

Nanoparticle size and surface Chemistry Effects on the dynamic behavior of nano-reinforced polymers: a mechanochemical tuning for more durable materials

NICE-LEEGO

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Objectifs et description du projet

• Intellectual merit

Materials behave very differently at high deformation rates, such as when a bullet hits a polymer fabric or a composite. The scientific objective of the NICE project is to explain this difference in terms of the structural changes that occur at several length scales in polymers and nanocomposites. The technological objective is to enable the development of smart materials to prevent macroscale dynamic damage in polymers and composites used in load-bearing applications. Our innovation will consist of developing an integrated multiscale approach covering synthesis, testing, and modeling. We will develop (1) methods to monitor *in situ* the structural changes of the weakest links, tagged when possible, during deformation, (2) molecular-level techniques that signal impending failure, and (3) processes to fabricate materials that prevent or tolerate local damage before the damage becomes global. The program will also advance the methodology for developing quantitative property-prediction relationships in polymer and nanocomposites toward more durable and secure materials.

• Scientific objectives

The difficulty and the uncertainty in using polymeric materials in crucial components are partly because the nature of microdamage under dynamic loading is not fully understood¹. The difficulty is mostly related to the complex hierarchical structure, which distinguishes polymers and nano-reinforced polymers from other materials.

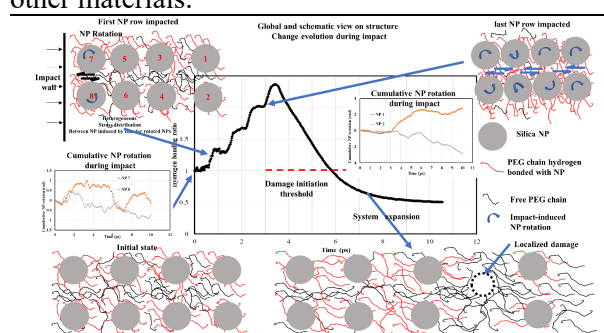


Figure 1: Sequence of hydrogen bonding kinetics and impact-wave-induced damage on PEG-Silica nanocomposites (work in progress)²

Unlike composite materials, nano-composite behavior depends on the size of the reinforced nanoparticles (NPs). By reducing NP size, we drastically increase the interfacial interaction between the NPs and the polymeric matrix³. Interfacial interaction through hydrogen bonding in the case of PEG-Silica systems turns out to be the driving parameter of the material damage during impact. The loss of the hydrogen bonds induces rotation and counter-rotation of the NP which in turn induces a material shear flow between NP leading to the early initiation of cavitation¹ (figure 1). In this

case, we did not have any control over the density of the hydrogen bonding energy. In this proposal, we target to work on binary systems where the hydrogen bonding density can be controlled. Therefore, we can tune the system to cover a wider range of configurations from weak to strong interfacial interaction. All this to answer one fundamental question: ***Does weaker or stronger interfacial interaction delay or accelerate material damage under high strain rate loading?***

• Research tasks

The interfacial interaction between the NPs and the surrounding matrix is a key parameter that governs the nano-composite properties. As polymer matrix and surface modifier, poly(2-hydroxyethyl methacrylate) pHEMA will be used due to its peculiar structure carrying a hydroxyl as well as an ester group both capable of H-bond interaction (figure 2). Compared to pMMA, which is only capable of accepting H-bonds *via* its

¹ E.M. Arruda, M.C. Boyce, R. Jayachandran, Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers, *Mech. Mater.*, 19 (2) (1995), pp. 193-212

² Qiuyun Yin, Fahmi Bedoui, Andres Jaramillo-Botero, Zhan Wange, Xianqian Wua, Chenguang Huang, William A. Goddard III; Transient tension-activated solidification of dense suspensions; work in process of submission to *Physical Review*.

³ Francisco Sebastian Navarro Oliva Mehdi Sahihi Luc Lenglet Alejandro Ospina Erwann Guenin Andres Jaramillo-Botero William A. Goddard III Fahmi Bedoui, Nanoparticle size and surface chemistry effects on mechanical and physical properties of nano-reinforced polymers: The case of PVDF-Fe₃O₄ nano-composites, *Polymer Testing* Volume 117, January 2023, 107851

ester group, pHEMA will then offer the opportunity of raising the interaction with silica, for a possibly more efficient energy dissipation *via* the complex interplay of H-bond *formation-breaking-exchange*.

