with magnetite nanoparticles: towards microwave metamaterial absorbers" Journal of Materials Chemistry C 4.15 (2016): 3290-3303.

3. Y. Danlée et al. "Thin and flexible multilayer polymer composite structures for effective control of microwave electromagnetic absorption" Composites Science and Technology 100 (2014): 182-188.

4. R. Jaiswar et al. "A thin ultra-wideband microwave absorbing structure printed on flexible substrate with resistive-ink made of multiwall carbon-nanotube" Metamaterials conf. (2017).

Acknowledgements: The authors thank the Walloon region, the "Communauté Française de Belgique" and FNRS FRIA for supporting this work.

CARBON BASED PHOTONICS CRYSTALS AND ELECTROMAGNETIC TUNABLE ABSORBERS

D. Bychanok(1), K. Batrakov(1), A. Paddubskaya(1),
P. Kuzhir(1), A. Celzard(2), Ph. Lambin(3)

(1) Research Institute for Nuclear Problems BSU, 11 Bobruiskaya Str., 220030 Minsk, Belarus
(2) Institut Jean Lamour-UMR Université de Lorraine-CNRS 7198, ENSTIB, 27 rue Philippe Seguin, CS 60036,88026 EpinalCedex, France
(3) Namur University, Physics Department, 61, rue de Bruxelles – B – 5000 Namur, Belgium

Periodic structures with photonic band gap or "photonic crystals" have attracted the attention of many researchers due to their outstanding combination of physical properties. The appearance of the band structure of the spectrum, including the prohibited area (gap) due to Bragg scattering in the periodic perturbation − is well known wave phenomenon. Nevertheless construction of 3-dimensional periodic structures may be difficult due to technological problems. The modern 3D-printing technology with high spatial resolution offers many promising opportunities for creating of complex 3 dimensional periodic polymer structures. In contrast to classical photonic crystals [1], it is interesting to estimate electromagnetic properties of lossy periodic structures with carbon-containing skeleton with finite conductivity.

Two classes of carbon-based periodic structures made by 3D-printing that could possess high absorption ability of electromagnetic radiation and resonance behavior in microwave-THz frequency ranges are discussed:

(i) Carbon based reticulated photonic crystals made by 3D-printed techniques (see e.g. [2]).
(ii) 3D printed sandwiches [3] and other 3D structures of sophisticated geometries made from a nanocarbon polymer composite fiber.

The peculiarities of EM response of both carbon-based materials are investigated; the advantages of each type of carbon structures along with CVD graphene/polymer sandwiches [4] and metasurfaces depending on particular application are emphasized.

References:
1. *E. Yablonovitch, JOSA B 10, 283 (1993).*
2. *A. Szczurek; A. Ortona; L. Ferrari; E. Rezaei; G. Medjahdi; V. Fierro; D. Bychanok; P. Kuzhir; A. Celzard, Carbon,* ***88****, 70 (2015)*
3. *A. Paddubskaya, N. Valynets, P. Kuzhir, K. Batrakov, S. Maksimenko, R.Kotsilkova, H. Velichkova, I. Petrova, I. Biró, K. Kertész, G. I. Márk, Z. E. Horváth, L. P. Biró, Journal of Applied Physics,* ***119****, 135102 (2016)*
4. *K. Batrakov, P. Kuzhir, S. Maksimenko, A. Paddubskaya, S. Voronovich, Ph Lambin, T. Kaplas and Yu Svirko, Scientific Reports,* ***4****,Article number:7191 (2014)*

Acknowledgements: This work was supported by Projects FP7-PEOPLE-2013-IRSES-610875 NAmiceMC H2020-MSCA-RISE-2016-734164 Graphene 3D.

EFFECT OF GRAPHENE QUALITY ON ITS HIGH-FREQUENCY ELECTROMAGNETIC PROPERTIES

A. Paddubskaya(1), K. Batrakov(1), P. Kuzhir(1), T. Kaplas(2), Y. Svirko(2), N. Reckinger(3),M. Lobert(3), O. Deparis(3), Ph. Lambin(3)

(1) Laboratory of NanoElectroMagnetics, Institute for Nuclear Problems of Belarusian State University, Bobruiskaya str. 11, 220030 Minsk, Belarus
(2)Department of Physics and Mathematics, University of Eastern Finland, Joensuu FI-80101, Finland
(3) Department of Physics, Université de Namur,61 Rue de Bruxelles, B-5000 Namur, Belgium

The CVD technique is the most promising approach for large-scale production of single- or few-layer graphene. But typically CVD graphene films have a polycrystalline structure with high density of graphene/grain boundaries resulting to variable transport, thermal and electronic properties [1]. In this context, understanding the influence of the graphene structure is not only a fundamental problem, but is also technologically important for future development of various graphene-based devices [2].

In this communication, the influence of average graphene grain size and boundaries width on the global electromagnetic properties of a graphene film has been investigated at high frequency range (from microwave up to several THz). In particular, the Rigorous Coupled Wave analysis (RCWA) method has been applied to analyze theoretically the influence of the graphene structure on the electromagnetic response of graphene films as well as graphene-based multilayers. The mean free path of electrons in graphene under high-frequency EM wave being small (~ 100 nm) as compared with a typical grain size of CVD graphene (several tens μm), the grains hardly affect the overall electromagnetic response of the graphene-based systems. From the experimental point of view, samples of CVD graphene with two grain sizes (~20 μm and ~ 400 μm) were synthesized. The results obtained experimental in the microwave and THz frequency ranges correlate well with theoretical simulations. To investigate the effects of grain boundary width on the total EM response of graphene, the measurements of THz transmittance spectra *versus* applied mechanical strain (up to 40%) were carried out. It has been shown that, in spite of the formation of high-density cracks, which are clearly seen by optical microscope under strain >10%, the effective ac-conductivity of graphene-based films doesn't change significantly. The weak sensitivity of CVD graphene EM properties on microstructure opens a new possibility for future development strain-tunable graphene-based devices operated at high frequency range.

References:
1. H. Zhou *et al*, Nat. Commun. 4, 2096 (2013).
2. T. Ma *et al*, Nat. Commun. 8, 14486 (2017)

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

ANISOTROPIC COMPOSITE MATERIALS BASED ON CARBON NANOTUBES FOR ELECTROMAGNETIC APPLICATIONS

A.V. Okotrub(1), O.V. Sedel'nikova(1) and L.G. Bulusheva(1)

(1) Nikolaev Institute of Inorganic Chemistry SB RAS,
pr. Lavrenteva, 3. Novosibirsk, 630090, Russia

Composite materials based on polymers matrix with various nanocarbon inclusions are promising materials for electromagnetic shielding. Electromagnetic characteristics of composite are governed by many factors, such as geometry, length, defectiveness, concentration and orientation of filler in the matrix. Arrays of aligned MWCNTs were synthesized on silicon substrates by CVD method in the reaction of catalytic thermolysis of ferrocene/toluene mixtures. Polystyrene/iron-filled MWNT composite films were prepared by solution processing, forge-rolling and stretching methods. Effect of fabrication on the structure of obtained carbon filler/polymer composite was discussed. The efficiency of stretching and forge-rolling for anisotropic composite production was demonstrated [1, 2]. Magnetic susceptibility measurements as well as records of isothermal hysteresis loops performed in three perpendicular directions of magnetic field confirmed that the nanotubes have a preferential alignment in the matrix. Strong diamagnetic anisotropy in the composites emerges not only from the MWCNTs but also from the polystyrene matrix. The polymer sticks to the honeycomb lattice through the interaction of the π-orbitals of the phenyl ring and those of the carbon nanotube, contributing to anisotropic diamagnetic response [3]. The contribution of iron nanoparticles to overall magnetic response strongly depends on nanotube concentration in the composite as well as on matrix-filler non-covalent stacking, which influences magnetic interparticle interactions. Interface interactions in multicomponent nanoparticles can affect electromagnetic properties of an absorbing system. We investigate the electromagnetic response of MWCNTs filled with iron-containing nanoparticles (ICNs) in the terahertz frequency range. Thin composite films were prepared from the iron-filled MWCNTs and polymethylmethacrylate (PMMA) by casting and stretching methods. The composites showed an enhanced permittivity and anisotropy in the transmittance spectra when iron content increased [4]. This behaviour was related to the mechanism based on electrical conductivity and polarization of ICNs and ICN/MWCNT interfaces. Since terahertz field penetrates inside MWCNTs, the filling of their cavities can be a way of varying the electromagnetic properties of MWCNT-containing composites.

