

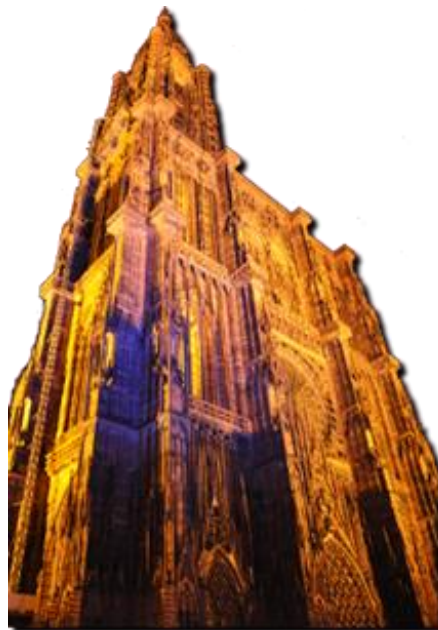


19^{ème} Journée Scientifique GFP Section Est

(Groupe d'Etude et d'Application des Polymères)

Strasbourg 12 Juin 2024

A l'Institut Charles Sadron



Présentation

La section du Groupe Français des Polymères (GFP) Grand-Est couvre les anciennes régions Alsace (Strasbourg, Mulhouse), Lorraine (Metz, Nancy, Epinal) Franche-Comté (Besançon) et Champagne-Ardenne (Reims), en s'étendant également au Luxembourg.

Chaque année la section organise une journée scientifique. Ce rendez-vous annuel concerne tous les polyméristes, thésards, chercheurs académiques et industriels du secteur des polymères et matériaux polymères. Cette journée a pour objectif de promouvoir et favoriser le développement des interactions dans ce domaine multidisciplinaire qui va de la chimie en passant par la physico-chimie, la physique et la mécanique, jusqu'aux procédés de polymérisation. Cette année la journée se tiendra le 12 Juin 2024 à l'Institut Charles Sadron (ICS) de Strasbourg.

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Contact: gfp@ipcms.unistra.fr

Tél: 03 88 10 71 45

Lieu: Institut Charles Sadron (ICS)- Bâtiment 75

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67034 Strasbourg Cedex 2

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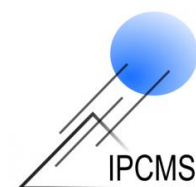
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Programme

8h30-9h00	Accueil des participants	
9h00-9h15	Khalid Ferji , Président du GFP Est Daniel Grande , Directeur de l'ICS	Ouverture et présentation de la journée
9h15-9h45	Conférencière invitée Jannick Rumeau-Duchet IMP Lyon	How thermosetting based composites could contribute to circular economy ?
9h45-10h05	Lorenzo Marradi , ICS & Soprema Strasbourg	Mechanical bond driven plasticization of PVC
10h05-10h25	Mariame Ezzehar , IS2M Mulhouse	Study of the surface functionalisation of composite substrates by plasma polymerisation to produce composite-elastomer assemblies
10h25-10h55	Pause – Session POSTERS	
10h55-11h15	William Fall , LPS Orsay & ICS Strasbourg	Branches, tie-chains and entanglements in polyethylene single crystals under uniaxial tensile strain
11h15-11h35	Mehdi Khoulood , Polytech. Univ. & IMED lab. Maroc, LPCM Nancy	Smart bio-based materials for enhanced agricultural fertilizer efficiency via pH responsiveness
11h35-11h55	Thomas Bugnard , ICS Strasbourg	Elastomère acrylate comprenant une phase cristalline
11h55-12h15	Laurent Farge , LRGP & LEMTA Nancy	Analyse des propriétés physiques et mécaniques de vitrimères à précurseur PBT
12h15-13h45	Pause Déjeuner Buffet	
13h45-14h15	Conférencier invité Christophe Wilmort MayFair Village, Aubagne	Quel impact de l'IA sur la R&D et l'industrie des polymères?
14h15-14h35	Capucine Loth , ICS & Inserm Strasbourg / ITODYS Paris	Ion triggered self-assembly of antibacterial Fmoc-based tripeptide: physical chemistry and MD simulation
14h35-14h55	Christophe SOARES , TA Instruments, Guyancourt	Comparison of the Ozawa-Flynn-Wall method with temperature-modulated thermogravimetry for lifetime predictions
14h55-15h15	Isabelle Royaud , IJL Nancy & M. Gandhi Univ. India	Development of bio-filler-interfaced electrospun PVDF based nanogenerator for mechanical energy harvesting
15h15-15h45	Pause – Session POSTERS	
15h45-16h05	Mehdi Vahdati , ICS, Inserm & Dentaire Strasbourg / Saint-Gobain Recherche Aubervilliers	Quasi-complex coacervates: single-phase viscoelastic analogues of complex coacervates
16h05-16h25	Valentine Lavaux , IS2M Mulhouse	Bio-based epoxy curing in mild conditions using catalytic systems: towards high performance materials
16h25-16h45	Axel Pinabiaux , ICS Strasbourg	Templated-synthesis of supramolecular polymers
16h45-17h00	Remise du prix de la meilleure communication orale – Clôture de la journée	

Communications orales

HOW THERMOSETTING BASED COMPOSITES COULD CONTRIBUTE TO CIRCULAR ECONOMY ?

Shi Ting, Wenyong Zhang, Gabriel Perli, Jean-François Gérard, Sébastien Livi,

Jannick Duchet-Rumeau

Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon,
Université Jean Monnet, F-69621 Villeurbanne Cédex, France

Thermosetting materials like epoxy constitute a new type of waste source since these materials have appeared in many industrial applications with relatively long life spans such as structural composites for aeronautics or automotive, coating or isolating materials for electronic applications. In this talk, different pathways will be described to show how these thermosetting polymers could contribute to the circular economy : i) The epoxy prepolymer was re-designed to be environmentally friendly while integrating the end of life : In this work, we have designed and engineered for the first time degradable multifunctional epoxy with a ionic liquid backbone [1] ; ii) The formulation of epoxy polymer was rethought by using clean process such as UV polymerization : cycloaliphatic epoxidized imidazolium ionic liquids were successfully synthesized with high yields and appear as promising candidates to replace bisphenol A derived polymers [2]; iii) The self-healing of epoxy materials can also be an alternative to the recycling by having the ability to heal the cracks and to prolong the life time. Two pathways of self healing used for repairing the carbon fiber/epoxy matrix composite. The first route will describe the effect of reversible bonds introduced in the interphase of carbon fiber reinforced composite in order to generate an ability of interfacial self-healing that will be evaluated by single fiber micro-droplet pull-out testing. The second route is the embedding of microcapsules into epoxy matrix which are previously filled with liquid healing agent [3]. All these epoxy networks were deeply investigated in terms of thermal and mechanical properties, hydrophobicity, fire resistance and shape memory to be sure to develop high-performance environmentally friendly new epoxy materials for the continuous progress of a circular economy.



