ISTITUTO PER I POLIMERI COMPOSITI E BIOMATERIALI

Joint Laboratory for Graphene-based Multifunctional Polymer Nanocomposites

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Final Report

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Joint Lab IPCB-CNR/SKPLME Sichuan University

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The "Joint Laboratory for Graphene-based Multifunctional Polymer Nanocomposites", established between the Institute of Polymers, Composite and Biomaterials of the National research Council (IPCB-CNR) and the State Key Laboratory of Polymer Engineering Materials of Sichuan University (SKPLME), was approved at the end of July 2015 by CNR (Prot 0002710-IPCB, 23rd July 2015) and it has been operating in the last years focusing on the development of graphene-based polymer composites, covering the whole chain from the fundamental research to the preparation and validation of prototypes for applications in sectors including automotive, packaging and environment protection. The main scope of this report is to summarize the results of most important activities, the main scientific outputs and the networking activity which have been carried out during the last four years, starting from the overall objectives of the Joint Lab as initially stated in the proposed project.

1. General Summary of Joint Lab Objectives and Research activity

The general objective of the Joint Lab was the development of the fundamental and technological knowledge for the rational designing, preparation and validation of multifunctional polymeric nanocomposites based on chemically modified graphenes (CMGs), including graphene oxide, reduced graphene oxide and their derivatives. In this view, the Joint Lab research activity has been addressed to the understanding of the correlation among graphene hierarchical morphology, polymer/graphene interactions and process and its effect on the functional and structural properties of the resulting graphene-based composites. In particular, the attention has been devoted to the exploitation of the potentials of the so called "segregated morphology", obtained through a well-established control of the spatial localization of the carbonaceous filler to realize the layered-structure as well as the three-dimensional network within the bulk polymer. The correlations between the filler-morphology and the procedures adopted to control the spatial localization of filler were exhaustively studied and represent a promising background useful for all young students involved in the research activities.

From a scientific point of view, the Joint Lab has represented a favourable research-hub which has allowed to pursuit the excellence in the field of graphene-based composites (as testified by the large number of published papers and the establishment of several further funded research projects) and overcome the scientific lacks which have limited the widespread diffusion of graphene-based polymer nanocomposites. Some of materials developed within the Joint Lab, with specific attention to the materials based on natural rubber, on chitosan and materials for 3D printing technology, as well as the knowledge related to designing and preparation of composites with control of the morphology represent a valuable solutions to the current challenges faced by the stakeholders in strategic sectors such as automotive, packaging and environment protection wherein it is continuously required the presence of innovative materials with high performances for antistatic, EMI shielding, gas barrier applications as well as biocompatibility and electrical and optical applications.

The main activities carried during the project, have been realized in the framework of the following Workpackages (which, for sake of completeness, are briefly reported from the project technical Annex):
WP1: Development of chemically modified graphenes (CMGs) including graphene oxide, reduced graphene oxide and their derivatives by novel chemical oxidation and exfoliation approaches. Main target: High quality CMGs. (Principal Research Team: SKLPME, Subordinated team: IPCB-CNR).
WP2: Development of graphene-based nanocomposites by using rubber, thermoplastic polyurethane and proteins. Target: Tailoring of CMGs morphology within the polymer. (Principal Research Team: SKLPME, Subordinated team: IPCB-CNR).
WP3: Development of nanocomposites based on high amorphous vinyl alcohol polymers and proteins by Layer-by-Layer or vacuum assisted deposition approaches to realize the alignment of graphene in 2D layered morphology. Target: Tailoring of 2D layered CMGs morphology within the polymer (Principal Research Team: IPCB-CNR, Subordinated team: SKLPME).
WP4: Morphological, physical and thermo-mechanical characterization as well as mechanical, electrical and EMI shielding properties of graphene-based nanocomposites. Target: Extensive characterization of nanocomposites. (Research Team: SKLPME and IPCB-CNR).
WP5: Exploration of the potentials of selected graphene-based composites in specific applications. Target: Development of prototypes at lab scale with specific application properties (TRL 4-5). (Research Team: SKLPME and IMCB-CNR).
WP6: Dissemination (Research Team: SKLPME and IPCB-CNR).

The WP1 research activity, mainly addressed to the development of a suitable experimental approaches for the production of chemically modified graphenes (CMGs) through oxidation of graphite and subsequent chemical reduction, was carried out during the 1st and 2nd year. The activity led to the definition of robust procedures for the preparation of high quality CMGs which have been used for the preparation of composites. At the same time, it was successfully explored the possibility to use a modified polyvinyl-alcohol (HAVOH) for the liquid exfoliation of graphite to graphene nanoparticles. It was possible to obtain an effective polymer masterbatch, useful for several applications.
The activities of WP2 and WP3 were mainly addressed to the development and characterization of innovative nanocomposites. Several research activities were implemented during the three years of the Joint Lab project with the aim to investigate the fundamentals for the preparation of effective nanocomposites with enhanced structural and functional properties (i.e. the tailoring of the graphene and its derivatives morphology to improve the functional and structural properties). The activities were performed according to the planned project. However, new research directions were added with respect to those described in the technical Annex, being considered more interesting in the international scenario and in the light of new opportunities arising from the international projects wherein both IPCB and SKPLME were involved as partners, ie 3D Graphene which is a MarieCurie project and GRAPE-MAT and GINSENG projects which are Grande Rilevanza projects from MAECI and Chinese Institutions (more info about the projects are reported in the last section of the report).
The activities of WP4 were addressed to the exhaustive characterization of composites whereas the WP5 activity was addressed to the validation of composites with respect to specific application in strategic sectors, ie food and electronic packaging, materials for 3D printing technology, conductive materials, dye-adsorbing materials, ecc…Finally, as for the activity concerning the WP6 focused on

the Dissemination, twelve papers have been published in the framework of the Joint Lab with evident acknowledgement to the CNR for the founds. One additional paper is going to be submitted focused on the layered composite for EMI shielding applications whereas several abstracts have been presented in some national and international workshops. Additional evidences about the dissemination activity are provided in the last section of this report.