References:
1. A.V. Okotrub et al, Phys. Status Solidi B 248 (2011) 2568-2571.
2. N.R. Arutyunyan et al, Laser Physics Letters 13 (2016) N 065901.
3. T.L. Makarova et al,Carbon 96 (2016) 1077-1083.
4. O.V. Sedelnikova et al,Nanotechnology 29 (2018) N 174003.

THE MULTIPLE ROLES OF IONIC LIQUIDS APPLIED TO POLYMER/2D-MATERIALS NANOCOMPOSITES

A.P. Godoy(1), K.Z. Donato(1) and R.K. Donato(1)

(1) MackGraphe (Graphene and Nano-Material Research Center), Mackenzie Presbyterian University, Rua da Consolação 896, São Paulo - SP - 01302-907 - Brasil

Ionic liquids (ILs) are organic salts with low melting points that are often liquid at room temperature and present several intrinsic properties, e.g., low volatility, high thermal and chemical stability, insignificant flammability, good thermal conductivity, high ionic mobility and moisture resistance. The imidazolium based IL present, besides the previous mentioned properties, a strong affinity with carbon based materials. A "π– π stacking" of the IL cations at the π-electronic surface of the sp2 carbon network allows it to act as both a solvent and a surfactant due to the IL's amphiphilic structure.[1] These features make IL ideal for exfoliating/stabilizing graphene through a solution irradiation process, allowing much broader experimental conditions in comparison to the usual organic solvents.

This approach allows functions such as unrolling and dispersing MWCNT or the direct exfoliation of graphite ore into few-layers graphene sheets.[2]

Recently, the application of ILs or their polymerized species (PILs) has also shown promising results for structural and properties control of nanocomposites. They allow stable dispersions of several different 2D-materials, such as grapheme, hBN and MoS2, and their combinations directly into polymeric systems.[3] These materials can be assembled into complex nano-engineered composites presenting very desirable properties such as thermal/electrical conductivity, non-flamability, sensing, responding and actuating.

Thus, this presentation will give an overview about the many different tasks that ILs/PILs can assume when applied into 2D materials exfoliation. Moreover, applications where the IL-2D materials are further applied into polymer matrices, forming nanocomposites with properties strongly influenced by these ionic additives, will be presented.

References:

1. *R. D. Rogers, Nature, 2007, 447, 917; T. Fukushima and T. Aida, Chem.–Eur. J., 2007, 13, 5048.*
2. *A. C. Kleinschmidt, R. K. Donato, et al. RSC Adv., 2014, 4, 43436; H. Benes, R. K. Donato, et al. RSC Adv., 2016, 6, 6008.*
3. *X. Wang and P. Wu ACS Appl. Mater. Interfaces, 2018, 10,2504.*

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D and MackPesquisa 2017.

PLA/GRAPHENE/MWCNT COMPOSITES WITH IMPROVED ELECTRICAL AND THERMAL PROPERTIES FOR 3D PRINTING APPLICATIONS

E. Ivanov(1,2), R. Kotsilkova(2), H. Xia(3), Y. Chen(3), R. K. Donato(4), K. Z. Donato(4), A. P. Godou(4), C. Silvestre(5), S. Cimmino(5), R. Di Maio(5)

(1) Research and Development of Nanomaterials and Nanotechnologies (NanoTech Lab Ltd.), Acad. G. Bonchev Str. Block 4, 1113 Sofia, Bulgaria
(2) Open Laboratory on Experimental Micro and Nano Mechanics (OLEM), Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Block 4, 1113 Sofia, Bulgaria
(3) State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China
(4) MackGraphe - Graphene and Nanomaterials Research Center, Mackenzie Presbyterian University, Rua da Consolação 896, São Paulo 01302-907, SP Brazil
(5) Istituto per i Polimeri, Compositi e Biomateriali (IPCB), Consiglio Nazionale delle Ricerche (CNR), Via Campi Flegrei 34 Olivetti, 80078 Pozzuoli (NA), Italy

The main idea of this study was investigation of the effect of filler concentrations and various combinations of GNP and MWCNT on the electrical and thermal conductivity of nanocomposites. The PLA polymer was doped with low cost industrial graphene and multiwall carbon nanotubes. The electrical and thermal properties of as prepared composites were examined as well as the dispersion of nanofillers in polymer matrix was investigated by scanning electron microscopy (SEM) and Raman. These graphene-polymer composites were further extruded into 1.75 mm diameter filaments to fit the needs of commercialized 3D printers of composite filament with improved electrical and thermal properties.

Generally, the results show that at maximum filler content (6 wt%) electrical conductivity increases with almost 7-8 decades for the mono-filler systems with GNP and MWCNT compared with pure PLA but this effect is more pronounced for PLA/MWCNT composites. On the other hand, some of the bi-filler composites with PLA/MWCNT/GNP shows a synergetic effect on electrical conductivity with the values higher than these obtained for the maximum filler content of 6 wt% for the mono-filler systems. Thermal conductivity and diffusivity of GNP nanocomposites were improved by addition of graphene nanoplatelets by 181 % and 214 %, respectively.

The results indicate that there is a close relationship between the electrical and thermal properties with the morphology of the as prepared nanocomposites. As the graphene or MWCNTs loading kept growing, a continuous and denser network was formed in the polymer matrix. Composites with more MWCNT fillers showed higher electrical conductivity, while the composites with higher content of GNP showed higher thermal conductivity. These graphene-polymer composites were further extruded into 1.75 mm diameter filaments to fit the commercialized 3D printer. This work was done during the secondments of the first author within the frame of Graphene 3D project.