Different routes contributing to circular economy of polymer materials

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Study of the surface functionalisation of composite substrates by plasma polymerisation to produce composite-elastomer assemblies

Mariame Ezzehar¹, Clara Esteve¹, Aissam Airoudj¹, Gautier Schrodj¹, Vincent Roucoules¹, Florence Bally-Le Gall¹

¹IS2M, UMR 7361 CNRS, Université de Haute-Alsace, F-68057 Mulhouse Cedex, France

The conventional approach to improving adhesion between composite materials and elastomer often requires the use of solvent-based adhesion primers, containing dangerous substances classified as CMR (carcinogenic, mutagenic and reprotoxic). Motivated by the search for more environmentally-friendly practices, and in compliance with REACH regulations, an environmentally-friendly surface functionalization strategy has been developed. Plasma polymerization, a solvent-free technique for functionalizing surfaces [1], has been identified as a promising alternative to the use of adhesion primers. Indeed, it has already been demonstrated that plasma polymerization can improve adhesion between different materials such as metal and elastomer [2] [3] [4]. The aim of this study is to apply this technology to adhesion between composite materials and elastomers. For this reason, we are developing a plasma polymerization functionalization method that generates functional groups able to react with rubber, creating covalent bonds between substrate and rubber during crosslinking. More precisely, plasma polymers containing anhydride groups have been deposited on composite substrates and post-modified by aminolysis in vapor phase to graft alkene groups. Surface functionalization has been characterized by FTIR-ATR and contact angle measurements, and adhesion properties by a 90° peel test. In addition to improving adhesion between these two materials, this study aims to better understand the influence of different plasma polymerization functionalization parameters on adhesion mechanisms.

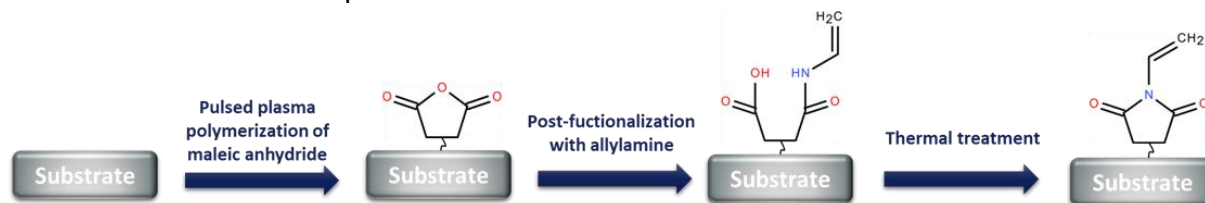


Figure 2: Representation of the different substrate functionalization stages

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Branches, Tie-Chains and Entanglements in Polyethylene Single Crystals under Uniaxial Tensile Strain

William S. Fall,¹ Jörg Baschnagel² & Hendrik Meyer²

¹ Laboratoire de Physique des Solides, CNRS, Université Paris-Saclay, Orsay, France;

² Institut Charles Sadron, Université de Strasbourg & CNRS, Strasbourg, France.

Résumé

Short chain branched, bimodal polyethylene resins possess slow crack growth resistance, making them ideal for hazardous applications such as high-pressure pipelines. Flaws induced during manufacture can result catastrophic failure but bimodal PE resins are relatively resistant. The relationship between chain architecture and the mechanical properties of such resins is however poorly understood. Using coarse-grained molecular dynamics simulations and a united-monomer model of PE¹, single well-aligned multi-lamella PE crystals are grown, using self-seeding and drawn to mimic uniaxial tensile testing. During deformation, the crystallinity, tie-chain and entanglement content are monitored and correlated with the stress-strain curves. In addition, the dependence of all metrics on the deformation rate and drawing direction are investigated. Such a study is only possible with homogeneously aligned PE crystals². The elastic modulus is strongly dependent on the direction of deformation and at large strains, the inclusion of branches prevents disentanglement, shear induced alignment, chain sliding and craze. Peak stress is found to be proportional to the change in number of tie chains³. In the equivalent multi-domain systems, grown by continuous-cooling, such trends are almost completely hidden. Finally, the motivation for coarse-grained models of more complex polymers will be discussed and how simple machine learning algorithms can aid in their development.

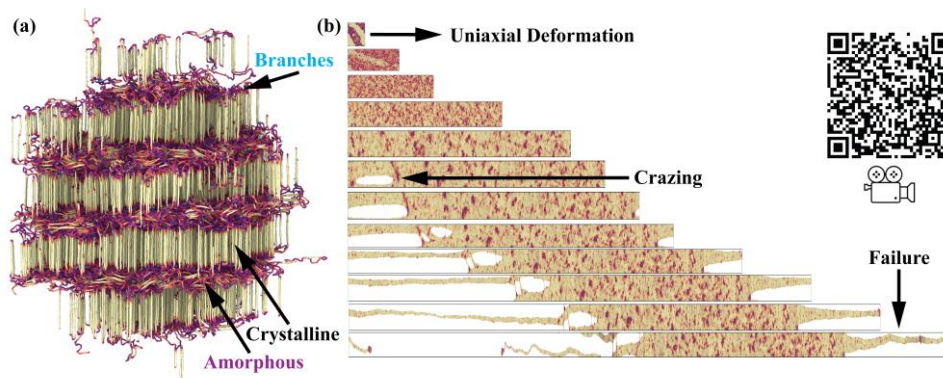


Figure. (a) Aligned single PE crystal grown via self-seeding (b) the PE crystal in (a) drawn uniaxially. Beige and purple coloured regions are crystalline and amorphous respectively.

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Smart Bio-based Materials for Enhanced Agricultural Fertilizer Efficiency via pH Responsiveness

Mehdi Khouloud,^{1,2} Redouane Beniazza,³ Mohamed Lahcini,^{2,4} Khalid Ferji,¹ Jean-luc Six,¹

¹ CNRS, LCPM, F-54000, Université de Lorraine, 1 rue Grandville, Nancy 54001, France

² Department of Chemical and Biochemical Sciences, Green Process Engineering (CBS), University Mohammed VI Polytechnic, Benguerir 43150, Morocco

³ Institute of Science, Technology & Innovation (IST&I), Mohammed VI Polytechnic University (UM6P), Ben Guerir 43150, Morocco

⁴ Cadi Ayyad University, Faculty of Sciences and Technologies, IMED Lab, 40000 Marrakech, Morocco

Résumé

The urgent need for more efficient agriculture in order to increase crop yields and ensure food security has highlighted the importance of optimizing fertilizer usage. Addressing this, our study introduces an innovative approach utilizing pH-sensitive copolymers derived from bio-based raw materials. We use Chitosan (CS), a biopolymer derived from chitin, in association with ϵ -caprolactone to synthesize grafted copolymers (Chitosan-g-poly(ϵ -caprolactone) (CS-g-PCL). These copolymers have tunable physical properties and pH-sensitivity suited for agricultural applications. The primary objective is to harness pH fluctuations near plant roots, which induce localized acidity from cation exchanges, thereby stimulating the CS-g-PCL based fertilizer for targeted nutrient release.