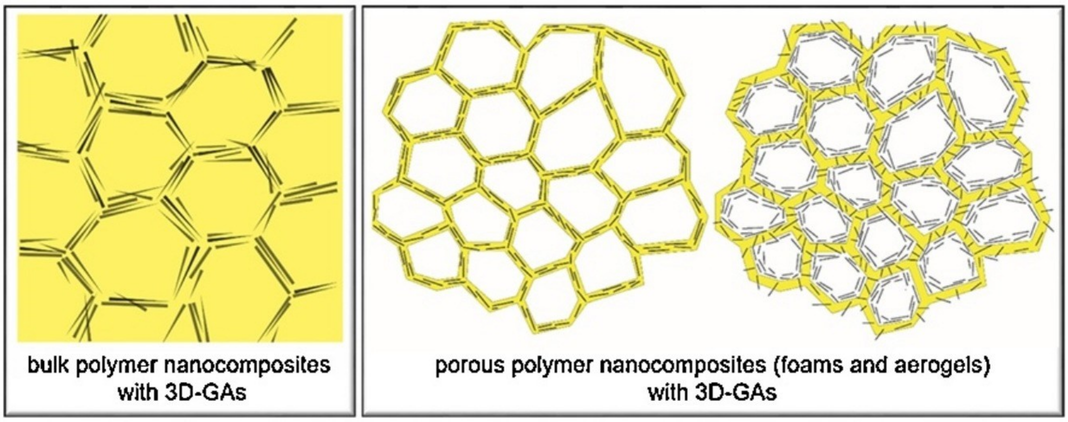
The main scientific results of the Joint Lab are the following ones:
a) Preparation of high-quality chemically-modified graphenes by liquid exfoliation in presence of a suitable polymer, ie High Amourphous PolyVinyl Alcohol, HAVOH;
b) Understanding of the fundamentals and technological aspects which allow to control the spatial localization of 2D filler within selected polymeric matrix: Natural rubber, thermoplastic polyurethane, high amorphous vinyl alcohol, proteins and chitosan;
c) Design and preparation of the graphene-based polymer nanocomposites by ultrasonic assisted graphene self-assembly latex mixing, layer-by-layer deposition, solution casting deposition and vacuum assisted filtration. Through the investigated techniques it has been possible to tailor-made the GCMs morphology from random dispersion, to 2D layered deposition up to 3D segregated network;
d) Validation of the multifunctional graphene-based nanocomposites by means of an extensive structural and functional characterization of the developed materials.
From a general and strategic point of view, the Joint Lab has also allowed to:
a) further strengthen the relationships between the CNR and the Sichuan University which is a world-class institution for quality and number of published papers and patents in the field of polymer science (Scimago data);
b) promote the exchange of permanent and young researchers;
c) integrate complementary research resources and facilities;
d) co-publish papers in the top impact Journals of polymer material science;
e) jointly participation in three international projects: 3D Graphene which is a MarieCurie project and GRAPE-MAT and GINSENG projects which are both Grande Rilevanza projects founded by MAECI (Minister of Foreign Affairs and International Cooperation) and Chinese Institutions as MOST (Minister of Science and Technology of China) and NSFC (Natural Science Foundation of China), respectively (more info about the projects are reported in the last section of the report).
f) promote the link with the Sichuan Province which was identified by the Italian Foreign Affairs Minister as a strategic region for the development of the research cooperation with China.

2. Graphene-based innovative composites through the literature analysis

In this section are presented the most significant scientific results related to the Development of graphene-based innovative composites which have been interested by a publication on ISI journal. In particular, for sake of brevity, for each paper are reported the title with the authors, TOC graph (or a significant figure from the main-text) and abstract. The first paper is a review published in Progress in Polymer Science journal which represents a clear overview of the state-of-art of composite materials realized by using graphene and its derivatives with a fine control of the morphology. This topic will represent the basis for future activities between IPCB-CNR and SKPLME, exploring different applications and different filler (ie. filler 1D as carbon nanotubes, other filler 2D as hexagonal boron nitride, *h*BN already investigated in the Joint Lab).

1. *Nanocomposite polymeric materials with 3D graphene-based architectures: from design strategies to tailored properties and potential applications*

Authors: M.Salzano de Luna, Y.Wang, T.Zhai, L.Verdolotti, G.G.Buonocore, M.Lavorgna, H.Xia, *Progress in Polymer Science* 89, pp. 213-249, *2019. ISSN: 0079-6700. DOI: 10.1016/j.progpolymsci.2018.11.002*



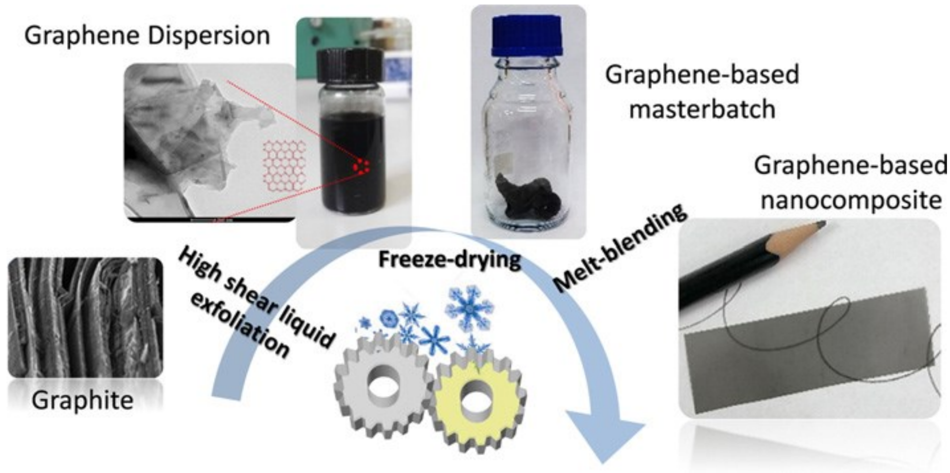
Graphical Abstract: Schematization of three-dimensional "segregated morphology" of graphene in bulk polymer nanocomposites. Yellow regions correspond to the polymer matrix.