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

A STATE OF ART FOR 3D PRINTING MATERIALS CHARACTERIZATION OF BLACK MAGIC PRODUCED BY GRAPHENE 3D LAB

M. Casa(1), M. Sarno(1), A. Paddubskaya(2),P. Kuzhir(2), P. Lamberti (3), G. Spinelli(3), P. Ciambelli(1)

(1) Narrando srl, Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy

(2) Research Institute for Nuclear Problems, Belarusian State University, Bobruiskaya Str. 11,220030 Minsk, Belarus,

(3) Università degli Studi di Salerno,Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy

3D printing creates bottom - up three-dimensional objects by adding material layer by layer, through the so-called Additive Manufacturing (AM), recognized as a disruptive technology for a wide variety of applications. However, despite great effort and significant progress made in AM, technical challenges still remain, and the material selection has been identified as one of the key barriers for current AM processes and machines. The majority of materials used by current AM techniques are polymers, though some metal or ceramic materials are used in some high-end machines [1]. The weak mechanical and electrical property of the polymers and poor surface quality of the metal parts has hindered a wider progress of AM technology. Paralleling the development of AM technology during the past decade, significant efforts have also been devoted to the development of polymer nanocomposites. By incorporating nanoparticles into polymers, the nanocomposites exhibit improved mechanical, thermal, electromagnetic and other properties [2]. Several fillers such as nanocarbons, fillosilicate, silica, and titania nanoparticles have been proposed to enhance the mechanical and thermal properties of materials for additive manufacturing printers, i.e. FDM and SLS technology.
Since 3D printing is an emerging technology and relevant materialsare still under study, only few companies have already launched nanocarbon-based materials on the market.Graphene 3D lab, Proto Plant and Directa plus have developed these type of exotic material using nanotechnology to improve the properties of printable polymer. In particular Graphene 3D lab claims that its graphene¬enabled 3D printing materials, the so-called Black Magic, set the record for the lowest electrical resistivity. For these reasons and aiming at setting a target reference material, a careful carachterization of Black Magic was carried out, by Raman Spectroscopy, XRD, Infra-Red spectroscopy, TGA, DSC, and SEM. Moreover, the electrical properties and electromagnetic response of the material in the GHz and THz range were measured.

References:
1. Additive Manufacturing Technologies - 3D Printing, Rapid, Ian Gibson, Springer
2. Lin, D. et al. Three-Dimensional Printing of Complex Structures: Man Made or toward Nature? ACS Nano 8, 9710–9715 (2014).

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application

SYNERGY EFFECTS IN POLYMER COMPOSITES WITH DIFFERENT NANOCARBONS

J. Banys[1], J. Macutkevic[1], I. Kranauskaite[1], N. Nunn[2], O. Shenderova[2]

(1) University of Vilnius, Sauletekio al. 9, LT-00122 Vilnius, Lithuania,

(2) International Technology Center, Raleigh, NC 27715, USA

Nowadays, investigations of electrically percolative polymer-based composites with various nanocarbon inclusions are very popular due their wonderfull electric, electromagnetic, mechanical and thermal properties in comparison with net polymer matrix properties. Many investigations of such composites were performed in narrow frequency range and at room temperature in order to find so called percolation threshold (minimal concentration of nanofillers at which composites are conductive). One important task is to reach as low as possible percolation threshold in order to preserve or reach optimal mechanical properties of polymers and to use minimal concentration of expensive fillers. The lowest percolation threshold was observed in carbon nanotubes (CNT) composites due to their high aspect ratio. However, CNTs usually exhibit the large agglomerates in polymer matrix because of the high van der Waals force between CNTs, leading to the increase of percolation threshold. Therefore, the percolation threshold in nominaly the same polymer matrix and for the same CNT can very significantly. Moreover, the percolation threshold in other composites, for example in carbon black composites, can be also very low. Thus investigations of composites with other less expensive inclusions are very promissing. Onion-like carbon (OLC), consisting of stable defected multishell fullerenes, exhibit high conductivity similar to CNT. In this work we will present results of broadband dielectric investigations of OLC/CNT mixed composites in wide temperature range (from 20 K to 500 K). It was established that the percolation threshold sustainable decrease in OLC composites after addition of small amount of carbon nanotubes, so it is observed significant synergy effect. This is due favourable distribution of OLC and carbon nanotubes CNT clusters inside composite (confirmed by electron microscope investigations), so that the electrical transport occurs in both networks simultaneously. Above percolation threshold electrical conductivity occurs mainly via electron tunneling between OLC and CNT clusters, while at higher temperatures (above matrix glass transition temperature) transport in polymer matrix is also very important. At low temperatures (below 200 K) electrical conductivity in all investigated composites follows tunneling model law. Both potential barrier height and mean distance between carbon particles decreases after addition of small amount of carbon nanotubes. These results demonstrate the potential of OLC/CNT based percolative composite for use as highly dielectric and conductive material in electronic applications.

SLS 3D PRINTING OF FLEXIBLE POLYMER MATERIALS

H.S. Xia[(1)], M. Lavorgna[(2)], X.P. Gan[(1)], G.X. Fei[(1)], Z.H. Wang[(1)]
(1) State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute Sichuan University, Chengdu 610065, China
(2) Institute of Polymers, Composites and Biomaterials, National Research Council, P.le Fermi, 1-80055 Portici, Italy

Selective laser sintering (SLS) 3D printing can directly turn complex 3D models into real objects. The flexible thermoplastic polyurethane (TPU) and polydimethylsiloxane (PDMS) powder was prepared and optimized for SLS 3D printing. Also the flexible TPU and PDMS conductor was prepared by 3D printing using self-made carbon nanotubes (CNTs) wrapped polymer powders. The SLS printing, as a shear-free and free-flowing processing without compacting, provides a unique approach to construct conductive segregated networks of carbon nanotubes in the polymer matrix. The electrical conductivity for the SLS 3D printed flexible CNTs/elastomer composite specimen reached 10^{-1} S/m at 1 wt% CNTs content, which is seven orders of magnitude higher than that of conventional injection-molded CNTs/polymer composites at the same CNTs content. And it had a percolation threshold of 0.2 wt%, much lower than those prepared by conventional pressing and injection molding. The 3D printed CNTs/elastomer specimen could maintain good flexibility and durability, even after repeated bending for 1000 cycles, the electrical resistance can keep at a nearly constant value. The flexible conductive CNTs/elastomer composite articles with complicated structures and shapes like porous piezoresistors can be easily obtained by this approach.

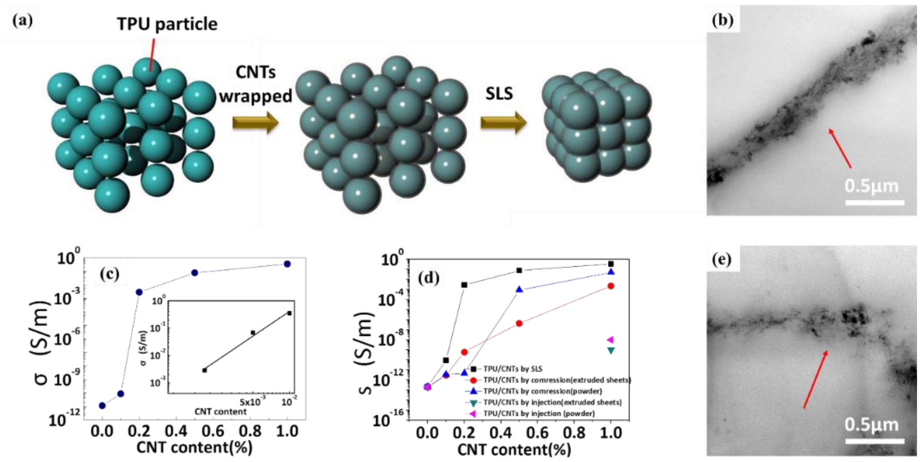


Fig 1. Preparation, structure and conductive properties of TPU/CNTs composites by SLS

References:
1. Z.C. Li, Z.H. Wang, X.P. Gan, D.H. Fu, G.X. Fei, H.S. Xia, **Macromol. Mater. Eng**. 2017, 302, 1700211.*
2. J. Zhao, R. Xu, G.X. Luo, J. Wu, H.S. Xia*, **J. Mater. Chem**. B, 2016, 4, 982*
*3. W.L. Pu, D.H. Fu, Z.H. Wang, X.P. Gan, X.L. Lu, L. Yang, H.S. Xia, **Adv. Sci.** 2018, 1800101*

Acknowledgements: This work was supported by the project of National Science Foundation of China (51433006) and the Project H2020-MSCA-RISE-2016-734164 (Graphene 3D).

