



Séminaire du 11 avril 2024



Mécanique et microstructure
des polymères

Photo-curable Thermosets with Microstructure Formed by Polymerization-Induced Phase Separation

Catalin R. Picu^a

^a Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Photopolymerization-induced phase separation (photo-PIPS) is used in conjunction with an acrylic-based polymeric network with various additives for the purpose of creating microstructure and improving the thermoset toughness. Additive-rich sub-domains form immediately after the onset of polymerization and their size decreases with continued exposure. The microstructure is probed by monitoring the sample transmittance and by direct microstructural observations. A significant increase of toughness is observed when using as additives epoxy-based end-group terminated PDMS (hydroxy-terminated PDMS (OH-PDMS) and diglycidyl ether-terminated PDMS (epoxy-PDMS)). These are crosslinked through a thermal step after UV exposure and phase separation to create nanoscale elastomeric subdomains within the thermoset. Enhanced toughness is not obtained when using PDMS or polypropylene glycol (PPG) as phase separating additives. The reaction kinetics and the resulting mechanical properties are evaluated for various sets of process and material parameters.

Mécanismes de rupture séquentielle d'un tri-couche de polymères sous flexion 4 points dynamique rapide, pour application au déploiement d'airbags

Gaultier LEFAY ^a, Nicolas AMOUROUX ^b, Christophe GERMAIN ^c, Grégory MARTIN ^b, Cristian OVALLE-RODAS ^a, et Lucien LAIARINANDRASANA ^a

^a Mines Paris, Université PSL, Centre des Matériaux (MAT), UMR7633 CNRS, 91003 Évry, France

^b Westlake Compounds Holding, 1bis rue Maurice Hollande, 51100 Reims, France

^c Samvardhana Motherson Reydel Companies, Rue Léon Duhamel, 62440 Harnes, France

Mots-clés : Impact, corrélation d'images, ouverture d'entaille, faciès de rupture

Le déploiement des airbags dans l'industrie automobile est strictement contrôlé pour assurer la sécurité des passagers en cas d'accident. La libération du sac airbag dans l'habitacle est conditionnée par la rupture maîtrisée de trois matériaux polymères superposés constituant le tableau de bord : un support en polyoléfin thermoplastiques (TPO) muni d'une entaille (canal de frappe), une mousse en polyuréthane (PU) et un revêtement en polychlorure de vinyle (PVC) plastifié. Pour que les essais en laboratoire soient représentatifs des conditions réelles (vitesse d'impact, températures de -25 à 85 °C, mêmes séquences de déformation et de rupture), deux campagnes d'essais à l'échelle 1 instrumentés ont été réalisées. Ceux-ci ont ainsi permis de mesurer des vitesses d'impact de l'ordre de 23 m/s, et ont servi de base pour la mise en place d'essais de flexion 4 points en laboratoire sur éprouvettes TPO seules et tri-couches (PVC+PU+TPO). Lors de ces essais nous avons pu observer les mécanismes de rupture grâce aux données d'une caméra vidéo rapide (Photron FASTCAM, 30 000 à 100 000 Hz) et suivre l'ouverture d'entaille (Notch Opening Displacement, NOD) sur le TPO seul ainsi que sur le TPO dans le système tri-couche, pour construire et analyser les courbes Force-NOD. Des observations fractographiques ont également été réalisées pour qualifier le type de rupture rencontrée.

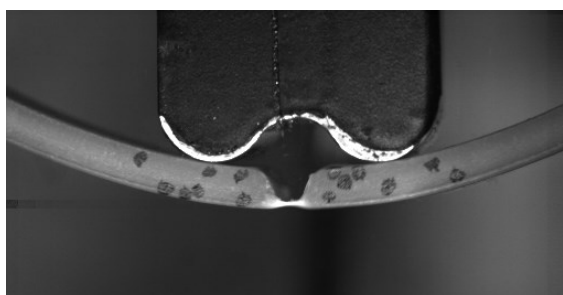


Figure 1 : Flexion 4 points sur éprouvette TPO à 23 m/s et 23 °C

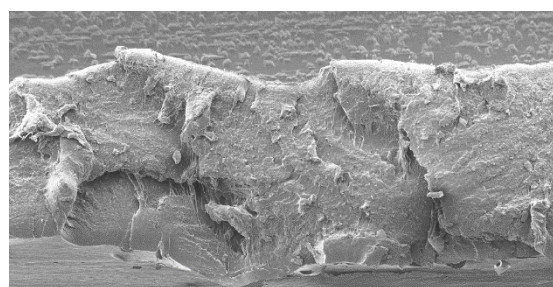


Figure 2 : Micrographie MEB du TPO après rupture à 23 m/s et 23 °C.

