PROGRAMME INSTITUTS ET INITIATIVES

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

iMAT – Institut de Science des Matériaux

Intitulé du projet de recherche doctoral (PRD): I
Investigation of nanoparticle size effect on the properties of nano-reinforced polymers

Directrice ou directeur de thèse porteuse ou porteur du projet (titulaire d'une HDR) :

NOM : BEDOUI Prénom : Fahmi

Titre : MCF HDR

e-mail : fahmi.bedoui@utc.fr

Adresse professionnelle : Université de technologie de Compiègne, Rue Roger Couttolenc
(site, adresse, bât., bureau) CS 60319,

Unité de Recherche :

Intitulé : ROBERVAL

Code *(ex. UMR xxxx)* : A préciser XXX

École Doctorale de rattachement de l'équipe (future école doctorale de la doctorante ou du doctorant) :
ED71

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) :

Sebastian Francisco Navarro-Oliva, 2019, 50%

Co-encadrante ou co-encadrant :

NOM : Lisiecki Prénom : Isabelle

Titre : DR-CNRS HDR OUI

e-mail : isabelle.lisiecki@sorbonne-universite.fr

Unité de Recherche :

Intitulé : MONARIS

Code *(ex. UMR xxxx)* : UMR 8233

École Doctorale de rattachement : ED 388

Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : /

NOM : Ngo Prénom : Anh-Tu

Titre :IE ou HDR non

e-mail : anh-tu.ngo@sorbonne-universite.fr

Unité de Recherche :

Intitulé : MONARIS

Code : UMR 8233

École Doctorale de rattachement : ED 388

Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : /

Co-encadrante ou co-encadrant :

NOM : Kondo Prénom : Djimédo

Titre : **Professeur**

e-mail : djimedo.kondo@sorbonne-universite.fr

Unité de Recherche :

Intitulé : Institut Jean Le Rond D'Alembert

Code : UMR 7190

École Doctorale de rattachement : ED391 Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) :

3 dont 1 Cifre (avec EDF) et 1 cotutelle ;

1- Mr KPOTUFE Kossivi, doctorant inscrit SU en Novembre 2017, en cotutelle avec l'Université de Lomé. Quotité d'encadrement 50 %

2- Mlle BEN EL BARGHIA Ghita, inscrite à SU en Octobre 2019, Quotité 100 %

3- Mr BACQUAERT Goustan, inscrit Novembre 2020, thèse Cifre avec EDF, Quotité d'encadrement 50 %

4- Mr KAMAGATE Banouho, inscrit en Décembre 2920, cotutelle avec l'Université Houphouet Boigny, Abidjan, Côte d'Ivoire.

Cotutelle internationale : Oui, précisez Pays et Université : **Togo, Université de Lomé**

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?
Non

Description du projet de recherche doctoral *(en français ou en anglais) :*

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.

Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées.
Indiquer les publications/productions des encadrants en lien avec le projet.
Préciser le profil d'étudiant(e) recherché.

Short summary

This thesis project is dedicated to the study of the size effects of nanoparticles and their surface chemistry on the macroscopic properties (thermal, mechanical, etc.) of nano-reinforced polymeric materials. These new materials will be developed through the controlled dispersion of nanoparticles of variable diameter ranging from 3 to 20 nm and of variable surface chemistry, which will depend on the polymer matrix used. Recent experimental work carried out previously shows an improvement in the mechanical properties of this class of materials when the size of the particles decreases. However, only sizes greater than 15 nm could be studied. In addition, more recent modeling work (theoretical, atomistic simulations) show that this effect is significantly accentuated when the size becomes less than 10 nm. To date, this effect has not been explored experimentally for such small sizes. In addition, at nanoscopic scales where the main deformation mechanisms are at play, the nature of the interfaces plays an important role. To understand the mechanisms responsible for the observed improvements, the elaboration of model materials with nanoparticles characterized by well-controlled size and surface chemistry as well as an adequate choice of polymer matrix are of great importance. Beyond the effect on the mechanical properties, the materials obtained will allow a more general observation of the size effect: thermal, electrical etc. The project challenge lies on how to link the key parameters at the nano-scale to the observed measurable properties (mechanical, thermal, electric etc.) on rigorously prepared model materials. Neither mechanical engineering nor physical chemistry researchers alone could address these issues. Therefore, a myriad of complementary expertise's will join the project: colloidal synthesis of nanoparticles with appropriate sizes and surface chemistry (Isabelle Lisiecki MONARIS-SU), polymer processing and multi-scale characterization of nano-reinforced polymers (Fahmi Bedoui ROBERVAL-UTC) and micromechanical modeling of nano-reinforced materials (Djimédo Kondo IJLRDA-SU). The micromechanical modeling tools will, when necessary, guide the interpretation of the results obtained and ultimately the determination of the optimal parameters for the development of these new materials.
This PhD. thesis will be intended for master's students who have strong foundation in polymer physical chemistry and are willing to venture outside narrow specialization and excel in interdisciplinary areas

Detailed Ph.D. proposal

Experimental data [1] along with molecular dynamics simulation [2] provided the evidence that unlike common composite materials, nano-reinforced polymers macroscopic properties do not only depend on the volume fraction and heterogeneity shape ratio, but also on the size of heterogeneous species (figure 1).