H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application

ELECTRICALLY CONDUCTIVE FILAMENTS BASED ON PLA REINFORCED WITH CARBON NANOPARTICLES FOR 3D PRINTING APPLICATIONS

G. Spinelli(1), P. Lamberti(1), R. Raimo(1), V. Tucci(1), R. Kotsilkova[2] and E. Ivanov[2,3]

(1) Department of Information and Electrical Engineering and Applied Mathematics, University of Salerno Via Giovanni Paolo II, Fisciano (SA) ITALY,

(2) Open Laboratory on Experimental Micro and Nano Mechanics, Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 4, Sofia, Bulgaria

(3) Research and Development of Nanomaterials and Nanotechnologies (NanoTech Lab Ltd.) Acad. G. Bonchev Str. Block 1, 1113 Sofia, Bulgaria

Currently, the improved availability of reliable and precise 3D printers has made 3D printing technology, aka additive manufacturing (AM), an increasingly cost-effective solution in different areas of research and development for the manufacturing of customized, multifunctional and complex 3D objects which are obtained layer by layer driven by computer-aided design (CAD) specifications [1]. More recently, the full potential of 3D printing can be exploited thanks to the remarkable advances due to introduction of nanotechnology in the AM field that offers a higher degree of customization leading also toward printing of electrically conductive structures.
Among the different additive manufacturing approaches, fused deposition modeling (FDM) seem to be one of the most promising being clean, simple-to-use and office-friendly although it is limited by the fact that its feedstock is a common thermoplastic polymer filament such as PLA, ABS, PET and nylon. The goal of the authors is to propose a non-conventional polymer nanocomposites, suitable for 3D printing applications, in which nanostructures, i.e. multi-walled carbon nanotubes (MWCNTs), graphene nanoplates (GNPs) and a combination of both fillers (MWCNTs/GNPs) are incorporated into Polylactic acid (PLA, Ingeo™ 3D850) as an attempt to overcome several limitations over traditional 3D manufacturing based on insulating materials. Overall, this study provides the results regarding an extensive electrical characterization carried out on the proposed formulations in order to support their concrete applicability thus paving the way for the design and fabrication of 3D printable conductive parts. This work was done during the secondments of the first author within the frame of Graphene 3D project.

References:
1. *Wei Gaoa et al. "The status, challenges, and future of additive manufacturing in Engineering", Computer-Aided Design 69 (2015) 65–89*
2. *R. Kotsilkova, Thermosetting nanocomposites for engineering application. Smithers Rapra Technology, UK, 2007.*

Acknowledgements: This work was carried out within the framework of the Marie Skłodowska-Curie Actions (MSCA) Research and Innovation Staff Exchange (RISE) H2020-MSCA-RISE-2016-734164 Graphene 3D.

H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application

NANOCOMPOSITES FOR DLP 3D PRINTING FROM MATERIALS ENGINEERING TO MATERIALS SCIENCE

I. Roppolo[(1)]

(1) Department of Applied Science and Technology, Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129, Torino, Italy

In the last years, 3D Printing (3DP) is increasing its importance both in science and in industrial applications due to the peculiar properties and manifolds advantages that the technologies that are included under this umbrella terms can offer.[1] Without going into details for each technology, it is implied the possibility to produce components with shapes impossible to obtain by classical subtractive manufacturing, saving at the same time both raw materials and energy.[2, 3]. Among polymeric 3D printing processes, light-based technologies (SLA and DLP) are generally known for being the fastest and most precise. However their main drawback consists in the limited palette of available printable materials, which restrict the possible applications.

Aiming to widen the range of printable materials for DLP, here we will show different strategies for producing 3D printable nanocomposites developed in our laboratories (Figure 1). The idea beyond consists in imparting improved mechanical properties or new functionalities to the printed objects maintaining at the same time a good printability. In this context we will show that a classical direct dispersion of fillers in a photocurable formulation followed by the optimization of printing parameters (what we call “the materials’ engineering approach”) could be overcome by an appropriate design of the photocurable mixture, adding a bit of materials’ science and chemistry. This allows to obtain objects with peculiar properties saving a high printability.

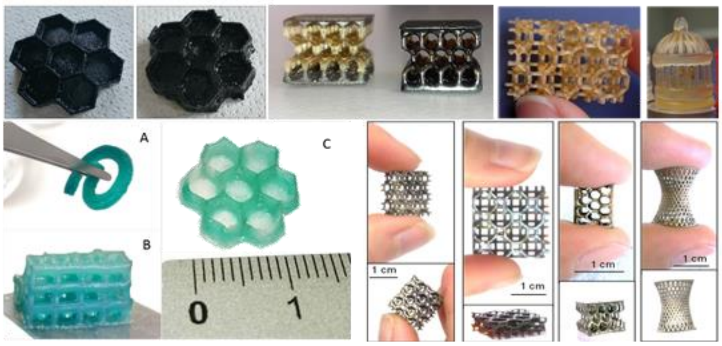


Figure 1 Different nanocomposites printed in our Labs

References:
1. T.A. Campbell, O.S. Ivanova, 3D printing of multifunctional nanocomposites, Nano Today, Vol. 8, 2013, 119-120.
2. F.P.W. Melchels, J. Feijen, D.W. Grijpma, A review on stereolithography and its applications in biomedical engineering, Biomaterials, Vol. 31, 2010, 6121-6130.
3. R.D. Farahani, M. Dubé, D. Therriault, Three-Dimensional Printing of Multifunctional Nanocomposites: Manufacturing Techniques and Applications, Advanced Materials, Vol. 28, 2016, 5794-5821.

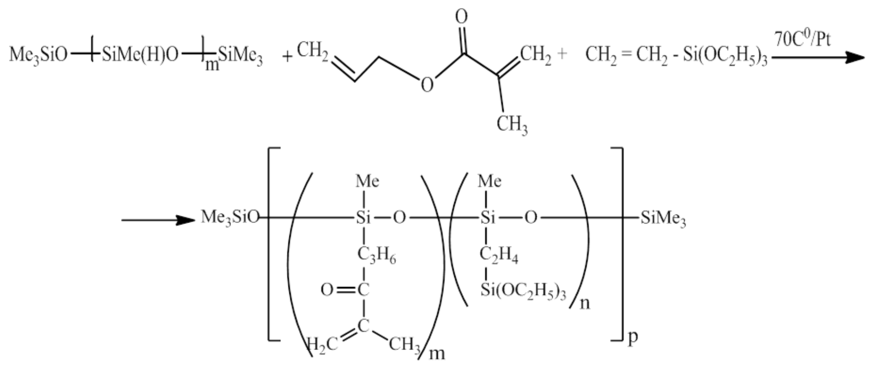
OBTAINING UV CURABLE PDMS BY HYDROSILYLATION REACTION

N. Jalagonia(1), N. Darakhvelidze(1), L. Kalatozishvili (1), A. Sichinava (1) P. Angelova(2) and E. Sanaia(1)

(1) Ilia Vekua Sokhumi Institute of Physics and Technology,
7 Mindeli str., Tbilisi, Georgia
(2) Open Laboratory on Experimental Micro and Nano Mechanics, Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 4, Sofia, Bulgaria

Photopolymers are light sensitive polymeric materials, which changes their physical or chemical properties by sources. They can change liquid substance to solid plastic like substance. These polymers are using in several printing technologies such as inkjet printing, Stereolithography (SLA) technology and other. Elastomer based on polydimethysiloxanes (PDMS) are important class of materials, because of properties such as chemical inertness, flexibility, optical transparence, also they have a very low surface tension (20.4 mN/m) and glass transition temperatures (146 K). It is possible to print a support material that holds the PDMS prepolymer in place until it can be cured by UV light using a photoactive cross-linking agent. It is possible to graft photoactive group on PDMS backbone and obtain new UV curable polymer [1-2]. It is known in the literature, those carbon nanostructures into various polymer gives totally new properties to obtain composite.