"In the last decade, a great deal of research has been devoted to the design and development of graphene-based polymer nanocomposites characterized by a prescribed arrangement of the graphene-based nanosheets into spatially segregated 3D architectures. The formation of a continuous filler network obtained by confining the nanosheets into a constrained volume of the polymeric matrix is particularly attractive from a technological point of view. The preparation of segregated 3D graphene-based architectures facilitates the proper tailoring of the overall performance of the resulting polymer nanocomposites, providing significant improvements in terms of structural (i.e., mechanical properties) and functional (electrical properties, sensing ability, and adsorption/absorption capacity) features. This review focuses on polymer-based nanocomposites in two categories, namely bulk and porous (foam and aerogels) systems. These all share the common distinctive feature that relies on the peculiar arrangement of the graphene-based nanosheets in the form of a segregated yet continuous 3D assembly. For each class of materials, the main preparation strategies are presented and the resulting structure-property correlations are

highlighted and discussed, together with the technological implications, and possible future directions."

2. *Graphene-based masterbatch obtained via modified polyvinyl alcohol liquid-shear exfoliation and its application in enhanced polymer composites*

Authors: DA.Simon, E.Bischoff, GG.Buonocore, P.Cerruti, MG.Raucci, H.Xia, HS.Schrekker, M.Lavorgna, L.Ambrosio, RS.Mauler, *Materials and Design, Volume 134, Pages 103-110 (2017). ISSN: 02641275, doi: 10.1016/j.matdes.2017.08.032*



Graphical Abstract: Schematization of process from graphite to graphene dispersion, graphene masterbatch up to graphene-based nanocomposite.

"A simple and inexpensive method for the production of graphene-based masterbatch via polymer-assisted shear exfoliation of graphite in water was comprehensively investigated. In detail, a modified polyvinyl alcohol (mPVOH) characterized by surface energy comparable with that of graphene was used as surfactant for the production of graphene-like particles. The proposed approach allowed a yield in graphene-like particles higher than that obtained by using common surfactants, along with a narrower size distribution. AmPVOH-masterbatch containing 4.38wt% of graphene-like particles was produced by removing the aqueous solvent from a dispersion and directly used for production of polymer nanocomposites by melt processing. Films prepared by blending the masterbatch with polyvinyl alcohol in order to have a graphene-like particles content equal to 0.3 wt% showed a 78% reduction in water permeability and a 48% increase in storage modulus as compared with pristine polymers. Improved barrier properties were also observed for polylactic acid (PLA) and low-density polyethylene (LDPE)-based composite films, whereas an increment of about 520% in the storage modulus was observed for the composite obtained with PLA. The obtained results are very relevant and the proposed process will open up a new pathway for using graphene-based masterbatch in the packaging industry."

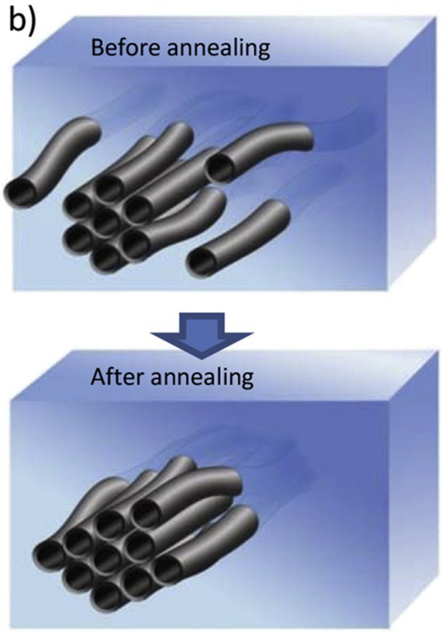
3. ***Reduction of graphene oxide by UHV annealing***

Authors: S.Kaciulis, A.Mezzi, P.Soltani, T.de Caro, H.Xia, Y.L.Wang, T.Zhai, M.Lavorgna, *Surface and Interface Analysis, 2018, V50(11), pg 1089-1093, 2018. ISSN: 1096-9918. DOI: 10.1002/sia.6424*

"A series of chemically treated graphene oxide (GO) samples, destined for the preparation of several composite materials, was studied by X-ray photoelectron spectroscopy (XPS). From their comparison, the 3-mercaptopropyl trimethoxysilane was identified as the most effective reducing agent among the used procedures. The influence of ultrahigh vacuum annealing up to 600°C on the chemical composition and carbon electronic configuration in reduced GO samples was further investigated by XPS and Auger electron spectroscopy. All the samples before and after thermal treatments were analyzed in situ by XPS and Auger electron spectroscopy, paying a particular attention to the shape of C KVV spectra described by the values of D parameter. The changes of chemical composition and carbon configuration reflected in the D parameter revealed the full reduction of GO to graphene after annealing in ultrahigh vacuum at 600°C. The successful reduction of GO to graphene was also confirmed by Raman spectroscopy. Obtained bulk samples of graphene aggregates remained stable in air, testifying the irreversibility of this reduction."

4. ***Relationship between electrical conductivity and spatial arrangements of carbon nanotubes in polystyrene nanocomposites: The effect of thermal annealing and plasticization on electrical conductivity***

Authors: G.Fei, Q.Gong, D.Li, M.Lavorgna, H.Xia, *Composites Science and Technology 146, 99–109* (2017). *ISSN: 0266-3538, doi: 10.1016/j.compscitech.2017.04.020*



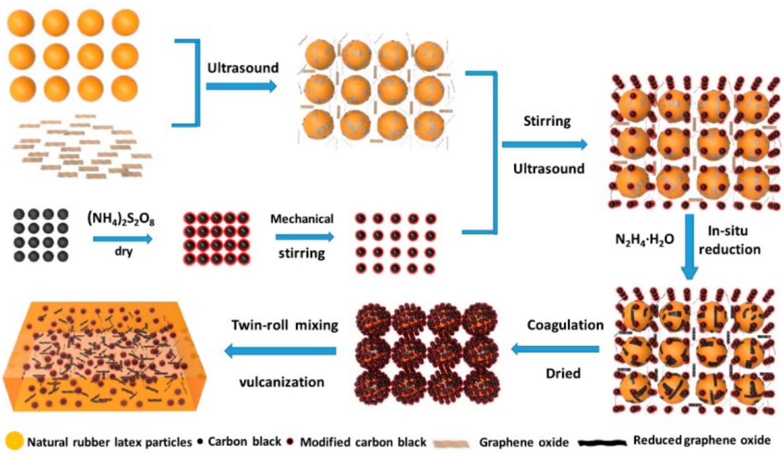
Graphical Abstract: Schematization of carbon nanotubes aggregation process induced by thermal annealing.

