European Cooperation in Science and Technology (COST) is a funding organization for the creation of research networks, called COST Actions.

EsSENce Cost Action CA19118

Project Title:

"High-performance Carbon-based composites with Smart properties for Advanced Sensing Applications"

Deliverable No	4.2
Deliverable Title	Joint papers on advanced sensing applications
Working Group	WG 4 "Sensing applications and smart sensor development"
Originator	HTWK Leipzig (Robert Böhm), Thales R&T (Paolo Bondavalli)

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1 Summary

The goal of the EsSENce Cost Action is to develop a scientific and technological innovation hub at European and International level, focusing on advanced composite materials reinforced with carbon-based nanomaterials (CNM) for sensing applications.

The main focus of the scientific community is to combine advances in manufacturing technologies with the development of innovative nano-enabled composite materials for the fabrication of lightweight smart devices with structural performance and improved and/or added new functionalities including sensing and detection.

Working Group 4 is seeking to explore properties of CNMs in sensing and smart sensors platforms. Research in the area of design and fabrication of sensors and/or composite materials with sensing properties as well as in actuators to enhance standard inspection techniques, has become of great interest to a variety of scientific communities ranging from biological and chemical sciences to engineering communities. Several tools and techniques for detection, based on the latest trends in NMs, and micro- and nanotechnologies are offering new opportunities for the development of composites with sensing properties. CNMs are emerging as reliable and powerful tools for sensing various compounds (e.g. heavy metals, phenolic compounds and pesticides) being offered at the same time as efficient destroying agents with interest for industrial applications. Moreover, CNMs with optical properties (e.g. carbon quantum dots) could be considered for smart sensing applications. Through EsSENce WG4, knowledge will be exchanged between partners engaged in the NMs and nanocomposite synthesis and partners with expertise in sensors development. This integration will lead to scientific contributions in sensing technologies with advantages such as high sensitivity and selectivity, rapidness, and cost efficiency.

The deliverable 4.2 (D4.2) entitled "Joint papers on advanced sensing applications" was developed within WG4. Several bilateral and multilateral discussions in the WG about sensing applications with CNM have already produced joint collaborations which resulted in publications that are either already published or in the planning phase. This report collects the abstracts and the bibliographic data of the published joint papers. Additionally, the planned joint papers are listed.

This deliverable received contribution from the following WG4 members: Sara Fateixa, Beate Krause, Petra Pötschke, Oğuzhan Öztürk, Shanmugam Kumar, Antonio J. Paleo, Müslüm Kaplan and Robert Böhm.

2 Published papers

The following papers have been published in the reporting period so far:

[1] OKAY ALTUNTAŞ, I.; ÖZTÜRK, O.; WAGNER, C.; KAHNT, A.; BÖHM, R.: Self-sensing properties of different carbon nanomaterial based composites for sustainable infrastructures. *20th European Conference on Composite Materials (ECCM 20),* Lausanne (Switzerland), 26.-30.06.2022

[2] FATEIXA, S.; SCHNEIDER, J.; KUMAR, S.; BÖHM, R.: 3D-printed graphene-based polymer composites for optical detection of water pollutants. *20th European Conference on Composite Materials (ECCM 20),* Lausanne (Switzerland), 26.-30.06.2022

[3] PALEO, A.J.; KRAUSE, B.; CERQUEIRA, M.F.; MUÑOZ, E.; PÖTSCHKE, P.; ROCHA, A.M.: Nonlinear thermopower behaviour of n-type carbon nanofibers and their melt mixed polypropylene composites. *Polymers,* 2022, 14(2), 269, https://doi.org/10.3390/polym14020269

[4] PALEO, A.J.; KRAUSE, B.; CERQUEIRA, M.F.; MUÑOZ, E.; PÖTSCHKE, P.; ROCHA, A.M.: Electronic features of cotton fabric e-textiles prepared with aqueous carbon nanofiber inks. *ACS Applied Engineering Materials*, 2022, https://doi.org/10.1021/acsaenm.2c00023

[5] PALEO, A.J.; KRAUSE, B.; CERQUEIRA, M.F.; MUÑOZ, E.; MELLE-FRANCO, M.; PÖTSCHKE, P.; ROCHA, A.M.: Thermoelectric properties of polypropylene carbon nanofiber melt-mixed composites: exploring the role of polymer on their Seebeck coefficient. *Polymer Journal* 2021, 53, 1145–1152, https://doi.org/10.1038/s41428-021-00518-7

[6] KAPLAN, M.; KRAUSE, B.; PÖTSCHKE, P.: Polymer/CNT nanocomposite composites and filaments for smart textiles: melt mixing of composites, 2022/333/91-96, https://doi.org/10.4028/p-3g2wph , in: Solid State Phenomena, ISSN: 1662-9779, https://www.scientific.net/SSP.