The aim of presented work is obtaining of photopolymers based on PDMS [3]. For purpose, we have conducted hydrosilylation reaction of polymethylhydrosiloxane (PMHS) with allyl acrylate and vinyltriethoxysilane in the presence Karstedt's catalyst in Toluene. Obtained polymer is liquid which are well soluble in organic solvents with specific viscosity $\eta_{sp} \approx 0.4$. The end of reaction was tested by FTIR, where peak at 1260 cm^{-1} disappears which belongs to Si-H bonds. After this the polymer distilled in vacuum, cross-linking agent was add about 1 % and curried by UV during 1 h.



Scheme 1. Hydrosilylation reaction of PMHS, Allyl metacrylate and vinyltrietoxysilane

Second step is addition of photoinitiator which is dissolved in monomer and reduced graphene oxide. Nanocompmosite has obtained by solution mixing method.Then polymer surface was treated by Ar and curing by UV during 2-3 h. Obtained curried polymers were studied by SEM, optical microscope, FTIR, ^{1}H NMR spectra data, DSC, TGA, DMTA.

References

[1] J. T. Sheridan, Photopolymers Materials (Light Sensitive Organic Materials): Characterization and Application to 3D Optical Fabrication and Data Storage. [Online] Available at: http://www.ucd.ie/t4cms/Photopolymers%20Materials_%20Characterization%20and %20Application%20to%203D%20Optical%20Fabrication%20and%20Data%20Stora ge.pdf. [Accessed: 07.10.2013].
[2] B. Thavornyutikarn, R. Nonthabenjawan, P. Ngamdee, W. Janvikul. Synthesis, Characterization and Crosslinking of Dual-Curable Siloxane Copolymers. Journal of Metals, Materials and Minerals. 18, 2, 213-218, 2008.
[3] *N. Jalagonia, I. Esartia, T. Tatrishvili, E. Markarashvili, J. Aneli, O. Mukbaniani. Siloxane matrix with methylpropionate side groups and polymer electrolyter membranes on their basis. Oxid. Commun., 39, 2, 1282-1292, 2016;*

Acknowledgments: This work was supported by the H2020 MCA RISE project "Graphene-3d", Grant No. 734164, funded by the European Union.

H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application

RHEOLOGY OF POLYLACTIC ACID COMPOSITES FILLED WITH MULTI-WALLED CARBON NANOTUBES AND GRAPHENE NANOPLATES FOR 3D PRINTING APPLICATION

Rumiana Kotsilkova[a], Sonia Tabakova[a], Evgeni Ivanov[a,b], Radost Ivanova[a], Clara Silvestre[c], Rosa Di Maio[c]

[a]*OLEM, Department of Fluid Mechanics, Institute of Mechanics, BAS, Sofia, Bulgaria,*

[b]*NanoTech Lab Ltd., Institute of Mechanics, BAS, Sofia, Bulgaria,*

[c]*Instituto per i Polimeri, Compositi e Biomateriali, CNR, Napoli, Italy*

The materials used for the 3D printing must possess appropriate properties connected with the stability of the jet produced during the fused-deposition modelling (FDM). In this work two types of nanocomposites together with a neat polylactic acid (PLA) have been analysed: two mono-filler systems, graphene nanoplates (GNP)/PLA and multiwall carbon nanotubes (MWCNT)/PLA and bi-filler system GNP/MWCNT/PLA nanocomposites with the filler contents varying from 0 to 12 wt%. The rheological behaviour in steady and oscillatory flows has been studied at constant temperature above the melting point.

The steady experiments show that all the composites up to 6 wt% GNP/PLA have a generalized Newtonian flow behavior similar for that of the matrix PLA, whose viscosity is well described by the Carreau viscosity model. However, the 9 – 12 wt% GNP/PLA composites and all the composites MWCNT/PLA represent pseudo-plastic flow behaviour. This change in the rheological behaviour of the different composites is related to the rheological percolation threshold, determined by the oscillatory experiment. It occurs that the nanocomposites MWCNT/PLA show the lowest percolation threshold, which can be referred to the particle size and shape dependence, i.e., the GNP nanoplates form much stronger network in the PLA matrix than that of the MWCNT nanotubes.

The printability windows of the shear rate ($\dot{\gamma}$)/stress (τ) diagrams for each material are constructed, based on the power law relation $\tau = \alpha\dot{\gamma}^n$. The lowest value of *n*is achieved in the bi-filler system 3%GNP/9%MWCNT/PLA,associated with the highest degree of dispersion. Obviously, this combination gives the best dispersion as an optimal interpenetration between both nanofillers, leading to a strong network structure of nanofillers in the polymer.

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

RHEOLOGY AND PROCESSING OF POLYMER NANOCOMPOSITES WITH GRAPHENE AND OTHER 2D MATERIALS

L. G. Amurin [1], Y. D. C. de Oliveira[1], P. A. R. Múnoz[1], C. L.C. Rodriguez [1], G. J. M. Fechine[1], R. J. E. Andrade [1*]

(1) Graphene and Nanomaterials Research Center, Mackenzie Prebyterian University, São Paulo, Brazil.

Bi-dimensional (2D) nanomaterials became of great interest, scientific and technologically, due to their unique properties, after graphene was isolated in 2004. These unique properties make them extremely appealing to process polymer nanocomposites, due to their polymer-nanofiller interactions. These nanocomposites have been found to possess promising properties such as mechanical, barrier, thermal, and electrical. These properties are advantageous for applications in the field of 3D printing among others. Between the different methodologies of incorporate 2D nanofillers in a polymer matrix, melt blending is usually the most economical and industrial approach when compared with others. However, the effective reinforcement of polymers is still a challenge due to the poor dispersion and the strong interfacial adhesion between the nanofiller and the polymeric matrix. In this study, we used different strategies to disperse 2D materials into polymer matrix by using a twin screw extruder. The influence of the methods, processing parameters, particles concentration, level of particles dispersion and polymer nanocomposite properties were evaluated with the aim to understand the thermodynamics and the physical-chemical interactions that are involved in the mixing and dispersion process, with special attention to the rheological properties. Actually, it was observed these particles have a significant influence depending on their preparation and pre-exfoliation, which influences the nanocomposites rheological behavior.

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene, from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), grants 2014/22840-3 and 2012/50259-8. P.A.R.M. and L. G. A. are supported by a fellowship from FAPESP, 2015/16591-3 and 2017/07244-3, respectively. This work was also partially funded by Fundo Mackenzie de Pesquisa (MackPesquisa).