"The effect of both thermal annealing and plasticization of the polymeric matrix by low molecular weight compounds on the electrical conductivity of the polystyrene based carbon

nanotubes (CNTs) composites were investigated. It was found that the electrical conductivity of the samples filled with 3 wt% of CNTs increased by nearly 2 orders of magnitude after thermal annealing for 10 h at 150 °C, and it further increased with increasing plasticizer content. The effect of the hierarchical CNT morphology on the electrical conductivity of composites was elucidated by in-situ Raman and Synchrotron Radiation Small Angle X-ray Scattering investigations. The synergistic effect between thermal treatment and matrix plasticization contributes to efficiently eliminate the residual stress at the interface between polymeric matrix and carbon nanotubes. This leads to the formation of a more effective CNTs network featured by denser bundles, exhibiting a larger number of contacts between the CNTs which contributes to significantly enhance the electrical conductivity of composites."

5. ***Graphene/carbon black/natural rubber composites prepared by a wet compounding and latex mixing process***

Authors: J.Wang, K.Zhang, Z.Cheng, M.Lavorgna, H.Xia, *Plastics, Rubber and Composites, 47, 9, 398-412, 2018. ISSN: 14658011, doi: 10.1080/14658011.2018.1516435*

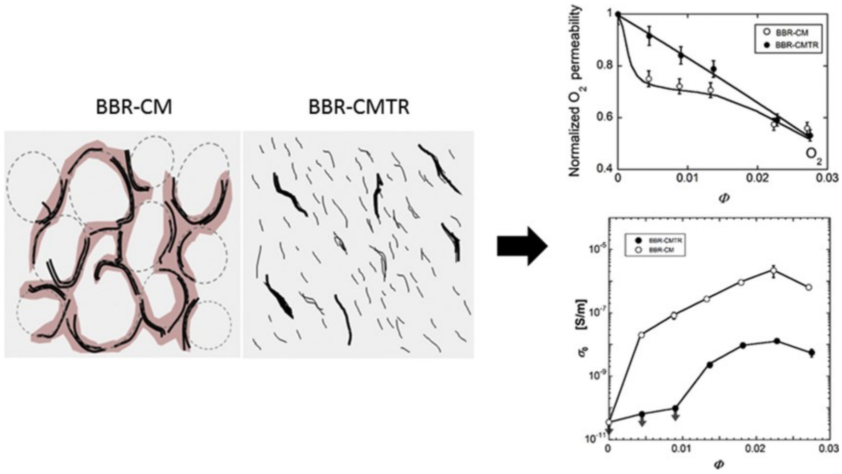


Scheme 1 (present in the paper). WCL method for the preparation of rGO/CB/NR composites.

"The extensively used latex mixing approach to prepare graphene can improve the graphene dispersion but meets some challenges in the preparation of high content carbon black filled rubber system like a rubber tire. Owing to the high melt viscosity of the rubber/graphene masterbatch, the dispersion of carbon black is not perfect during twin-roll mixing and some aggregates will be formed. Here we proposed a wet compounding process, combined with ultrasonically assisted latex mixing, named as the WCL method to prepare reduced graphene oxide/carbon black/natural rubber (rGO/CB/NR) composites. The morphological observations confirmed that both graphene and carbon black can be evenly dispersed in the rubber composites. The incorporation of rGO also improves the hardness, thermal conductivity and anti-aging properties of the composites. The rGO/CB/NR composites prepared by the WCL method possess better mechanical properties compared to conventional latex mixing. The entanglement-bound rubber tube model was utilised to understand the reinforcing mechanism."

6. *Tailoring gas permeation and dielectric properties of bromobutyl rubber–Graphene oxide nanocomposites by inducing an ordered nanofiller microstructure*

Authors: F.He, G.Mensitieri, M.Lavorgna, M.Salzano de Luna, G.Filippone, H.Xia, R.Esposito, G.Scherillo, *Composites Part B: Engineering, 116, 361-368, (2017)*, ISSN: 1359-8368*, DOI: 10.1016/j.compositesb.2016.10.076*

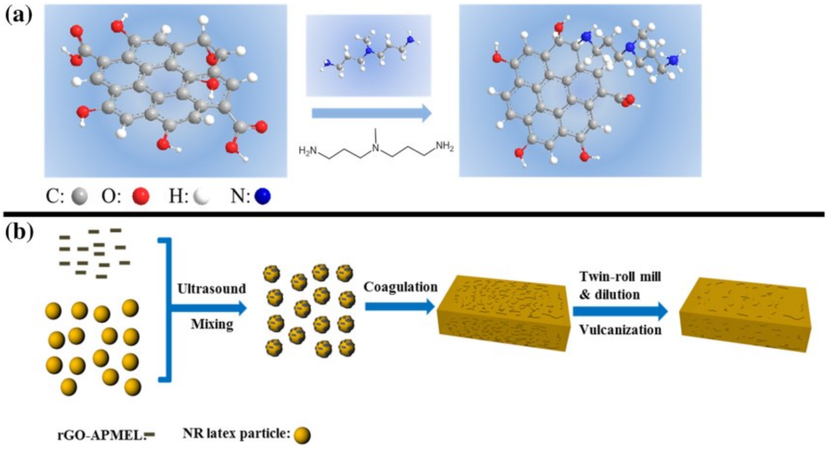


Graphical Abstract: Correlation between segregated morphology and dielectric properties of rubber-based composites.

"The spatial distribution of graphene oxide (GO) nanoplatelets in a bromobutyl rubber (BBR) matrix has been tailored by exploiting the rubber latex mixing process to confine nanoparticles among latex microspheres, thus obtaining a segregated arrangement. The gas transport properties and the dielectric behavior of these nanocomposites displaying a 'segregated' morphology have been compared, for different filler contents, to those of BBR/GO nanocomposites in which the nanoparticles are uniformly dispersed within the rubber matrix. Relevant qualitative and quantitative differences emerge from the comparison of the properties of the two families of GO-based samples. It has been found that the segregated morphology enables a significant enhancement of the barrier properties of pristine rubber already at low levels of nanofiller loading. In addition, an exceptionally low value of the electrical percolation threshold has been detected, which is more than one order of magnitude lower than in the case of uniform filler dispersion. These effects are a direct consequence of the assembly and confinement of nanoparticles among the rubber latex microspheres."