Effects of clay filler contents and a high voltage electric field on the microstructure and mechanical response of 3D-printed PVDF composites

Nelly PONS^{a,b}, Séverine A.E. BOYER^a, Alain BURR^a, Cristian OVALLE^b, Karim INAL^a, Lucien LAIARINANDRASANA^b

^a Mines Paris, PSL University, Centre for material forming (CEMEF), UMR 7635 CNRS, 06904, Sophia Antipolis, France

^b Mines Paris, PSL University, Centre for material sciences (MAT), UMR 7633 CNRS, 91003, Evry, France

Nelly.Pons@minesparis.psl.eu

PVDF is a smart polymer that exhibits electroactive properties in its β and γ phases. Both the processing and the addition of fillers can induce this phase transition, starting with the non-electroactive α phase. In this study, PVDF and PVDF-clay composites (0.5, 2.0, and 10 wt.%) were processed and shaped using an Ender3 v2 3D printer. Along with the four material combinations, the printing orientation (longitudinal or transverse) and the use of a high voltage electric field were varied in the study. The obtained specimens were one-layer deposited films (100 μm thick) with a dog-bone geometry. The bead width ($\sim 400 \mu\text{m}$) was determined by using optical microscopy, and using SEM observations, the multiscale anisotropy (microstructure and macrostructure) has been underlined. Engineering stress-strain curves, from repeated uniaxial tensile tests on each configuration, allowed retrieving characteristics parameters: the Young's modulus, the yield stress, and the stress at break and the corresponding deformations. This study highlights on the evolution of these parameters with respect to the clay filler content as well as to the addition of a high electrical field during the 3D printing process.

High T_g vitrimers. Time-temperature superposition rheology provides insight on the network topology

Paolo EDERA^a, Selene CHAPPUIS^a, Michel CLOITRE^a, Francois TOURNILHAC^a

^a C3M Lab, ESPCI, Paris

Polymeric materials are classically divided in two families: *thermosets* and *thermoplastics*. For the first one, the shape fixity is provided by a permanent space-spanning network, with covalent crosslinks. For the second one, the shape fixity is given by weaker bonds, raising the temperature the bonds are undone, the material loses its rigidity and can be remodeled in a new shape.

Vitrimers are polymeric networks where the crosslinks are at the same time covalent and exchangeable. This unique combination of microscopic mechanisms makes them a promising class of materials that combines good shape fixity at low temperature, and reprocessability above a certain activation temperature T_v .

Roughly speaking we can say that at low temperatures (below the glass transition temperature T_g) the response is dominated by the friction between polymer chains. Above T_g , rubbery behavior, with a transient elastic plateau is observed. And at even higher temperatures, above T_v , where the link-exchange reaction is activated, stress-relaxation is observed.

The thermomechanical properties of such systems (the values of the elastic moduli, the T_g and the T_v , the viscosity in the final stress relaxation regime, *etc.*) stem from a complex interplay between dynamic link exchange, the polymer chains relaxations, and the network architecture (topology).

In this seminar I will show how torsional rheology can be used to thoughtfully characterize vitrimers mechanical behavior from room to processing temperature. Secondly, I will show how the mechanical relaxation spectrum can be modeled to have insight on the microscopic network topology^[1].