Abstracts for POSTERS

DIELECTRIC/ELECTRICAL PROPERTIES OF GRAPHITE, MWCNT AND HYBRID MWCNT/GNP COMPOSITES

I. Kranauskaite(1*), J. Macutkevic(1), A. Borisova(2), A. Martone(3), M. Zarrelli(3), A. Aniskevich(2), V. L. Kuznetsov(4), S. I. Moseenkov(4), V. Fierro(5), A. Celzard(5), and J. Banys(1)

(1) Vilnius University, Physics Faculty, Radiophysics Department, Vilnius, Lithuania
(2) Institute of Polymer Mechanics, University of Latvia, Riga, Latvia
(3) Institute for Composite and Biomedical Materials, National Research Council, Portici, Italy
(4) Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
(5) IJL – UMR Université de Lorraine – CNRS 7198, ENSTIB, Épinal, France
**Corresponding author: ieva.kranauskaite@ff.vu.lt*

Polymer composites with various carbon inclusions like multiwalled carbon nanotubes (MWCNT), graphite or graphene are interesting for fundamental reseach and are attractive for various applications [1]. The electrical percolation threshold of these composites could be very low and it is important to obtain as low percolation threshold as possible in order to reach optimal mechanical properties of composites and to use minimal concentration of expensive fillers. Adding several different fillers in the matrix the percolation threshold can decrease in comparison with single filler composites due to synergy effect between the different components [2].

In this contribution the dielectric/electrical properties of composites filled with different fillers were investigated: graphite filler (concentration 0-2 wt.%), MWCNT filler (0-4 wt.%), hybrid MWCNT/GNP filler (total concentration 0.3 wt.%). The measurements were performed in frequency range from 20 Hz to 3 GHz at room temperature and at low frequencies (20 Hz – 1 MHz) in temperature range from 30 K to 300 K. The percolation threshold for graphite composites is high except exfoliated graphite for which percolation threshold is similar to MWCNT composites. Combining two types of carbon fillers MWCNT and GNP the quantitative synergy effect on the material electrical conductivity was obtained.

In this presentation the results of dielectric/electrical investigations of polymer composites filled with different fillers will be presented, compared and discussed in wide frequency and temperature range.

References:
[1] W. Bauhofer, J. Z. Kovacs, Composite science and technology 69, 1486 (2009).
[2] J. Chen, X. Ch. Du, W. B. Zhang, J. H. Yang, N. Zhang, T. Huang, Y. Wang, Composite science and technology 81, 1-8 (2013).

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application

CONTRIBUTION OF NANOTECHLAB LTD. TO GRAPHENE 3D PROJECT FOR PRODUCTION OF GRAPHENE-BASED NANOCOMPOSITES, FILAMENTS AND 3D PRINTING OF TEST SAMPLES

V. Georgiev(1), E. Ivanov(1), C. Silvestre(2), S. Cimmino(2), R. Di Maio(2) and R. Kotsilkova(3)

(1) NanoTechLab Ltd., Acad. G. Bonchev str., Block. 4, 1113 Sofia, Bulgaria.
(2) IPCB/CNR, Campi Flegrei, 34 Pozzuoli, Napoli, Italy,
(3) Institute of Mechanics – Bulgarian Acad. Sc, Acad. G. Bonchev str., 1113 Sofia, Bulgaria

NanoTechLab Ltd. as a partner in "Graphene 3D" project contributes by obtaining the graphene containing polymer nancomposites, fabrication of filaments and 3D printing of model structures implementing our composites. Two- and three-component nanocomposite materials based on PLA, containing graphene nanoplatelets (GNP) and carbon nanotubes (CNT) have been produced so far. Compositions were obtained in collaboration with the laboratory of Dr. Silvestre, Institute of Polymers and Biopolymers, Pozzuoli, Italy. The materials were prepared with different concentrations of the individual components by the hot melt extrusion (HME) method. Two-component granular compositions containing from 1.5 to 9 wt% GNP or CNT and ternary in combination of GNP and CNT from 1.5 to 7.5 wt% were produced. For this purpose, a twin-screw extruder with temperature control in 5 zones was used. Benefits of HME include the absence of solvents, fewer processing steps, and lower manufacturing costs.

Thereafter, the resulting materials were subjected to extrusion for producing a 1.75 ± 0.05 mm diameter reinforced filament. The extrusion was carried out in the laboratory OLEM, Institute of Mechanics-BAS and NanoTechLab Ltd, by means of a single-screw extruder with control over 4 temperature zones and a nozzle with a diameter of 1.75 mm. Filaments were produced using all the composite materials under the following production conditions: barrel zones T_1-165 °C, T_2-170 °C, T_3-175 °C, T_4-170°C; screw speed 20 rpm; water temperature 60 °C.

The resulting filaments containing different amounts of nanofillers were used for 3D printing of model objects designed by Prof. Lambin, University of Namur, Belgium. We found out the following printing parameters as the most suitable for our models: nozzle temperature-205 °C; layer thickness-0.1 mm; printing speed 2500 mm/min; heated bed-70 °C; outline overlap 15%.

Since the project is in progress, further we are going to employ the composite filaments fabricated in Mackenzie university, Sao Paulo, Brazil, for 3d printing purposes. This work was done during the secondments of the first author within the frame of Graphene 3D project.

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

THE EFFECT OF GRAPHENE AND MWCNTS ON ELECTRICAL AND ELECTROMAGNETIC PROPERTIES OF PLA NANOCOMPOSITES PRODUCED BY SOLUTION BLENDING AND MELT EXTRUSION

P. Angelova[1], P.Kuzhir[2] , P.Lamberti[3]

(1) Open Laboratory on Experimental Micro and Nano Mechanics, Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 4, Sofia, Bulgaria
(2) Research Institute for Nuclear Problems, Belarusian State University, Bobruiskaya Str. 11, 220030 Minsk, Belarus
(3) Department of Information and Electrical Engineering and Applied Mathematics, University of Salerno, Italy

Nanocomposites with graphene (GNP) and MWCNTs (supplied by Times Nano, China) in polylactic acid (PLA), from Nature Works, USA were prepared by two different methods – solution blending (SB), at IMech-BAS, and melt extrusion (ME), at IPCB-CNR, Pozzuoli. Various formulations of monofiller composites (GNPs/PLA and MWCNT/PLA) and bi-filler composites GNP/MWCNT/PLA at filler contents 0-12 wt% were produced based on Robust Design pre-planning. Electromagnetic properties in GHz and THz wave range were measured at INP BSU, Minsk, and the electrical characterizations were performed at Narrando Srl, Salerno, in collaboration with UniSa.

It was found that in the microwave range, 32-33 GHz, the EMI absorption is ~ 33% for 6wt% MWCNT/PLA (ME) and ~ 38% for the 6wt% GNP/PLA (SB). In the THz wave range (0.3 THz), the GNP/PLA composites demonstrate much better absorption ability then the MWCNT/PLA. The higher aspect ratio of GNP and MWCNTs, the higher absorption is achieved for the nanocomposites. Interestingly, in the THz wave range the bi-filler composites of 6wt% GNP/MWCNT/PLA show very high EMI shielding efficiency (97-100%), with absorption ~ 49%, compared to the monofiller composites at 6wt% filler content.