7. ***Simultaneous reduction and surface functionalization of graphene oxide and the application for rubber composites***

Authors: J.Wang, K.Zhang, S.Hao, H.Xia, M.Lavorgna, *Journal of Applied Polymer Science* 136(15),47375, *2019. ISSN: 0021-8995. DOI: 10.1002/app.47375*

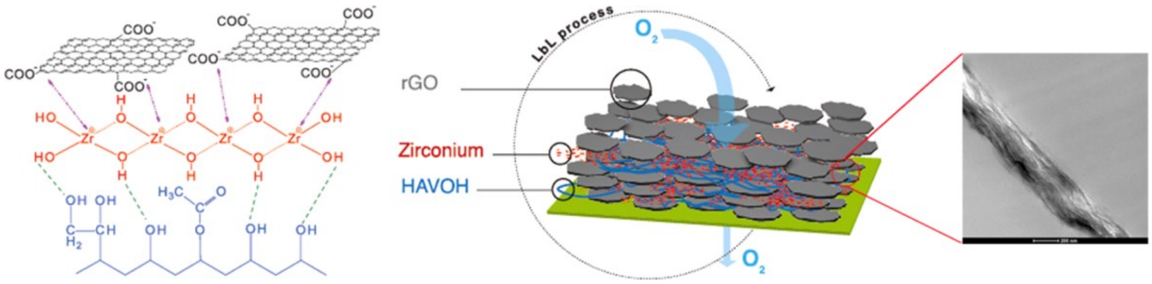


Scheme 1 (present in the paper). Scheme 1. (a) Functionalization of GO by grafting reaction with APMEL and (b) preparation of NR/rGO composites through a latex mixing using the APMEL-functionalized GO aqueous dispersion.

"The simultaneous reduction and functionalization of graphene oxide (GO) was realized through a chemical grafting reaction with a functionalization agent N,N-bis(3-aminopropyl)methylamine (APMEL). The reduced and functionalized reduced GO (rGO-APMEL) sheets can be well dispersed in water without any added surfactant and the formed stable rGO aqueous dispersion can be kept for a long time, which can be used for the preparation of rubber–graphene (GE) composites by latex mixing. The electrostatic interaction between rGO–APMEL (positively charged) and natural rubber latex particles (negatively charged) leads to the formation of NR/rGO–APMEL composites with strong interaction. Compared with blank NR, the tensile strength and modulus for NR/rGO–APMEL increase with the rGO–APMEL loading. Especially, when the filler content is 5 phr, the tensile strength of NR/rGO–APMEL-5 increases by 32.7%, as a control the tensile strength of NR/GO-5 and NR/rGO-5 decrease by 20.1 and 15.6%, respectively. The entanglement-bound rubber tube model was used to analyze the reinforcing effect of GE on NR/rGO–APMEL nanocomposites at a molecular level. This study may provide us a novel approach to prepare well dispersed and exfoliated rGO–polymer nanocomposites."

8. Borate cross-linked graphene oxide–chitosan as robust and high gas barrier films

Authors: N.Yan, F.Capezzuto, M.Lavorgna, GG. Buonocore, F.Tescione, H.Xia, L.Ambrosio, *Nanoscale, 8, 10783-10791 (2016), ISSN 2040-3364, DOI: 10.1039/C6NR00377J*



Graphical Abstract: Schematization of the layered structure realized by the layer-by-layer approach.

"Gas-barrier materials obtained by coating poly(ethylene terephthalate) (PET) substrates have already been studied in the recent literature. However, because of the benefits of using cheaper, biodegradable, and nonpolar polymers, multilayered hybrid coatings consisting of alternate layers of reduced graphene oxide (rGO) nanosheets and a novel high amorphous vinyl alcohol (HAVOH) with zirconium (Zr) adducts as binders were successfully fabricated through a layer-by-layer (LbL) assembly approach. Atomic force microscopy analysis showed that rGO nanoplatelets were uniformly dispersed over the HAVOH polymer substrate. Scanning and transmission electron microscopies revealed that multilayer (HAVOH/Zr/rGO)n hybrid coatings exhibited a brick-wall structure with HAVOH and rGO as buildings blocks. It has been shown that 40 layers of HAVOH/Zr/rGO ultrathin films deposited on PET substrates lead to a decrease of 1 order of magnitude of oxygen permeability with respect to the pristine PET substrate. This is attributed to the effect of zirconium polymeric adducts, which enhance the assembling efficiency of rGO and compact the layers, as confirmed by NMR characterization, resulting in a significant increment of the oxygen-transport pathways. Because of their high barrier properties and high flexibility, these films are promising candidates in a variety of applications such as packaging, selective gas films, and protection of flexible electronics."

9. Stretchable conductive films based on carbon nanomaterials prepared by spray coating

Authors: Q.Bu, Y.Zhan, F.He, M.Lavorgna, H.Xia, *Journal of Applied Polymer Science*, 133, 43243, (2016), ISSN: 1097-4628*, DOI: 10.1002/app.43243*

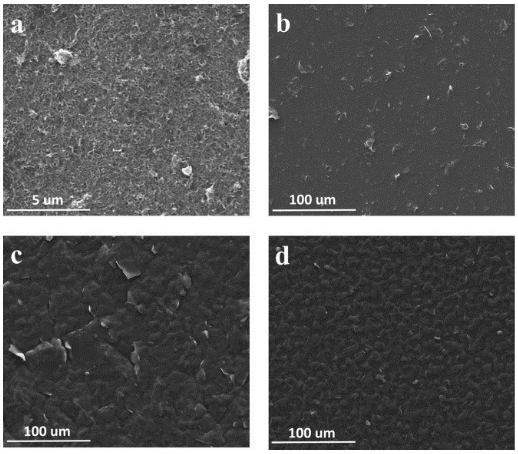


Figure (present in the paper). SEM images of the surfaces of PDMS films coated with (a) CNTs, (b) GE, (c) GO, and (d) rGO by spray coating. The carbon nanomaterial concentration for all of the spraying dispersions was 0.075 mg/mL.