To preserve the pH-responsive amine functions of chitosan, they are initially protonated. Subsequent in-situ ring-opening polymerization of ϵ -caprolactone (CL) is initiated by the hydroxyl groups of chitosan in the presence of a catalyst. This method allows preferential grafting of PCL from the chitosan, preserving the copolymer's pH-sensitive amine functionality.

Our strategy not only maintains the copolymer's pH-sensitivity but also enhances its physicochemical properties critical for controlled nutrient release. We employ a bulk polymerization process varying the ratios of chitosan to ϵ -caprolactone to produce copolymers that effectively combine hydrophilic (protonated chitosan) and hydrophobic (PCL grafts) components. The successful preservation of amine functionality highlights the potential of this approach in developing smart materials for targeted and efficient fertilizer delivery in agriculture.

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Elastomère acrylate comprenant une phase cristalline

Thomas Bugnand

Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg

Résumé

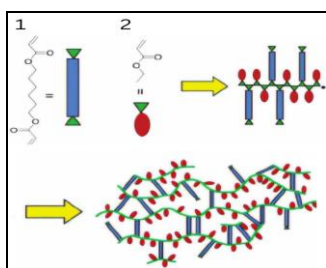
Les matériaux polymères acrylates fonctionnels sont très largement utilisés dans l'industrie en raison de leur grande variété chimique et de leur large spectre de propriétés. Ils peuvent donc trouver de multiples applications.

Dans cette étude, nous nous concentrons sur la synthèse et la caractérisation de composites élastomères acryliques comprenant une phase semi-cristalline. Ces matériaux jusqu'ici très peu décrits dans la littérature offrent pourtant de réelles opportunités d'applications. Il s'agit donc dans ce travail de comprendre l'influence du taux de cristallisation dans le matériau. L'intérêt est porté sur leurs propriétés thermomécaniques originales.

L'objectif principal de ce travail est donc de synthétiser tout d'abord des réseaux d'élastomères semi-cristallins dont la température de transition vitreuse est maintenue pratiquement constante tout en contrôlant précisément leur taux de réticulation et de cristallisation. Ceci est réalisé en utilisant des mélanges de monomères acryliques mono- et difonctionnels en proportions variables.

Le poly(éthylène glycol) méthyl éther acrylate avec une longue chaîne d'éthylène glycol (PEGMEA9) est utilisé pour former le squelette semi-cristallin. Sa copolymérisation avec l'acrylate de butyle (BA) ou l'acrylate de 4-hydroxybutyle (HBA) utilisés comme espaceur entre les chaînes de PEGMEA9 permet d'ajuster le ratio de la phase semi-cristalline. Le poly(éthylène glycol) diacrylate est utilisé comme réticulant. Son taux d'incorporation dans la chaîne principale permet de contrôler finement la masse molaire moyenne entre deux nœuds de réticulation. L'ajout de dodécane thiol comme agent de transfert permet de moduler davantage la densité de réticulation et d'améliorer la flexibilité.

L'élaboration des composites avec ces matériaux spécifiques est réalisée par incorporation de charges minérales sous forme de poudre de dimensions parfaitement connues (tailles moyennes et dispersion). La variation des propriétés mécaniques par l'ajout de ces charges solides est précisément étudiée.



1. Monomère Di acrylate
2. Monomère Mono acrylate

Figure 1 Formation d'un réseau par polymérisation radicalaire des monomères (di)acrylates

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Analyse des propriétés physiques et mécaniques de vitrimères à précurseur PBT

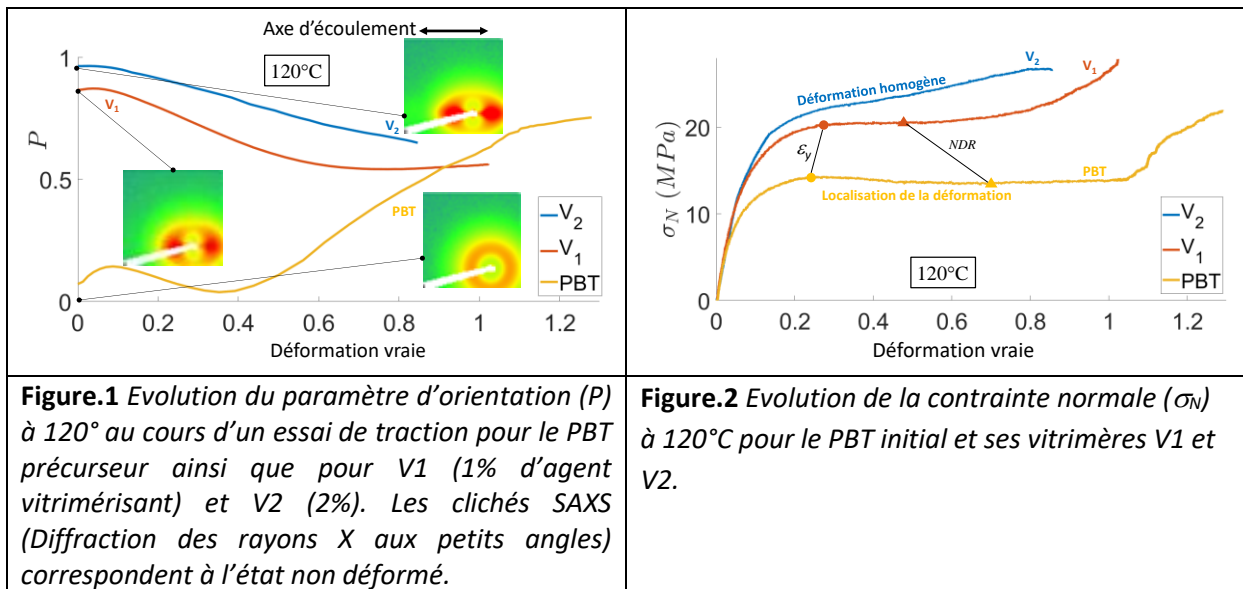
Quentin-Arthur POUTREL², Laurent FARGE¹, Sandrine HOPPE², Stéphane ANDRÉ²