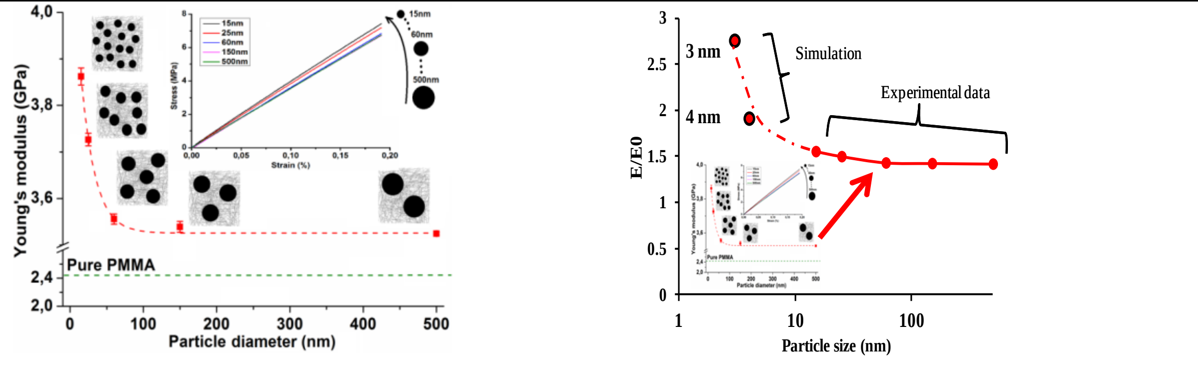

Figure 1: Expperimental [1] and simulation [2] evidence of size effect in nano-reinforced polymers : case of PMMA-SiO_2 composites

The results provided new insight into the interaction modes taking place at key material length scales for simple combination of O-H terminated silica and PMMA polymer. Simulations show that the most important size-related enhancement is expected below 10nm. However, there is no experimental evidence of such an effect (for sizes less than 10nm) in real systems. This is probably due to the difficulties to produce NPs with low size polydispersity in such a range of sizes, with an adequate surface chemistry, while ensuring their good dispersions in polymeric matrix. Nonetheless full understanding of the configuration of rigorously prepared model materials will allow a detailed understanding of the mechanisms involved to explain the drastic improvement in observed macroscopic properties.

MONARIS partner, who has great expertise in colloidal chemistry of inorganic NPs, will be involved in the synthesis of maghemite (*gamma*-Fe_2O_3) NPs by using the thermal-decomposition approach [3]. NPs will be characterized by tunable diameters varying from 3 to 20 nm, and a low size dispersion, less than 10%.

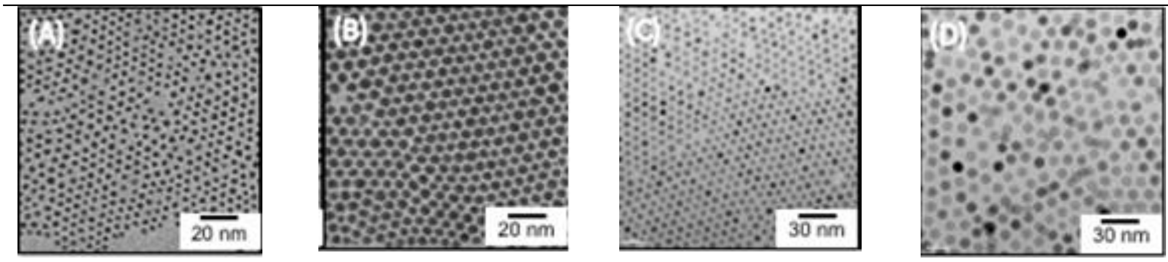

Figure 2 : Metallic Co (cobalt) nanoparticles with a mean diameter equal to (A) 4.5 nm (σ: 11%) and (B) 7.7 nm (σ: 11%). γ-Fe_2O_3 (maghemite) nanoparticles with a mean diameter and size dispersion equal to (C) 8 nm (σ: 6%) and (D) 11 nm (σ: 6%) [3].