"Stretchable conductive films consisting of a layer of carbon nanomaterials, that is, carbon nanotubes (CNTs), mechanically exfoliated graphene (GE), or chemically reduced graphene oxide (rGO), deposited on polydimethylsiloxane (PDMS) films were prepared by spray coating. The correlations among the concentration of the carbon nanomaterials, the electrical resistance and the optical transmittance of the spray-coated films were investigated. The results show that the conductivity of the CNT coatings was better than that of the GE-based coatings. When the CNT concentration of the dispersion for spraying increased from 0.01 to 0.075 mg/mL, the surface electrical resistance decreased from 7.8 3 103 to 6.7 3 102 X, whereas for the GE or rGO coatings, the electrical resistance was several orders higher than that of the CNT coatings. The CNT spray-coated films exhibited an optical transmittance of about 60% at a wavelength of 550 nm; this was higher than that of the GE or rGO spray-coated films. The electric heating behaviors of the stretchable conductive films as functions of the applied voltage and the concentration of carbon nanomaterials and the electrical conductivity under tensile and bending strains were also investigated. The surface temperature of the CNT-coated films rose rapidly up to 2008C within about 40 s when the applied voltage was 110V. The stretchable conductive films have potential as electric heating elements because of their excellent conductive properties."

10. *High piezo-resistive performances of anisotropic composites realized by embedding rGO-based chitosan aerogels into open cell polyurethane foams*

Authors: T.Zhai, L.Verdolotti, S.Kaciulis, P.Cerruti, G.Gentile, H.Xia, M.Stanzione, GG.Buonocore, M.Lavorgna, *Nanoscale (2019) 11, 8835-8844, ISSN 2040-3364, DOI: 10.1039/C9NR00157C*

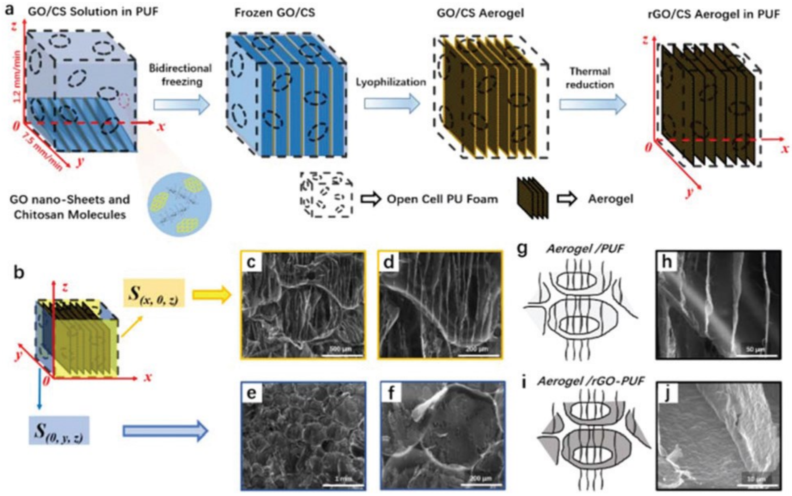


Figure (present in the paper). (a) Schematic preparation of the aerogel/polyurethane foam composite. (b) Scheme of the resulting aerogel/PUF composite with the 3D orthogonal coordinates. SEM images showing the aligned lamellar structure of the aerogel/PUF composites observed from surface S(x, 0, z) at low (c) and high (d) magnifications, and the flat wall structure observed from surface S(0, y, z) at low (e) and high (f) magnifications. Scheme of the aligned lamellar structure of aerogel/PUF (g) and aerogel/rGO-PUF (i) composites. High magnification SEM images show the bonding interface between the aerogel lamellae and the polyurethane foams for the aerogel/PUF (h) and aerogel/rGO-PUF (j) composites.

"Anisotropic aerogel-foam composites were developed by embedding a reduced graphene oxide (rGO)/chitosan aerogel directly into an open-cell polyurethane foam through an in situ bidirectional freezedrying process. The resulting aerogel–foam composites possess both excellent compression-resilience performance and stable piezo-resistive properties due, respectively, to the excellent mechanical properties of polyurethane foams and to the presence of a chitosan-based aerogel loaded with rGO. The latter, indeed, provides outstanding electrical properties due to its conductive and parallel flat lamellar structure. It has been proven that both mechanical and piezo-resistive properties are stable even after 1000 loading/unloading cycles and a reduction of the electrical resistance of about 86% is observed upon the application of a 60% strain. The high sensitivity, long cycling life, and reliable performance over a wide strain range make this unique anisotropic aerogel-foam composite a highly promising candidate for the production of wearable sensors and healthcare monitoring devices."

11. Borate cross-linked graphene oxide–chitosan as robust and high gas barrier films

Authors: N.Yan, F.Capezzuto, M.Lavorgna, GG. Buonocore, F.Tescione, H.Xia, L.Ambrosio, *Nanoscale, 8, 10783-10791* (2016), ISSN 2040-3364, *DOI: 10.1039/C6NR00377J*

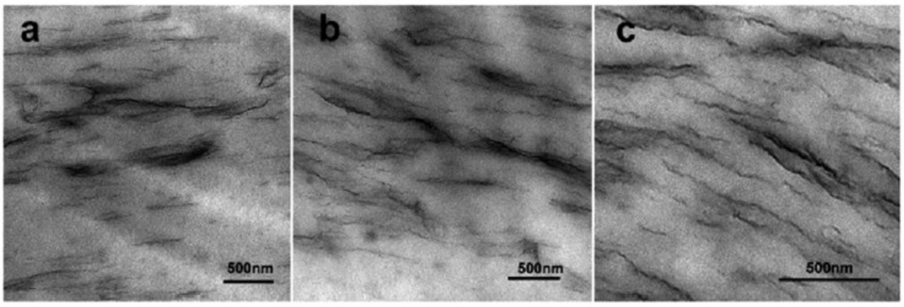
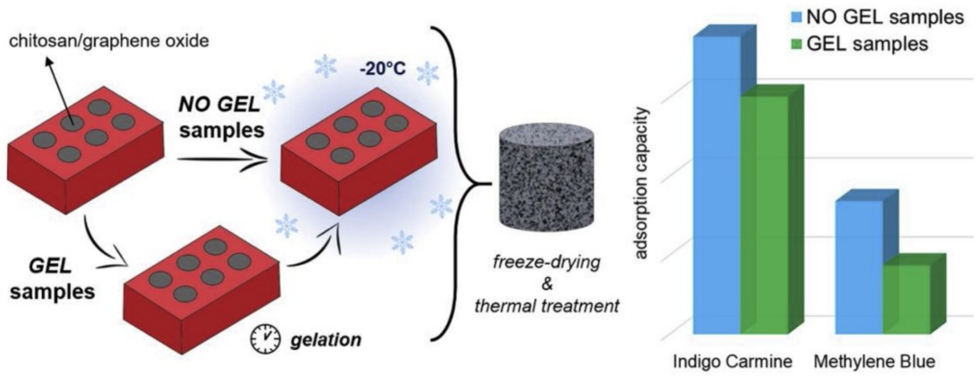


Figure (present in the paper). Transmission electron microscope cross-sectional images of chitosan composite films for (a) CS/GO-T, (b) CS/B/1GO and (c) CS/B/1GO-T.