2.1 Collection of Abstracts

Self-Sensing Properties of Different Carbon Nanomaterial Based Composites for Sustainable Infrastructures

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Abstract: Recently, various studies have focused on the cement-based composites doped with carbon-based materials to provide non-structural functional properties without compromising engineering properties. Some of the most important non-structural functional properties are self-sensing performance of cement-based composites, such as damage, strain, structural vibration, and durability monitoring. Generally, the term attained as “self-sensing” is related to the function of cement-based material to exhibit its piezoresistive ability. Accordingly, self-sensing capability of the cement-based composites can be attained and structural or/and material health monitoring can be provided without the need external integrated. In this study, the mixtures of cement-based composites functionalized with self-sensing ability was addressed. The paper focuses on the production techniques, engineering performance and multifunctionality properties of small-size specimens to large-scale trial specimens. Challenges of the current methods as sensory materials are also discussed together with other cement-free composites.

Keywords: Carbon-based materials; Multifunctionality; Self-sensing; Structural Health Monitoring.

3D Printed Polymer Nanocomposites Engineered with Graphene and Metallic Nanoparticles for Optical Detection of Water Pollutants

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Abstract: The development of novel low-cost materials capable of exhibiting high performance, sensitivity and reproducibility are highly desirable for environmental quality monitoring of emerging chemical pollutants (ECPs). Their presence in water can be harmful and have unpredictable consequences for the environment and human health. Therefore, monitoring such ECPs is critical to improving water quality and preventing the increased incidence of several diseases. Here, we explore the performance of 3D printed polymer nanocomposites comprising graphene and gold nanoparticles (AuNPs) to detect ECPs in water using surface-enhanced Raman scattering (SERS). Fused filament fabrication additive manufacturing will fabricate samples using nanoengineered filaments comprising graphene and AuNPs. Nanoengineered filaments are prepared by melt blending using a twin-screw extruder. The composites' capability to detect the ECPs is evaluated using conventional and portable Raman instruments. Imaging techniques, namely confocal Raman microscopy, are used to optimize the Raman signal of the ECPs on the substrates.

Keywords: 3D printed polymer nanocomposites; graphene; SERS; emerging pollutants.

Nonlinear Thermopower Behaviour of N-Type Carbon Nanofibres and Their Melt Mixed Polypropylene Composites

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Abstract: The temperature dependent electrical conductivity σ (T) and thermopower (Seebeck coefficient) S (T) from 303.15 K (30 °C) to 373.15 K (100 °C) of an as-received commercial n-type vapour grown carbon nanofibre (CNF) powder and its melt-mixed polypropylene (PP) composite with 5 wt.% of CNFs have been analysed. At 30 °C, the σ and S of the CNF powder are ~136 S m^{-1} and -5.1 $\mu V\ K^{-1}$, respectively, whereas its PP/CNF composite showed lower conductivities and less negative S-values of ~15 S m^{-1} and -3.4 $\mu V\ K^{-1}$, respectively. The σ (T) of both samples presents a $d\sigma/dT < 0$ character described by the 3D variable range hopping (VRH) model. In contrast, their S(T) shows a $dS/dT > 0$ character, also observed in some doped multiwall carbon nanotube (MWCNT) mats with nonlinear thermopower behaviour, and explained here from the contribution of impurities in the CNF structure such as oxygen and sulphur, which cause sharply varying and localized states at approximately 0.09 eV above their Fermi energy level (E_F).

Keywords: polypropylene; carbon nanofibers; thermoelectric properties; n-type polymer composites; variable range hopping

Electronic Features of Cotton Fabric e-Textiles Prepared with Aqueous Carbon Nanofiber Inks