¹Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

²Université de Lorraine, CNRS, LEMTA, F-54000 Nancy, France

Résumé

Nous avons étudié les conditions de synthèse ainsi que les propriétés physiques et thermo-mécaniques de vitrimères à précurseur PBT (polytéréphtalate de butylène). Des mesures obtenues par rhéométrie ont permis de mesurer l'augmentation de la viscosité du polymère fondu induite par la réticulation du réseau. Dans le cas d'une mise en forme par « moulage-injection », l'augmentation de la viscosité entraîne une modification drastique des conditions de cristallisation (voir clichés SAXS sur la Figure 1). En réalisant des mesures *in situ* sur synchrotron au cours d'essais de traction, nous avons montré que les mécanismes de déformation des polymères formés sont également drastiquement modifiés par le processus de vitrification (voir paramètre d'orientation P sur la Figure 1). Logiquement, cela entraîne une modification significative des propriétés mécaniques macroscopiques (Figure 2).¹ Dans la perspective du remplacement du PBT « classique » par sa version vitrifiée, nous avons également étudié les conditions de synthèse de ces matériaux sur une extrudeuse semi-industrielle. Lorsque la viscosité du polymère et la vitesse des vis augmentent, le cisaillement qui intervient dans les zones de mélange de l'extrudeuse est susceptible d'induire des ruptures de chaînes, et donc d'entraîner une dégradation significative des propriétés du polymère.²



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Quel impact de l'IA sur la R&D et l'industrie des polymères?

Christophe Wilmort

Mayfair Village, Aubagne

christophe.wilmort@mayfairvillage.io

L'Intelligence Artificielle, aujourd'hui, impacte sensiblement l'industrie chimique d'une manière globale. La chimie des polymères n'est pas épargnée par ce phénomène grandissant.

Au cours de sa présentation, Christophe WILMORT, ingénieur chimiste de l'ECPM Strasbourg et Expert métier IA Chimie chez MAYFAIR Village présentera un panorama des travaux de recherche actuels réalisés grâce à des méthodes d'apprentissage automatique (Machine Learning) et d'apprentissage profond (Deep Learning) pour améliorer la R&D dans le domaine des polymères mais aussi leur production à l'échelle industrielle.

Grâce à Chemy Lane[®], outil de revue littérature automatisée et d'extraction d'informations ciblées pour le chimiste développé par l'équipe de R&D de MAYFAIR Village et basé également sur des technologies d'IA récentes (NLP, LLM, ...), Christophe présentera comment l'IA peut se révéler être un outil décisif dans les choix de pistes de recherche en les rendant plus vert(ueus)es mais aussi dans l'amélioration des chaînes de production en éclairant les prises de décisions. Il partagera également son regard et ses retours d'expériences sur l'intégration de technologies d'IA et ce que cela implique pour les entreprises ayant fait ce choix.

Enfin, en tant que membre du consortium de l'European Digital innovation Hub Polytronics, il présentera un financement européen visant à faciliter l'accès à l'IA pour les entreprises du secteur des polymères.

Ion triggered self-assembly of antibacterial Fmoc-based tripeptide: physical chemistry and MD simulation

Capucine Loth,¹ Florent Barbault,² Delphine Chan-Seng,¹ Lydie Ploux,³ and Fouzia Boulmedais¹

¹ CNRS, Institut Charles Sadron UPR 22, Université de Strasbourg, F-67000 Strasbourg, France ;

² Université Paris Cité and CNRS, ITODYS, F-75006 Paris, France ;

³ Biomaterials Bioengineering INSERM/Université de Strasbourg U1121, Centre de Recherche en Biomédecine de Strasbourg, Faculté Dentaire, CNRS, F-67000 Strasbourg, France.

Résumé

Hydrogels are materials with a high-water content, which makes them similar to natural tissues. They can be used as an injectable matrix directly on the infected site, making them suitable as drug delivery platforms. Small peptides as hydrogelators are of interest due to their high biocompatibility, degradability and ease of synthesis. They are formed upon solubility decrease induced by an external stimulus such as a change of solvent, pH switch or enzymatic modification.^{1,2,3} Our group already demonstrated the formation of a hydrogel based on the self-assembly of Fmoc-FFpY (Fmoc : fluorenylmethoxycarbonyl, F: phenylalanine; pY: tyrosine phosphate) with a polycation (PAH) through π - π stacking and electrostatic interactions.⁴ The study presented here aims to investigate the use of simple cations such as Fe^{3+} as counterions. This work was investigated through four major aspects: (i) structural characterization of the gel, (ii) study of its mechanical properties, (iii) molecular dynamic simulation and (iv) antibacterial assays. Spectroscopic analysis was carried out to highlight the secondary structure, and fiber structure. Rheological properties with self-healing tests showed a mechanical stiffness close to extra-cellular matrices, making it promising for cytotoxicity assays. The hydrogels showed an antibacterial activity against *S. aureus* probably due to the enhanced production of ROS induced by the presence of high concentration of FeCl_3 .

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Comparison of the Ozawa-Flynn-Wall method with temperature-modulated thermogravimetry for lifetime predictions

Frédéric HOPPENOT¹, Christophe SOARES^{1*}, Kylian HALLAVANT², Marie-Rose GARDA²,
Allisson SAITER-FOURCIN², Antonella ESPOSITO², Carlton G. SLOUGH³

¹ TA Instruments, Guyancourt, France

² Groupe de Physique des Matériaux - UMR 6634 (Univ Rouen Normandie, INSA Rouen Normandie, CNRS), 76000 Rouen, France

³ TA Instruments, New Castle, DE, USA

*christophe_soares@waters.com

Résumé

Keywords: thermal stability, activation energy, decomposition kinetics, degradation, TGA

Most of the current research efforts aim to develop and characterize materials that could be more efficient but also more ecological, i.e., with increased resistance over time, to avoid overconsumption of raw materials and unnecessary accumulation of waste. As a result, being able to evaluate the decomposition kinetics of a material as a function of its service (or storage) temperature becomes crucial, and indeed it could eventually help making a choice between different materials and formulations during the design phase.

Thermogravimetric analysis (TGA) is a well-established experimental technique that has been used for many years now for the evaluation of the kinetic parameters of thermal degradation [1] of materials. The work by Ozawa, Flynn and Wall [2,3] allowed to develop a method that uses several heating rates to determine a value of activation energy, which could then be used to predict the material's lifetime as a function of its service temperature [4,5].

Based on the experience previously accumulated about temperature modulation applied to DSC measurements [6], TA Instruments decided to extend this approach to thermogravimetry as well [7], thus allowing to estimate, through a single thermogravimetric test, the activation energy of thermal decomposition phenomena as a function of temperature. This presentation compares the results obtained experimentally by modulate-temperature thermogravimetry (MT-TGA) with lifetime predictions based on the Ozawa-Flynn-Wall model [8].