"Chitosan (CS) is one of the most promising polymers due to its biocompatibility, biodegradability, and natural abundance. However, its poor mechanical and barrier properties make it difficult to satisfy a wide range of applications. Herein, borate ions, originating from the hydrolysis of sodium tetraborate decahydrate (borax), have been used to crosslink chitosan and graphene oxide (GO) nanocomposites. Chitosan films consisting of 1.0 wt% boron and 1.0 wt% GO exhibit a significant improvement in both the toughness and oxygen barrier properties compared to pristine chitosan. In particular, the tensile strength of the samples after thermal treatment increases by ~160% compared to pristine chitosan, whereas their oxygen permeability reduces by ~90%. This is ascribed to the chemical crosslinking between chitosan and GO nanoplatelets through borate ions, as well as the formation of a layered morphology with graphene nanoplatelets oriented parallel to the sample surface. The exceptional robust and high gas barrier film has promising application in the packaging industry. The borate-crosslinking chemistry represents the potential strategy for improving properties of other polymer nanocomposites."

12. Optimization of dye adsorption capacity and mechanical strength of chitosan aerogels through crosslinking strategy and graphene oxide addition

Authors: M.Salzano de Luna, C.Ascione, C.Santillo, L.Verdolotti, M.Lavorgna, G.G.Buonocore, R.Castaldo, G.Filippone, H.Xia, L.Ambrosio, *Carbohydrate Polymers* 211, pp. 195-203, *2019. ISSN: 0144-8617. DOI: 10.1016/j.carbpol.2019.02.002*



Graphical Abstract: Schematization of the procedure for the preparation of aerogels and their effectiveness in adsorption of pollutants.

"Chitosan (CS) aerogels were prepared by freeze-drying as potential adsorbents for water purification, and the effect of the strategy of crosslinking was investigated by varying the amount of crosslinker (glutaraldehyde) and the sequence of steps for the preparation of the aerogel. Two procedures were compared, in which the crosslinking step was carried out before or after the freeze-drying of the starting CS solution. When crosslinking was postponed after the freeze-drying step, the adsorption capacity towards an anionic dye, such as indigo carmine, considerably increased (up to +45%), reaching values as high as 534.4 ± 30.5 mg g−1. The same crosslinking strategy ensured a comparable improvement also in nanocomposite aerogels containing graphene oxide (GO), which was added to enhance the mechanical strength and provide adsorption capacity towards cationic dyes. Besides possessing good mechanical strength (compressive modulus higher than 1 MPa), the CS/GO aerogels were able to bind also cationic pollutants such as methylene blue. The maximum uptake capacity increased from 4.3 ± 1.6 to 168.6 ± 9.6 mg of cationic dye adsorbed per gram of adsorbent with respect to pristine CS aerogels."

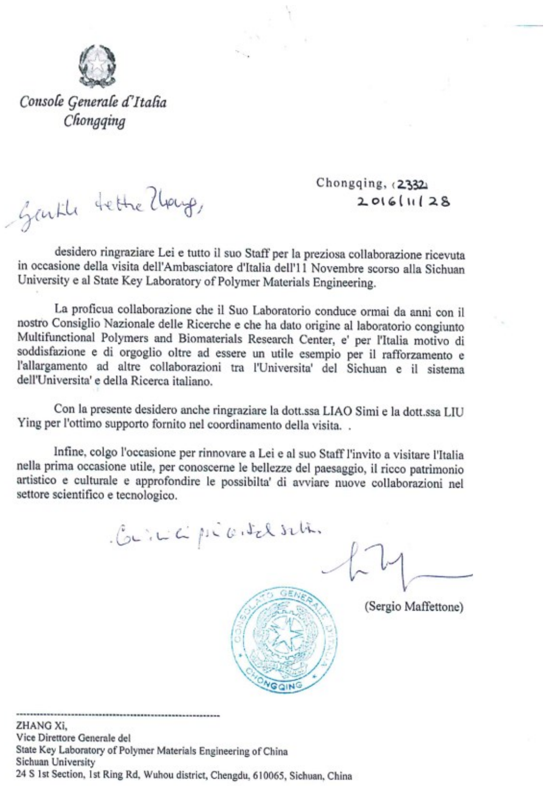
3. **Additional Info concerning the international cooperation**

The scientific collaboration between IPCB-CNR and SKLPME started in 2009; since then, several common papers focused on carbonaceous filler-based polymer nancomposites, co-authorized by Dr. Lavorgna and Prof. Xia, with the participation of several permanent and young researchers from both sides, have been published.
In November 2013 the Multifunctional Polymers and Biomaterials Research Center between the DSCTM-CNR and the Sichuan University (Prot DSCTM 70792 of 20/11/2013) was established. It was inaugurated in May, 2014 in Chengdu by the President of CNR (prof L.Nicolais) and President of Sichuan University, with the participation of delegates from Italian Embassy.
In 2015, a research project leaded by prof Xia funded by MoST (Grant 2015DFA51110) was identified as a key project in the field of Nanotechnology and Advanced Materials in the framework of cooperation agreement between China and Italy Foreign Affairs Ministers.