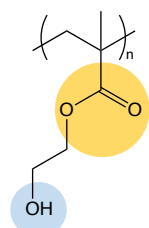


Figure 2: Structure of pHEMA representing the ester (orange) and hydroxyl (blue) moieties.

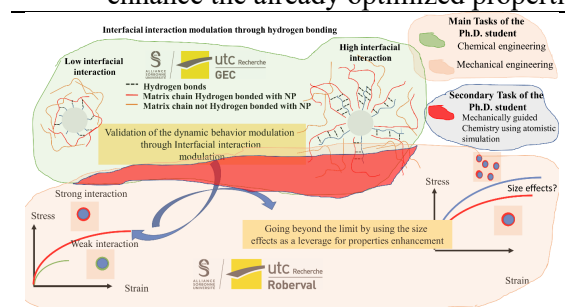
The project will thus deal with comparing the effect of size (ex 11 nm silica versus 70 nm silica) and surface functionalization (i.e. base silica versus pHEMA-grafted silica) of silica NPs used as fillers in pHEMA/SiO₂ nanocomposites. This silica will also be used for surface functionalization, following a conventional protocol consisting in (1) surface functionalization with APDMES, (2) coupling of an NHS-activated RAFT agent (3) RAFT polymerization of HEMA as reported for instance by Benicewicz and co-workers⁴⁵. Using RAFT polymerization will also allow controlling the degree of polymerization (DP) of pHEMA, thus tuning the molecular weight (MW) of the grafted chains. Bare silica as well as pHEMA-grafted silica will then be dispersed in a pHEMA matrix by either electrospinning or solvent casting.

A full set of characterization techniques will be available to explore the materials behavior at the different length scales: XRD, FTIR, DLS for materials microstructure, and DMA for the dynamic behavior of the polymer and the composite systems. Available modeling routines will be put into practice to help the student understand the observed behavior and also guide his material preparation methodology.

• Project organization

The main questions we would like to answer are:

- 1- How does the hydrogen bonding between the NP and the matrix modulate the material's performance under high strain rate loading, and how can this be monitored?
- 2- Could we use the grafted chain length and nanoparticle size as leverage to go beyond the limit and enhance the already optimized properties?



Proposed interfacial molecular architecture and size effects to modulate the interaction strength between NP and the matrix.

The Ph.D. student's tasks within the proposal will be:

- 1- **Synthesis of the NP with optimized surface chemistry**
- 2- **Optimize the process to fabricate samples made of NP-polymer mixes where the NPs are well dispersed**
- 3- **Physico-chemical characterization of the materials**
- 4- **Contribution to the modelling of the material**

The Ph.D. student will have access to well-established simulation tools to help him/her understand and/or guide his experimental results. The student will not be required to develop the simulation tools, he/she will be a wise user and will be assisted by his advisor and postdocs working on a close topic. The hired student will benefit from expert advisors in polymer chemistry (Karsten Haupt) and nano-reinforced polymer mechanics (Fahmi Bedoui). In addition, the hired student will benefit from strong interaction with the most knowledgeable research group (MSC CalTech W.A. Goddard III group) in atomistics through the LEEGO chair program.

Positioning of the project within the objectives of the initiative MSTD

The use of polymeric-based materials for load-bearing applications is desirable due to the weight reduction this will imply. However, unless we can predict the behavior of such materials so that we can prevent catastrophic failure, polymeric-based materials will be automatically excluded. Therefore, our target is to develop approaches that could enable the development, through full understanding of this class of materials, of durable and secure technological devices. From this perspective, this proposal fully complies with the MSTD initiative research philosophy.

⁴ *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; 4 ed.; John Wiley and Sons: New York, 1999.

⁵ Zheng, Y.; Huang, Y.; Abbas, Z. M.; Benicewicz, B. C. Surface-Initiated Polymerization-Induced Self-Assembly of Bimodal Polymer-Grafted Silica Nanoparticles Towards Hybrid Assemblies in One Step. *Polym. Chem.* **2016**, *7*, 5347–5350.