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Development of Bio-filler-Interfaced Electrospun PVDF based Nanogenerator for Mechanical Energy Harvesting

Isabelle Royaud^{1*}, Sreelakshmi Moozhiyil Purushothaman¹, Ponnas Sathiyathan², Chitra Lekha C S², Maïté Fernandes Tronco¹, Marc Ponçot¹, Sabu Thomas², Nandakumar Kalarikkal², Didier Rouxel^{1*}

¹ Université de Lorraine, CNRS, IJL, F-54000, Nancy, France

²International and Interuniversity Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Kerala, India

E-mail (corresponding author): isabelle.royaud@univ-lorraine.fr

Sustainability of our energy sources are crucial as we work to meet the expanding energy requirements. Owing to this, electroactive polymers, especially Polyvinylidene fluoride (PVDF), is increasingly being used in the development of nanogenerators (NG) to harvest the otherwise lost mechanical (or other forms of) energy. The electroactive properties and therefore the energy harvesting and sensing capabilities of PVDF are distinct characteristics of its polar phases, especially the β phase. Electrospinning is one of the best methods for manufacturing PVDF films with very high fraction of β phase [1]. The effect of bio-fillers such as nanocellulose in increasing the fraction of beta phase, enhancing the piezoelectric and viscoelastic properties of PVDF without hindering its non-toxicity or biocompatibility has brought bio-based PVDF-nanocomposites into the limelight [2]. When nanocellulose is incorporated into PVDF matrix by electrospinning, the synergic effect of electrospinning and the filler can alter the semicrystalline microstructure of PVDF. As all the principal crystalline phases of PVDF (namely α , β and γ) have characteristic vibrational bands, Raman and Fourier Transform Infrared (FT-IR) spectroscopies allow the precise identification and quantification of PVDF crystalline polymorphism. Therefore, this study is focused on the Raman and FT-IR analysis of electrospun PVDF-nanocellulose films and hence on estimating their piezoelectric performance. Additionally, the effect of nanocellulose on the dynamics of the macromolecular chains of PVDF and its dielectric properties are interpreted through Broadband Dielectric Spectroscopy (BDS). Finally, the durability and real-time performance of the films as NG is evaluated using a home-made test bench under various conditions. The NG's capacity to produce a consistent output from simple human movements such as finger tapping demonstrates its practical applications and its ability to serve as a fine model of sustainable engineering.

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Quasi-Complex Coacervates: Single-Phase Viscoelastic Analogues of Complex Coacervates

Jialin She^{1,2}, Axel Bourdette Kaya¹, Francisco J. Cedano-Serrano², Pierre Schaaf^{3,4}, Fouzia Boulmedais¹,

Mehdi Vahdati^{1,*}

¹ Université de Strasbourg, CNRS, Institut Charles Sadron, 67200 Strasbourg, France

² Saint Gobain Recherche Paris, 93300 Aubervilliers, France

³ Institut National de la Santé et de la Recherche Médicale, INSERM Unité 1121, CRBS, 67085 Strasbourg Cedex, France

⁴ Université de Strasbourg, Faculté de Chirurgie Dentaire, 67000 Strasbourg, France

Résumé

The occurrence of phase separation is a major practical limitation for the large-scale production and manipulation of complex coacervate-based materials for potential applications. Based on the phase behavior of a moderately hydrophilic model system, we introduce quasi-complex coacervates (quasi-CC), i.e. salty solutions of fully-doped oppositely-charged PEs that specifically mimic the viscoelastic response of their phase-separated CC counterparts *without* phase separation. Starting from an arbitrary reference formulation producing a phase-separated liquid-like CC, we explore different regions of the phase diagram by systematic changes in the added salt concentration (category **I**), PEs concentration (category **II**), or both. We show that the suppression of the phase separation via both categories (**I** and **II**) results in more liquid-like solutions than the reference CC in systems with negatively-tilted tie lines. Increasing the PEs concentration beyond the binodal boundary slows down the dynamics to some extent; however, the most concentrated solution (at the solubility limit of the PEs) remains more dynamic and liquid-like than the reference CC. It is proposed that obtaining the quasi-CC of a reference CC is only possible by lowering the added salt concentration in very concentrated PEs solutions. By investigating unexplored regions of the complex coacervation phase diagram, this study opens new avenues of exploration in the research on polyelectrolytes-based materials.

Bio-based epoxy curing in mild conditions using catalytic systems: towards high performance materials

Valentine Lavaux,¹ Jacques Lalevée,^{1,2}

¹ Université de Haute-Alsace, IS2M UMR 7361, F-68100 Mulhouse, France

² Université de Strasbourg, France

Résumé

Epoxides are the monomers of choice in the preparation of a large range of high-performance materials with exceptional thermal and mechanical properties ^[1] e.g. showing excellent surface adhesion, low shrinkage, and high corrosion resistance. Therefore, they cover a wide range of applications, including coatings, composites, or adhesives. As epoxy curing agents (hardeners), amines and anhydrides were and are still widely used in the industry due to their good curing speeds and their excellent resulting materials performances (e.g. glass transition temperature - T_g). For high performance materials, monomers/oligomers based on the bisphenol-A scaffold are, by far, the most important category of epoxides but now suffer from high toxicity concerns. ^[2] The same is true for hardeners. Therefore, the development of new epoxy systems (bisphenol-A free) that can be polymerized under mild conditions (at low temperature, under air, without monomer purification) and without hardeners is a huge scientific/ecological and societal challenge. In this context, the aim of our work is to propose new bio-based epoxy systems that can be polymerized with a catalytic system based on natural compounds. The polymerizations were performed in the mildest possible conditions. Full curing can be obtained in less than 20 minutes at 70°C and high T_g were obtained for bisphenol-A-free epoxy polymers. This approach corresponds to a breakthrough in the polymerization of bio-sourced epoxides which often leads to low T_g materials. Markedly, these systems showed good stability when developed in two component (2K) cartridges.

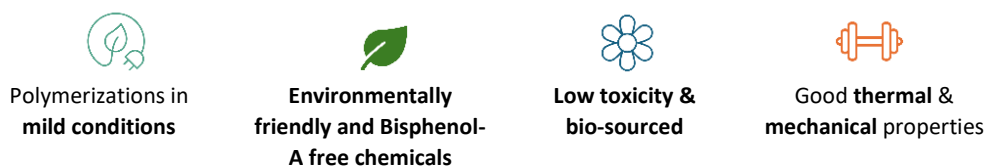


Figure. Purpose of the research subject and expected properties.