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Abstract: Cotton woven fabrics functionalized with aqueous inks made with carbon nanofibers (CNFs) and anionic surfactant are prepared via dip-coating followed by heat treatment, and their electronic properties are discussed. The e-textiles prepared with the inks made with the highest amount of CNFs (6.4 mg mL^{-1}) show electrical conductivities (σ) of ∼35 S m^{-1} and a negative Seebeck (S) of −6 μV K^{-1} at 30 °C, which means that their majority carriers are electrons. The $\sigma(T)$ of the e-textiles from 30 to 100 °C shows a negative temperature effect, interpreted as a thermally activated hopping mechanism across a random network of potential wells by means of the 3D variable range hopping (VRH) model. Likewise, their $S(T)$ from 30 to 100 °C shows a negative temperature effect, conveniently depicted by the same model proposed for describing the negative Seebeck of doped multiwall carbon nanotube mats. From this model, it is deduced that the cause of the negative Seebeck in the e-textiles may arise from the contribution of the impurities found in the as-received CNFs, which cause sharply varying and localized states at approximately 0.085 eV above their Fermi energy level (E_F). Moreover, the possibility of a slight n-doping from the cellulose fibers of the fabrics and the residuals of the anionic surfactant onto the most external CNF graphitic shells present in the e-textiles is also discussed with the help of the $\sigma(T)$ and $S(T)$ analysis.

Keywords: carbon nanofibers, cotton fabrics, aqueous conductive inks, surfactant, e-textiles, Seebeck coefficient, variable range hopping

Thermoelectric properties of polypropylene carbon nanofiber melt-mixed composites: exploring the role of polymer on their Seebeck coefficient

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Abstract: The effect of polypropylene (PP) on the Seebeck coefficient (S) of carbon nanofibers (CNFs) in melt-extruded PP composites filled with up to 5 wt. % of CNFs was analyzed in this study. The as-received CNFs present an electrical conductivity of ~320 S m^{-1} and an interesting phenomenon of showing negative S-values of −5.5 μVK^{-1}, with 10^{-2} $\mu W/mK^2$ as the power factor (PF). In contrast, the PP/CNF composites with 5 wt. % of CNFs showed lower conductivities of ~50 S m^{-1}, less negative S-values of −3.8 μVK^{-1}, and a PF of 7×10^{-4} $\mu W/mK^2$. In particular, the change in the Seebeck coefficient of the PP/CNF composites is explained by a slight electron donation from the outer layers of the CNFs to the PP molecules, which could reduce the S-values of the as-received CNFs. Our study indicates that even insulating polymers such as PP may have a quantifiable effect on the intrinsic Seebeck coefficient of carbon-based nanostructures, and this fact should also be taken into consideration to tailor conductive polymer composites with the desired thermoelectric (TE) properties.

Polymer/CNT Composites and Filaments for Smart Textiles: Melt Mixing of Composites

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Abstract. Textile products are of great importance in the dissemination of newly developed communication devices and flexible electronics in conjunction with the advantages of covering the entire human body and being used all day long by all individuals in society. Various approaches have been developed to ensure the required electrical conductivity of textiles. Our research deals with melt spinning of carbon nanomaterial-based composites (CNCs) into electrically conductive filaments. By combining the various composite structures and property profiles with a conductive filler at high concentration, specific morphological structures can be achieved that offer a much higher potential for the development of new functional fibers for different smart textile applications. This study aims to produce nanocomposites from polyamide 6 (PA6) and polyethylene (PE) matrices with single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) by using a small-scale mixing device that provides short mixing time, and material savings in the first stage of the research.

Keywords: carbon nanotube, melt mixing, polyamide 6, polyethylene, composite, electrical conductivity, smart textiles

3 Planned papers

The following papers are planned to be published in the next reporting periods:

[7] PEYROW HEDAYATI, D.; TROMPETA, K.; TERMINE, S.; CHARITIDIS, C.; BÖHM, R.; BONDAVALLI, P.: Carbon Nanomaterials (CNMs) for Sensing in Composite Applications.

Collaboration between: National Technical University of Athens (Greece); Thales Group (France); HTWK Leipzig (Germany)

[8] GEORGOPOULOU, A.; HARDMAN, D.; THURUTHEL, T.G.; IIDA, F.; CLEMENS, F.: Sensorized skin with biomimetic tactility features based on bi-modal soft resistive composites.

Collaboration between: EMPA Swiss Federal Laboratories for Materials Science and Technology Switzerland, Vrije Universiteit Brussel (VUB) Flanders Make Pleinlaan Belgium, Bio-Inspired Robotics Lab, Department of Engineering University of Cambridge UK

[9] YABAŞ, E.; ERDEN, F.; YAVUZ, E.; REKA, A.; BÖHM, R.: Phthalocyanines and Their Composites for Detection of Volatile Organic Compounds (VOCs) in Human Breath.

Collaboration between: Sivas Cumhuriyet University (Turkey), Erzincan Binali Yıldırım Üniversitesi Merkez (Turkey), University of Tetova (North Macedonia); HTWK Leipzig (Germany)