The electrical percolation threshold was obtained at 1.5 wt% for MWCNT/PLA and above 6wt% for GNP/PLA composites. The bi-filler systems GNP/MWCNT/PLA show electrical percolation below 3 w%. While saturation seems to achieve at 9wt% and 12 wt% filler contents, where the electrical conductivity of nanocomposites achieves 1-2.6 S/m. This study aims to select appropriate formulations with high conductivity and EMI shielding for 3D printing application.

References:
1. *D Bychanok , P Angelova, A Paddubskaya, D Meisak, L Shashkova,M Demidenko, A Plyushch, E Ivanov, R Krastev, R Kotsilkova, F Y Ogrin and P Kuzhir. "Terahertz absorption in graphite nanoplatelets/polylactic acid composites", J. Phys. D: Appl. Phys, 2018) (in print)*

Acknowledgements: This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D, during the secondment of P. Angelova (ESR) from the Institute of Mechanics-BAS, to the INP BSU, Belarus Narrando Srl, Italy.

GRAPHENE 3D
H2020-MSCA-RISE 2016-734164
Multifunctional Graphene-based Nanocomposites with Robust Electromagnetic and Thermal Properties for 3D-printing Application
MARIE CURIE ACTIONS

SURFACE-MODIFIED 3D PRINTED ENVIRONMENT FOR CONTROL OF STEM CELL BEHAVIOR

L. Germain(1,2), A. des Rieux(1), C. Dupont-Gillain(2)

(1) Advanced Drug Delivery and Biomaterials, Louvain Drug Research Institute, Université catholique de Louvain, Brussel, Belgium
(2) Bio & Soft Matter, Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Louvain-la-Neuve, Belgium

Additive manufacturing techniques, commonly known as 3D printing, attract more and more interest in the field of tissue engineering. These low-cost and easy-to-implement techniques allow scaffolds with a tailored architecture to be produced, with a view to personalize grafts. Stem cells differentiation is known to be influenced, among others, by the physical environment provided by the substrate to which cells adhere. This project aims to study how a complex 3D-printed scaffold coated with a polymer with tunable mechanical properties impacts the behavior of adipose-derived mesenchymal stem cells (AMSC).

3D structures are built in poly(lactic acid) (PLA) by fused deposition modeling (FDM), according to a gyroid model. These scaffolds are then coated with a poly(dimethylsiloxane) (PDMS) layer, whose cross-linking level is varied to obtain different surface mechanical properties.

Printing conditions were optimized to obtain a match between the model and the printed scaffold (Fig.1a). Contrary to the orientation-dependent deformation of common strut-based scaffolds, gyroid scaffolds showed an isotropic behavior (Fig.1b). Degradation experiments showed that gyroid scaffolds maintained their integrity up to 52 weeks. PDMS presence was assessed through several experiments (selective dissolution, water contact angle measurements, X-ray photoelectron spectroscopy and electron microscopy). Ongoing work is centered on the characterization of the PDMS mechanical properties and on the study of AMSC behavior when grown on the scaffolds. Stem cells studies on such PDMS-coated scaffolds will bring new knowledge on the importance of surface mechanical properties in 3D environments suitable for tissue engineering approaches.

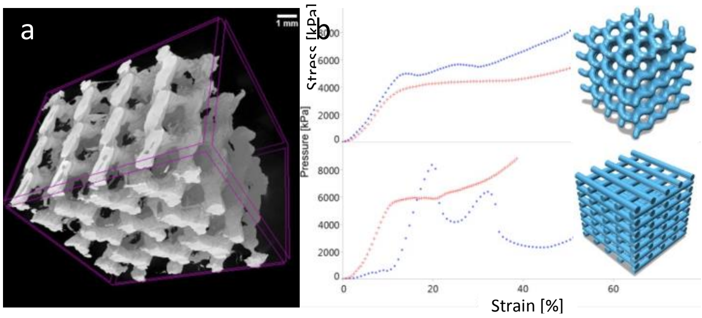


Figure 1:(a) Micro-CT scan of the gyroid sample and (b) stress-strain curves acquired in two perpendicular directions of (top) gyroid showing its isotropic behavior, and (bottom) control sample.

Acknowledgements: We thank Carlos A. Fuentes Rojas from the Department of Materials Engineering (KU Leuven) for the micro-CT scanning. This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

IONIC STRENGTH REVISITED IN MULTI-RESPONSIVE NANOCOMPOSITES

J. Odent[(1)], C. Samuel[(3)], S. Barrau[(4)], A. Enotiadis[(2)], T. J. Wallin[(2)], W. Pan[(2)], K. Kruemplestaedter[(5)], R. F. Shepherd[(5)], E. P. Giannelis[(2)], J.-M. Raquez[(1)], Ph. Dubois[(1)]

(1) Laboratory of Polymeric and Composite Materials (LPCM) - Center of Innovation and Research in Materials & Polymers (CIRMAP), University of Mons (UMONS), 23 Place du Parc, B-7000 Mons, Belgium

(2) Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA

(3) Department of Polymers and Composites Technology and Mechanical Engineering (TPCIM), Mines Douai, Rue Charles Bourseul 941, CS 10838, 59508 Douai, France

(4) Unité Matériaux et Transformations (UMET)−CNRS UMR 8207, Université Lille 1, 59655 Villeneuve d'Ascq, France

(5) Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853, USA

Despite extensive progress to engineer hydrogels for a broad range of technologies, practical applications have remained elusive due to their, until recently, poor mechanical properties and lack of fabrication approaches, which constrain active structures to simple geometries. To fully exploit engineered hydrogels we must, therefore, be able to rapidly fabricate complex structures with high resolution features. We herein demonstrate a family of ionic composite hydrogels with excellent mechanical properties that can be rapidly 3D-printed at high resolution using commercial stereolithography technology. The key to our formulation is the addition of anionically charged sulfonated silica nanoparticles to the cationic ammonium-containing pre-polymer acrylate solution, which endows the system with dynamic, reversible ionic interactions. The hybrid nature allows for their properties to be readily engineered by varying the amount of nanoparticles (from 0 to 10 wt%) and ammonium groups (from 0 to 50 mol%). When fabricated, the printed structures from our formulations are virtually optically transparent, exhibit fast gelling under near-UV exposure which allows rapid fabrication of macro-scale 3D objects and lead to an unprecedented set of properties. The new composite hydrogels combine within a single platform tunable stiffness (up to 114,500 Pa), toughness (up to 53.5 $kJ \cdot m^{-3}$), extensibility (up to 425 %) and resiliency behavior (up to 97 % strain energy recovered at 100 % strain for over 100 loading cycles) not reported previously in other engineered hydrogels. Hydrogels that are, simultaneously, *tough and resilient* are an important development. Using this technique, we printed not only a series of complex 3D hydrogel structures but also demonstrate the use of our system as a truly 3-dimensional compliant ionic conductor (conductivity up to 2.9 $S.m^{-1}$ at f = 1 MHz) or as a large and fast osmotically-driven actuator (swell rapidly over 60 % within 100 s) (**Fig.1**). Our work is a platform for designing other 3D-printed composite hydrogels beyond silica; the addition of other types of nanoparticles would add additional optical, electrical, or magnetic functionality to the as-printed devices. The design of such ionic composites, which combine a range of tunable properties provides opportunities for a variety of practical applications such as artificial tissue, soft actuators, compliant conductors and sensors for soft robotics. Fabrication of such hydrogels via additive manufacturing into complex geometries with high-resolution features represents another milestone, which, in our opinion paves the way for their use in advanced engineering applications.