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Templated-synthesis of supramolecular polymers

Axel Pinabiaux¹, Nicolas Giuseppone,^{1,2} Emilie Moulin¹

¹SAMS Research Group CNRS Université de Strasbourg Institut Charles Sadron UPR 22, Strasbourg

67000, France ; ²Institut Universitaire de France (IUF). Email: axel.pinabiaux@etu.unistra.fr

Résumé

The aim of the project is to propose a new way to produce self-assemblies of well-defined dimensions in organic solvents. The plan is to form triarylamine supramolecular polymers² with precise length and narrow dispersity by using a covalent polymer as template. This method got inspiration from DNA-templated strategies¹. During this presentation, we will describe the synthesis of well-defined copolyacrylamide bearing an accurate number of terpyridine pendant group, which will further serve as template for the anchoring of triarylamine molecules. We will also report on the synthesis of three different triarylamines, which will be subsequently used to form ruthenium heteroleptic complexes (Ru(Tpy)₂)³ with the covalent template. In particular, we will show how triarylamine trisamide with two norbornene groups can be used to freeze the self-assembled structure by ring opening metathesis polymerization (ROMP)⁴. The main assets of this methodology are three-fold: 1) the frozen triarylamine polymer can be dissociated from the template in order to study their physical properties;² 2) the template covalent polymer can be reused to form other triarylamine polymers; and 3) this methodology is potentially applicable to any building block able to form 1D supramolecular polymer.

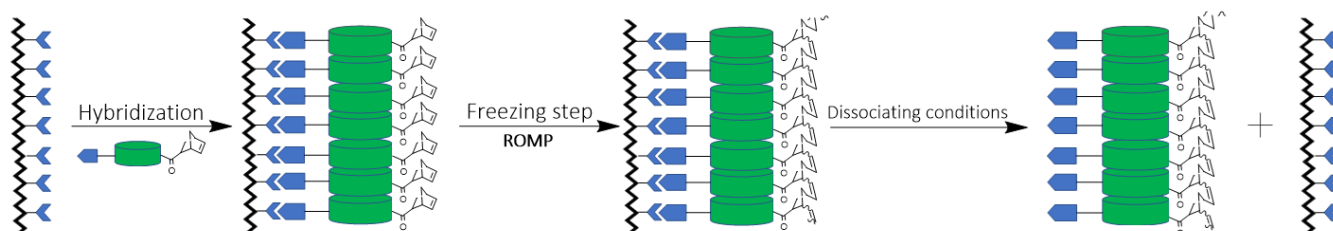


Figure 3 - Schematic representation of the

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Communications par affiche

The fabrication and doping of semiconducting/insulating polymer blend aerogels for thermoelectric applications

ESSADIKI Souhail^{1*}, FERTE Tom², COMBET Jérôme, CONSTANTIN Doru¹, CARVALHO Alain¹, BINIEK Laure¹

1 Université de Strasbourg, CNRS, Institut Charles Sadron UPR22, F-67000 Strasbourg, France

2 Université de Strasbourg, CNRS, Institut de physique et chimie des Matériaux de Strasbourg UMR7504, F-67000 Strasbourg, France

Résumé :

Conducting polymers have garnered significant attention in the field of thermoelectricity and researchers have made considerable breakthroughs in the charge transport properties of these materials. However, most of the research is dedicated to thin film study while few centimeters thick materials (e.g. aerogels) could be optimal for the fabrication of vertical thermoelectric generators. Meanwhile not a lot of focus is given thus is understood in terms of controlling thermal conductivity (κ) and the effect of doping on it. Our research group focuses on reducing κ by forming three dimensional conducting polymers and engineering their porosity. ^{[1][2]}

This current study aims to fabricate a new material composed of a blend of an insulating polymer, syndiotactic polystyrene (sPS) and a semiconducting polymer, poly(3-hexylthiophene (P3HT) polymers that will have a low thermal conductivity while maintaining acceptable power factor (PF) values. sPS is chosen for its ability to form mechanically robust gels and its supposed positive effect on the Seebeck coefficient. ^[3] Thermo-reversible gels of both polymers were obtained from thermally induced phase separation (TIPS). The P3HT/sPS aerogels with over 95% porosity and a thickness of 4-5 mm were fabricated through supercritical drying of the wet gels. The doping process was optimized to ensure homogeneous diffusion of the dopant within the few-millimeter-thick samples as confirmed by EDX measurements. a sequential doping (during the gel state of the blend) have been used utilizing F4TCNQ as a doping molecule.

We will describe here the measurement methods developed to characterize such new materials and the effect of doping conditions on the thermoelectric properties. In particular, we observed a decrease in thermal conductivity with a higher doping level, which is unintuitive. This leads to a low thermal conductivity ($\kappa = 25.2 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) compared to the values seen in other P3HT/sPS aerogels (where $\kappa = 36.1 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ^[3]) or in P3HT foam (where $\kappa = 135.5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ^[4]). The structure of the aerogels has been studied by WAXS/SAXS and EDX-SEM investigations, coupled with spectroscopic studies.

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Control of the π -interactions in (macro)molecular systems for (opto)electronic applications : the power of siloxane chains

L. Colin¹, J. Shaya¹, F. Mathevet², J.C. Ribierre³, B. Heinrich¹, L. Mager¹ and S. Méry¹

¹ IPCMS, UMR7504 23 rue du Loess, 67034 Strasbourg cedex

² IPCM, Sorbonne université, 4 Place Jussieu, 75252 Paris cedex

³ School of Physics and Astronomy, St. Andrew Univ.UK.

mery@ipcms.unistra.fr

The performance and stability of electronic and photonic devices are intimately linked to the way how molecules organize themselves and interact. Thus, the transport of charges in organic semiconductors takes place in a preferred direction where the stacks of π -conjugated systems are the most favorable. Conversely, in photoactive materials of electro-optical devices (light emitting diodes, laser diodes...), it is necessary to spatially separate the photoemissive systems to avoid luminescence quenching. This control of self-association can be achieved by acting on three parameters : i) the nature of the π -conjugated species, ii) the functionalization by flexible chains (usually aliphatics) and iii) the geometrical parameters.

In most cases, flexible chains that are used for functionalization are (branched) aliphatic chains. However, the use of siloxane chains have recently attracted much interest for their extreme flexibility and their strong ability to segregate from most chemical groups.