References :

[1] EDERA, Paolo, et al. Resolving the relaxation complexity of vitrimers: time-temperature superpositions of a time-temperature non-equivalent system. *Polymer* (2024) 126916
<https://doi.org/10.1016/j.polymer.2024.126916>

Exploring the sol/gel transition of thermosensitive hydrogels using time-resolved scattering techniques

Louanne POMMIER^{a,b}, Phuong-Anh DANG^{a,c}, Sophie NORVEZ^a, Stefano AIME^a, Laurent CORTÉ^{a,b}, Michel CLOITRE^a

^a Molecular, Macromolecular Chemistry and Materials, ESPCI Paris, CNRS, PSL University, France

^b Centre des Matériaux, MINES Paris, CNRS, PSL University, France

^c Équipe de Recherche sur les Relations Matrice Extracellulaire-Cellule, CY Cergy Paris Université, France

Thermosensitive hydrogels which are liquid at 20°C and solidify at body temperature are interesting systems for encapsulation and delivery of cells. They are studied as 3D matrices for in vitro models or injectable vectors for tissue engineering.^[1] A fine and robust control of their mechanical and microstructural properties is essential to ensure the proper survival and activity of cells.^[2] In this respect, scattering techniques are valuable tools to investigate the multiscale microstructure of such systems and their formation mechanisms.

In this work, we study mixtures of chitosan and glycerophosphate salts (CS/βGP). These materials can be held liquid at neutral pH and room temperature while exhibiting a rapid sol/gel transition at 37°C.^[3] For low enough concentrations in chitosan (0.5 - 1 wt%), the sol/gel transition of these mixtures results from a phase separation and produces a porous connected structure recalling that of colloidal gels with macroporosities having sizes of the order of 1 - 10 μm.^[4]

Here, we combine time-resolved small angle X-ray (SAXS) and light (SALS) scattering to investigate the emergence of the microstructure of CS/βGP hydrogels upon heating. On the mesoscopic scale, SALS reveals the formation of a heterogeneous microstructure of typical size 1 - 10 μm which can be related to the phase separation into polymer-rich and polymer-poor domains. At a smaller level, SAXS experiments on a synchrotron source shows a further structuration in polymer-rich domains of characteristic size 1 - 10 nm. We explain this structuration by the neutralization of CS chains upon heating, which induces their collapse and aggregation through hydrophobic interactions. Moreover, in situ SAXS experiments in a rheometer show that the structuration coincides with sol/gel transition. This multi-scale and time-resolved analysis provides keys to understanding the molecular and microscopic mechanisms at the origin of the emergence of the microstructural and mechanical properties of CS/βGP hydrogels.

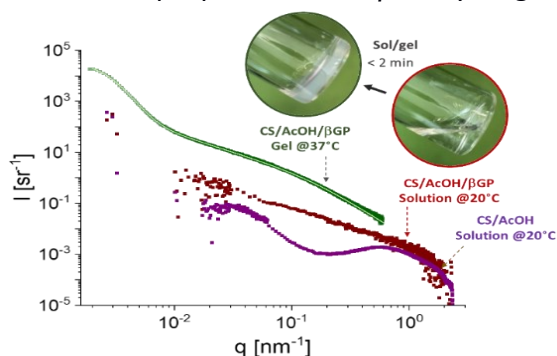


Figure 1: CS/AcOH and CS/AcOH/βGP solutions and gel by SAXS.

Références :

- [1] Zhou *et al.*, *Carbohydr Polym.* **2015**, *117*, 524-536
- [2] Annabi *et al.*, *Tissue Eng. Part B Rev.* **2007**, *16*, 371-383
- [3] Chenite *et al.*, *Biomaterials.* **2000**, *21*, 2155-2161
- [4] Dang *et al.*, *Carbohydrate Polymers.* **2022**, *277*, 118836



Vous pouvez nous contacter :

- Par courrier postal :

Centre des Matériaux Pierre-Marie Fourt
Mines Paris
CNRS UMR 7633, BP 87 91003 Evry, France

- Par téléphone : +33 (0)1 60 76 30 00
- Par courrier électronique : semteam@mat.mines-paristech.fr
- Site web : <https://www.mat.minesparis.psl.eu/seminaires/>

Equipe séminaire :

Clémence PINOT
Samuel EL HADDAOUI
Louise MARIOTON
Ayoub EL- HABYB
Mohammed FARTAS
Eliott DEGUILLES