Acknowledgements: This work was supported by the Belgian Federal Government Office of Science Policy (SSTC-PAI 6/27) and the National Science Foundation (Award No. DMR-1120296) for general support. This work was supported by the Project H2020-MSCA-RISE-2016-734164 Graphene 3D.

BIOINSPIRED PHOTONIC NANOSTRUCTURES WHAT CAN PHYSICISTS LEARN FROM BUTTERFLIES AND BEETLES?

G. I. Márk[(1)], K. Kertész[(1)], G. Piszter[(1)], Zs. Bálint[(2)] and L. P. Biró[(1)]

(1) Institute of Technical Physics and Materials Science, (MFA), Centre for Energy Research, P.O Box 49, H-1525 Budapest, Hungary, http://www.nanotechnology.hu

(2) Hungarian Natural History Museum, Baross utca 13, H-1088 Budapest, Hungary

Photonic nanostructures exhibit a broad range of optical phenomena: coloration, iridescence, photonic band gap, polarization, diffraction, total reflection, fluorescence, etc[1]. These materials have many existing and potential applications in technology, e.g. in communication, signal processing, computing, and as ecological friendly colorants. But biological evolution created photonic nanoarchitectures in living organisms more than 500 million years ago. The optical reflectance of butterfly wings and beetle elytra often show peculiar features, i.e. their Bidirectional Reflectance Distribution Function (BRDF) is markedly different from that of simple matte "painted" surfaces, with diffuse, Lambertian reflectance[2]. Butterfly wings and beetle elytra often have shiny, metallic appearance. Some butterflies, or beetles produce a very bright white or very dark black appearance. Indeed, these biological photonic crystals were found to be very efficient reflectors and showed an amazing flexibility. Subtle differences in the structures yield very different optical properties[3]. For example the cassidine beetles can undergo an active change of colour, controlled by the insect itself, as a reaction to events occurring in the environment. It is also possible to produce artificial bioinspired nanoarchitectures, with behaviours very similar to that of the living model, by nanomachining. Because of the scaling law of the classical electrodynamics similar structures with enlarged dimensions can produce similar reflection and transmission behaviour in a larger wavelength domain. This means that studying the micro- and nanostructure of the butterfly wing scales and beetle elytra together with their optical properties can be a valuable source of “blueprints” for designing more efficient devices active in the terahertz and microwave range. In this work we give some examples of such applications in the field of broadband absorption surfaces[4].

References:

1. http://www.nanotechnology.hu/online/2009_biophotonics_talk/index.html
2. L. P. Biró et al, Phys. Rev. E **67**, 021907-1 (2003)
3. G. Piszter et al, Anal. Methods, **3**, 78 (2011)
4. A. Paddubskaya et al, J. Appl. Phys. **119**, 135102-1 (2016)

Acknowledgements: This work was supported by the Hungarian OTKA K 115724 and OTKA K 111741. G.I.M., and G.P. wish to thank the Hungarian Academy of Sciences and the Belgian FNRS for financial support.

Participants list

	Title	First Name	Last name	Institution	Your E-Mail Address
1	Prof.	Ricardo	Andrade	MackGraphe	ricardo.andrade@mackenzie.br
2	Mrs.	Polya	Angelova	Bulgarian Academy of Sciences	polq_s_angelova90@abv.bg
3	Prof.	Juras	Banys	Vilnius University	juras.banys@ff.vu.lt
4	Mr.	Arvind Kumar	Bhakta	University of Namur	arvind.bhakta@unamur.be
5	Dr.	Yan	Busby	University of Namur	busbyan@gmail.com
6	Dr.	Marcello	Casa	Narrando	mcasa@unisa.it
7	Mrs.	Pauline	Castenetto	University of Namur	pauline.castenetto@unamur.be
8	Prof.	John	Chen	Sichuan University	johnchen@scu.edu.cn
9	Prof.	Paolo	Ciambelli	Narrando srl	pciambelli@unisa.it
10	Dr.	Yann	Danlée	Université Catholique de Louvain	yann.danlee@uclouvain.be
11	Mrs.	Karin	Derochette	University of Namur	karin.derochette@unamur.be
12	Dr.	Rosa	Di Maio	Istituto per i Polimeri, Compositi e Biomateriali	rosadimaio1988@libero.it
13	Dr.	Ricardo	Donato	MackGraphe	donatork@gmail.com
14	Dr.	Vladimir	Georgiev	NanoTechLab Ltd	vlado@ic.bas.bg
15	M.	Loïc	Germain	Université Catholique de Louvain	loic.germain@uclouvain.be
16	Prof.	Luc	Henrard	University of Namur	luc.henrard@unamur.be
17	Dr.	Evgeni	Ivanov	NanoTechLab Ltd	ivanov_evgeni@yahoo.com
18	Dr.	Rajkumar	Jaiswar	Université Catholique de Louvain	rajkumar.jaiswar@uclouvain.be
19	Dr.	Natia	Jalagonia	SIPT	nati.jalagonia@gmail.com
20	Prof.	Rumiana	Kotsilkova	IMech-BAS	kotsilkova@yahoo.com
21	Mrs.	Ieva	Kranauskaite	Vilnius University	ieva.kranauskaite@ff.vu.lt
22	Dr.	Polina	Kuzhir	Belarusian State University	polina.kuzhir@gmail.com
23	Prof.	Philippe	Lambin	University of Namur	philippe.lambin@unamur.be
24	Dr.	Geza	Mark	Institute of Technical Physics and Materials Science	mark@mfa.kfki.hu
25	Dr.	Jérémy	Odent	University of Mons	jeremy.odent@umons.ac.be
26	Prof.	Alexander	Okotrub	Russian Academy of Sciences, Siberian Branch	spectrum@niic.nsc.ru
27	Dr.	Ignazio	Roppolo	Politecnico di Torino	ignazio.roppolo@polito.it
28	Prof.	Ekaterine	Sanaia	SIPT	esanaia@gmail.com
29	Dr.	Giovanni	Spinelli	University of Salerno	gspinelli@unisa.it
30	Dr.	Sonia	Tabakova	IMech-BAS	stabakova@imbm.bas.bg
31	Dr.	Anna	Usoltseva	University of Namur	anna.usoltseva@unamur.be
32	Prof.	Hesheng	Xia	Sichuan University	xiahs@scu.edu.cn
33	Prof.	Chuhong	Zhang	Sichuan University	chuhong.zhang@scu.edu.cn

NOTES...

H2020-MSCA-RISE-2016-734164 - Graphene 3D

MULTIFUNCTIONAL GRAPHENE-BASED NANOCOMPOSITES WITH ROBUST ELECTROMAGNETIC AND THERMAL PROPERTIES FOR 3D-PRINTING APPLICATION

Start date: 01.01.2017
End date: 31.12.2020
Budget: 1 935 000 €

Coordinator: Institute of Mechanics, Bulgarian Academy of Sciences (Open Laboratory OLEM)

The RISE proposal Graphene 3D will set up an intercontinental and inter-sectoral network of organizations, working on a joint research program in the field of graphene-based polymer nanocomposite materials for additive manufacturing application. The project will enable staff exchanges and sharing of knowledge, this helping to turn creative ideas into innovative graphene-based products.

Graphene 3D Project flyer   Graphene 3D project slides   Graphene 3D Poster

Graphene 3D NewsLetter 2017

Secondment Report Form   Secondment Agreement Form

The project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie-Sklodowska Curie grant agreement N° 734164.