In this communication, we will illustrate the remarkable role of siloxane chains to control the π -interactions of molecular systems through two examples. In the first example, we will show how siloxane chains can improve the stacking of π -conjugated polymer semiconductors, ultimately leading to a significant enhancement of the charge transport properties.[1] In the second example, we will demonstrate the singular role of siloxane chains to prevent the cristallisation of oligofluorenes to lead to highly fluorescent non-volatile liquid semiconductors at room temperature.[2]

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Conductive PVA/PEDOT:PSS hydrogel foams for soft compressive strain sensors: impact of surfactants and dispersers on electrical and mechanical properties

Florian E. Jurin¹, Cédric C. Buron¹, Eleonora Frau², Stefan del Rossi², Silvia Schintke²

¹ Institut UTINAM, UMR 6213 CNRS-UBFC, Université de Franche-Comté (UFC), F-25030 Besançon Cedex, France

² Laboratory of Applied NanoSciences (COMATEC-LANS), HEIG-VD, University of Applied Sciences Western Switzerland (HES-SO), CH-1401 Yverdon-les-Bains, Switzerland

Résumé

Flexible strain and pressure sensors have garnered significant interest recently for various applications, including electronic skin and wearable electronics, such as sensors for healthcare, robotics, rehabilitation, and sports [1]. Conductive hydrogels are particularly promising for creating highly flexible sensor elements. This study compares conductive hydrogels and hydrogel foams for strain-sensing applications. We formulated conductive hydrogels using polyvinyl alcohol (PVA) and poly(3,4-ethylenedioxythiophene) (PEDOT:PSS). For hydrogel foaming, we explored the effects of using dodecylbenzenesulfonate (DBSA) as a foaming agent and incorporating air at different mixing speeds. Our results show that DBSA, even at a concentration of 1.12% wt, acts as an efficient surfactant, stabilizing air bubbles. This enables the creation of conductive PVA and PVA/PEDOT:PSS hydrogel foams with low density ($<400 \text{ kg/m}^3$) and high water uptake capacity (swelling ratio $> 1500\%$). The Young's modulus of these foams varies with the amount of air-bubble incorporation during mixing and is influenced by freeze-drying and rehydration. Using dielectric broadband spectroscopy under mechanical load, we found that PVA/PEDOT:PSS hydrogel foams exhibit a significant decrease in conductivity under mechanical compression, compared to dense hydrogels. The hydrogels' frequency-dependent conductivity shows two plateaus, one in the low-frequency range and one in the high-frequency range. Conductivity decreases linearly with pressure in both frequency regions, making the hydrogel foams highly suitable for compressive strain-sensing applications.

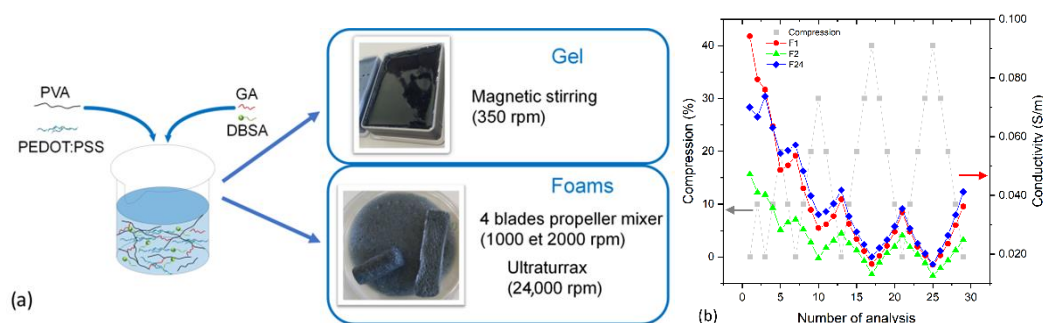


Figure 1. (a) Scheme showing the preparation process of PVA/PEDOT:PSS/DBSA hydrogels and (b) Conductivity measurements performed at different mechanical compressions

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Polyaniline based Flexible Sensors for pH monitoring

Catheline RAMSAMY,¹ Claire MAGNET,² Liam BIGNALL,¹ Sophie LAKARD,² Simon VASSAL,¹ Boris LAKARD,²

¹ Lixens Holding, 78200 Mantes-La-Jolie, France

² Université de Franche-Comté, CNRS, Institut UTINAM, 25030 Besançon

* boris.lakard@univ-fcomte.fr

Résumé

Advancements in pH sensor technology offer opportunities for improved sensitivity, accuracy, and miniaturization, enabling real-time monitoring in diverse environments, such as aqueous solutions, biological systems, and harsh industrial conditions. More specifically, oxidizing media, characterized by the presence of substances that readily accept electrons, such as chlorine or hypochlorite, are prevalent in various industrial processes like chemical manufacturing, water treatment, and environmental monitoring. pH measurement in such environments is crucial for ensuring product quality, process efficiency, and environmental safety.

With this in mind, we set out to develop flexible sensors using electrodeposited polymer films as pH-sensitive layers to manufacture pH sensors that are effective even in oxidizing environments. On one hand, the choice to use flexible sensors is explained by the fact that flexible sensors are becoming more and more important today due to their lightness, conformability, wearability, customizability, and versatility [1]. On the other hand, conductive polymers, such as polyaniline (PANI), are lightweight, resistant and can be deposited on flexible substrates either by chemical oxidation if the flexible substrate is insulating or by electrochemistry if the substrate is conductive [2].

Considering the advantages of using polyaniline and flexible electrodes, we therefore developed a potentiometric flexible sensor using a polyaniline film electrodeposited on a Cu/Ni/Au stack as the pH-sensitive material was developed. The pH sensor exhibited interesting detection performances in aqueous solution, leading to sensitive (73.4 mV per unit pH) and reproducible responses for pH values going from 3 to 8. However, these sensors were ineffective in solutions containing oxidizing hypochlorite ions, which made it necessary to incorporate Tritonx100 surfactant during the electrodeposition of the polyaniline film to make the sensitive material more stable in an oxidizing environment. The pH sensors based on polyaniline and Tritonx100 surfactant were then proved to be sensitive (62.3 mV per pH unit) and reproducible in aqueous solutions containing hypochlorite ions.

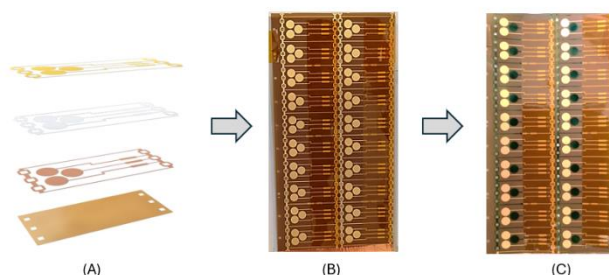


Figure 1. Fabrication process of Lixens® flexible sensors (a), pictures of the sensors before (B) and after (C) electrodeposition of polyaniline.