These particles will be stabilized thanks to the use of different type of ligands, which chemical nature (polar group and length chain) will be chosen as a function of the nature of the polymer. This will offer the possibility to determine the optimal combination passivated NP/polymer, that is to say the optimal compatibility between these two components, leading to adequate interactions. NP structural study (diameter and stability against aggregation and/or coalescence between the NPs) will be performed by transmission electron microscopy (TEM).

The ROBERVAL laboratory will focus on the one hand on the development of nano-reinforced polymers via the insertion of maghemite NPs into the polymer matrix and on the other hand on the study of their macroscopic properties. The electrospinning platform will be used to guarantee optimal dispersion of NPs regardless of their size. Previous work has made it possible to optimize this process on NPs sizes of 5 nm and 20 nm with a very homogeneous dispersion of the NPs [4]. The characterization of these new materials will be carried out at all key material lengthscales: from the molecular architecture (SAXS, WAXS and SANS) of the matrix, the dispersion of NPs in the matrix (SAXS and TEM) to the macroscopic properties: thermal (DSC TGA, etc.) mechanical (elastic, viscoelastic, viscoplastic etc.). For all the nano-reinforced polymer samples and thanks to the use of superparamagnetic NPs, a special attention will be paid to verify the amount of particles within the polymer as well as the absence of particle coalescence, by the use of a vibrating sample magnetometer (VSM).

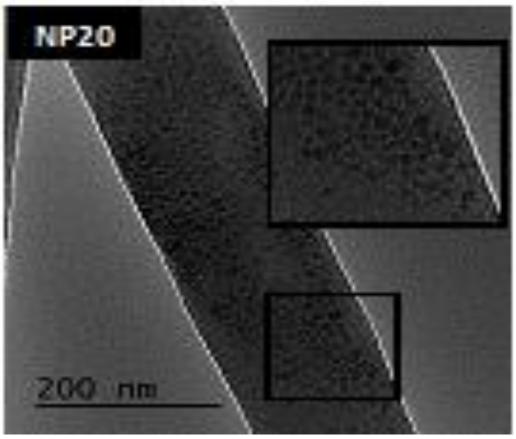

Figure 3 : TEM image of 10 nm Fe_3O_4 nanoparticles embedded in PVDF (polyfluorure de vinylidène) nano-fibers obtained by co-axial electrospinning[4]

The ultimate goal of this characterization step will be to establish unambiguously the possible links between NP size, NP-matrix interaction and macroscopic properties of the materials produced. Particular attention will be paid to *in situ* characterization combining X-ray diffraction and mechanical and / or thermal loading. This will allow access to both the overall response of the material as well as that of the matrix and the NPs separately. This will unambiguously quantify the effect of the size and surface chemistry of NPs on the neighboring matrix. This result is not yet available in the literature. It will allow a fine understanding of the effect of NP size in these materials. Integrating this result into a modeling approach will improve the predictive capacity of micromechanical models.

The Ph.D. thesis will be mostly rooted in experimental approach. The first aim will be to master the entire process of NPs synthesis, the materials processing and the very detailed understanding of the deformation mechanisms induced at the different length-scales. These items are part of the field of materials science and polymer physical-chemistry. In the modeling part of this thesis, we will focus on the use of **already established** and **proven approach** developed in Jean Le Rond D'Alembert Institute.

SORBONNE UNIVERSITÉ

[1] : A. S. Blivi, F Benhui, J. Bai, D Kondo, F Bedoui, Experimental evidence of size effect in nano-reinforced polymers: Case of silica reinforced PMMA, Polymer testing, 56, 337-343, 2016

[2] : Fahmi Bedoui, Andres Jaramillo-Botero, Tod A. Pascal,c and William A. Goddard III, Focus on the deformation mechanism at the interfacial layer in nano-reinforced polymers: a molecular dynamics study of silica - poly(methyl methacrylate) nano-composite, Submitted to Mechanics of Materials January, 2021.

[3] A-T Ngo, S. Costanzo, P-A Albouy, C. Salzemann, Johannes Richardi, I. Lisiecki. Formation of colloidal crystals of dodecanoic acid coated γ-Fe_2O_3: Experimental and theoretical investigations. Colloids and Surfaces A 560, 270 (2019)

[4] Francisco Sebastian Navarro Oliva Léo Picart Christopher Y. Leon-Valdivieso Ahmed Benalla Luc Lenglet Alejandro Ospina Jacques Jestin Fahmi Bedoui, Coaxial electrospinning process toward optimal nanoparticle dispersion in polymeric matrix, Just accepted in Polymer Composites, https://doi.org/10.1002/pc.25924

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cd_instituts_et_initiatives@listes.upmc.fr avant le 20 février.