However, as direct outputs of Joint Lab it is worth mentioning the following three international projects which represent a direct consequence of the research cooperation developed in the framework of the Joint Lab:

1) "Graphene related INnovative 2D materials for Sustainable ENerGetIcs and catalysis (GINSENG)" in the framework of the Progetto Grande Rilevanza, topic: New Materials, with particular reference to Two-dimensional systems and graphene, coordinator prof Granozzi (UNIPD) (come da https://www.esteri.it/mae/resource/doc/2017/11/joint_statement_maeci_nsfc_firmato.pdf). Both IPCB-CNR and SKPLME are partners of the projects (2018-2021) and M.Lavorgna and prf H.Xia are responsible of local research teams;
2) "Graphene and perovskite hybrid materials for energy and environment applications (GRAPE-MAT)- PGR00707", in the framework of the Progetto Grande Rilevanza, topic: Nanosciences and Advanced Materials granted by MAECI. Both IPCB-CNR and SKPLME were partners of the projects (2015-2018) and M.Lavorgna and prf H.Xia were responsible of local research teams;
3) "Multifunctional Graphene-based nanocomposites with robust electromagnetic and thermal properties for 3D-printing application, H2020-MSCA-RISE-2016-734164, Graphene 3D, coordinator Institute of Mechanics, Bulgarian Academy of Sciences (Open Laboratory OLEM). This is a project funded by the European Commission within the EU H2020 "MARIE SKŁODOWSKA-CURIE RESEARCH AND INNOVATION STAFF EXCHANGE" program. The 48-months project commenced on 01/01/2017 with coordination by the Institute of Mechanics, Bulgarian Academy of Sciences (IMech-BAS), the Open Laboratory on Experimental Micro and Nano Mechanics (OLEM). The main goals of Graphene 3D are: A) Develop and fabricate polymer nanocomposite material, doped by a mix of graphene and carbon nanotubes, with multifunctional property enhancement of the host polymer and high improvement potential, for 3D printing application. B) Use the multifunctional nanocomposite material to fabricate optimized 3D printed cellular structures with extraordinary electromagnetic wave absorption, high thermal conductivity, mechanical strength and lightness that have strong potential for application in new generation EM sensors, detectors, or heat exchange devices for power electronics. Both IPCB-CNR and SKPLME are partners of the projects (2018-2021) and M.Lavorgna and prf H.Xia are responsible of local research teams;

As a further result of the impact of research activity carried out within the Joint Lab, it is also worth mentioning the acknowledgement letter signed by the console of the Italian Embassy in Chongqing, who mentioned the strategic importance of the scientific activities between the SKPLME and the CNR in Chengdu:



Console Generale d'Italia
Chongqing

Chongqing, 2332
2016/11/28

Gentile Dottore Zhang,

desidero ringraziare Lei e tutto il suo Staff per la preziosa collaborazione ricevuta in occasione della visita dell'Ambasciatore d'Italia dell'11 Novembre scorso alla Sichuan University e al State Key Laboratory of Polymer Materials Engineering.

La proficua collaborazione che il Suo Laboratorio conduce ormai da anni con il nostro Consiglio Nazionale delle Ricerche e che ha dato origine al laboratorio congiunto Multifunctional Polymers and Biomaterials Research Center, e' per l'Italia motivo di soddisfazione e di orgoglio oltre ad essere un utile esempio per il rafforzamento e l'allargamento ad altre collaborazioni tra l'Universita' del Sichuan e il sistema dell'Universita' e della Ricerca italiano.

Con la presente desidero anche ringraziare la dott.ssa LIAO Simi e la dott.ssa LIU Ying per l'ottimo supporto fornito nel coordinamento della visita. .

Infine, colgo l'occasione per rinnovare a Lei e al suo Staff l'invito a visitare l'Italia nella prima occasione utile, per conoscerne le bellezze del paesaggio, il ricco patrimonio artistico e culturale e approfondire le possibilta' di avviare nuove collaborazioni nel settore scientifico e tecnologico.

(Sergio Maffettone)

CONSOLATO GENERALE D'ITALIA CHONGQING

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An additional result of the action of the Joint Lab, which deserves to be mentioned, is represented by the visibility which was dedicated to the Joint Lab Activity in the framework of the technical team China (Tavolo tecnico Italia-Cina) at the MAECI which was held on April, 24th 2018. In that meeting, dr M.Lavorgna was invited to show the main results of the activity which was established by the CNR with Sichuan Province and the Joint Lab was selected as principal case study for activity on Advanced Materials (between all the cooperation with China).

Again it is worth mentioning the visibility which was deserved to the Joint Lab during the CHINA-ITALY INNOVATION FORUM which was held on December 4th in Milan at the presence of the Italian and Chinese Ministers of the university and research. In that event, the Joint Lab presented some prototypes coming from the research activities as the graphene-based aerogels, the innovative materials for the 3D printing technology, the graphene-based rubber elastomer composites. Always in that event, dr M.Lavorgna and prof Luigi Ambrosio chaired a seminar focused on Advanced Materials to "highlight the important role in our society for their uniqueness in properties and extended application in various industries becoming the basis of modern science and technology. Advanced Materials, both in Italy and China are at the heart of many technological developments that touch our lives and find applications in many strategical sectors such as biomaterials for better health care, sensors for intelligent environment, energy materials for renewable energy and environment, packaging, composites and light alloys for better transportation, and more. This meeting will provide a platform for sharing the last advancement in new materials and innovation in technologies".

Figure. Some panels and the prototypes exposition during the China-Italy Innovation Forum

Finally, it is worth mentioning as a further output of the interaction with the Sichuan University, an agreement established and signed between CNR (the President, prof M.Inguscio) and the Talent Office of Sichuan Province (the President Fan Ruiping) on May 27th 2016, which states the mutual and reciprocal interests in the fields of the culture and scientific research and technological transfer. At the ceremony were present the Chinese delegation and for CNR, alongside with the President, prof Luigi Ambrosio, dr Virginia Coda Nunziante, dr Marino Lavorgna and for the Chinese consulate in Chongqing both dr S.Maffettone and dr F.Nicosia.

Figure. Some of the participants to the meeting at CNR

4. Conclusions

The main scientific results alongside with the several cooperation established between two research teams involved in the Joint Lab, IPCB-CNR and SKPLME-Sichuan University, represent a solid background to further foster additional scientific and cultural exchanges between the institutions and the countries. Dr Marino Lavorgna would also like to thank the Sichuan University and prof Hesheng Xia for supporting the Joint Lab with additional resources with respect to those dedicated by CNR (more or less 50000€ in three years, several young students involved in the common activities). More common projects will be submitted and (let's hope) founded in the future, but both responsible dr Marino Lavorgna and prof Hesheng Xia would like to thanks the National Research Council for having supported the Joint Lab and allowed to obtain great scientific results and realize a bridge connecting several people from both institutions and realize an effective research platform in the panorama of Advanced Materials.