Ammonia sensor based on electrodeposited polyaniline film

Aihemaiti KAYISHAER,^{1,2} Caroline DUC,¹ Nathalie REDON,¹ Claire MAGNETET,² Boris LAKARD,² Sophie LAKARD,²

¹ Université de Franche-Comté, CNRS, Institut UTINAM, 25030 Besançon

² Center for Energy and Environment, IMT Nord Europe, Institut Mines-Télécom, University of Lille, F-59000 Lille, France

* claire.magnenet@univ-fcomte.fr

Résumé

Due to its toxicity ammonia is problematic at high levels of concentration (the limit of exposure for humans is 35 ppm for 15 min). Moreover, this gas has long-term effects on environment and health at low concentrations [1ppb-1ppm]. Several gas sensors exist such as electrochemical sensors. But they are expensive (few hundreds of €), show some interferences to other gases and have a short lifespan (few months).

Resistive sensors based on conducting polymers (CPs) should be an alternative. Due to the π -conjugation along their chains, they provide a great potential as gas-sensing materials. Indeed, they allow the formation of a delocalised electron at the origin of the electrical conduction, modulated by redox or protonation reactions. Polyaniline (PANI) has been widely used during the last decade, since it is a highly stable compound, easily processed and it is simple to change its electrical conductivity by using chemical or electrochemical doping with various acids or additives.

Considering previous works, we decided to explore the response of flexible sensors based on a new composite film formed by electrochemistry from an aniline/CSA/Fluoral P solution. The electrothesized polyaniline film doped with CSA was successfully deposited on a gold-based sensor in the presence of fluoral-p and covered the interdigitated gold electrodes of flexible sensor devices. The resulting PANI-based sensors were then used to detect ammonia gas at room temperature in the range 50-200 ppb with a high sensitivity, good repeatability, and reversible response to humidity changes. The long-term stability is currently studied, and the preliminary results seem promising.

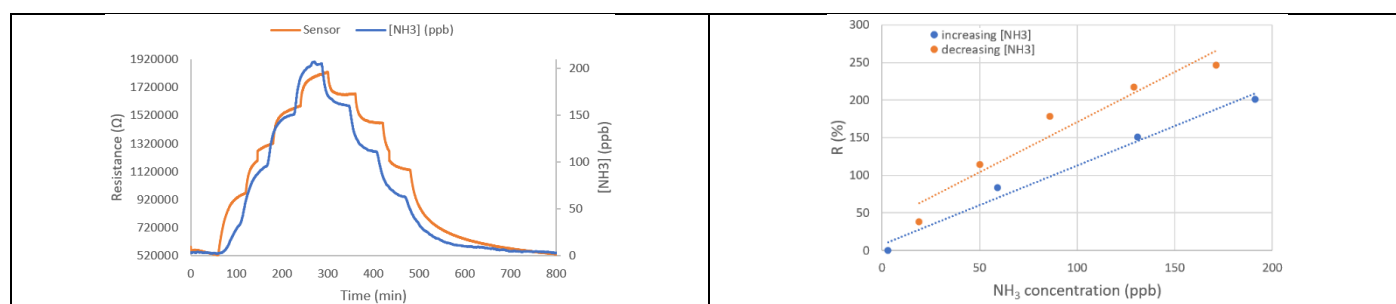


Figure 1. Resistance of the PANI/fluoral p-modified sensor as a function of the resistance of the sensor during exposition to increasing and decreasing concentrations of NH₃ from 50 to 200 ppb (a). Calibration curves calculated for the previous experiment (b). RH: 50%, T: 25°C.

Unexpected UCST behavior of a cationic comb polyarginine

Quentin BIEVELOT,¹ Amélie AUGÉ¹, Nicolas ZYDZIAK¹, Alain CHAUMONT², Philippe LAVALLE^{3,4}, Fouzia BOULMEDAIS¹,
Delphine CHAN-SENG¹

¹ Université de Strasbourg, CNRS, Institut Charles Sadron UPR22, F-67000 Strasbourg, France

² Université de Strasbourg, CNRS, Laboratoire de Modélisation et Simulations Moléculaires UMR7140, F-67000 Strasbourg, France

³ INSERM, UMR_S 1121 Biomaterials and Bioengineering, 11 rue Humann, 67085 Strasbourg, France

⁴ Université de Strasbourg, Faculté de Chirurgie Dentaire, 8 rue Sainte Elisabeth, 67000 Strasbourg, France

Résumé

Thermoresponsive polymers have gained increasing interest due to their ability to alter their physical properties under the effect of a stimulus. Temperature is a stimulus of choice because it can be triggered by various methods such as microwaves, ultrasound, radiofrequency, infrared illumination or magnetic fluid hyperthermia.¹ These smart materials can be divided in two categories; the first one exhibits a lower critical solution temperature (LCST) while the second presents an upper critical solution temperature (UCST).² LCST and UCST are the respective critical temperature points below and above which the polymer and solvent are completely miscible.³ While polymers with LCST are widespread and widely studied, polymers with UCST, although less numerous, have in recent years been gaining increasing interest in the biomedical field.² In this communication, the synthesis of comb polymers with oligoarginine pendent grafts, P(MA-hRx)_n, will be discussed along with their properties. These polymers exhibit an upper critical solution temperature (UCST) behavior that was not expected for a polyelectrolyte, but the phenomenon was attributed to the stacking of the guanidinium groups as supported by molecular dynamics simulation (Figure 1).⁴ Furthermore, polyarginines and polyguanidines are known to be antimicrobial⁵. Preliminary results showed that P(MA-hRx)_n exhibits an antimicrobial activity which could be used synergistically with its thermoresponsiveness for biomedical applications.

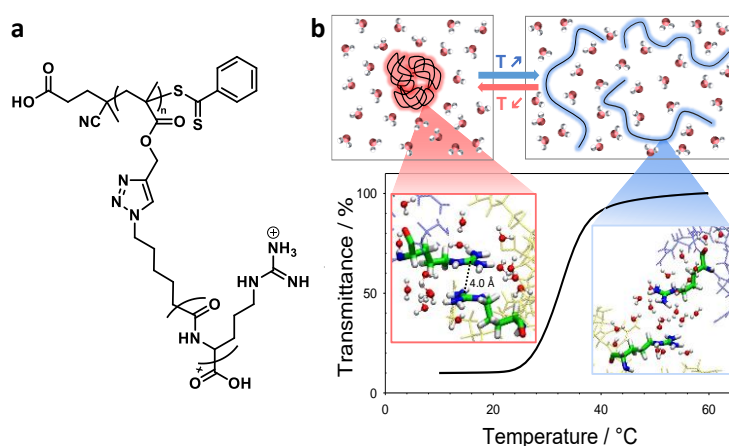


Figure 1. Comb polymers with pentaarginine pendent grafts (P(MA-hR5)_n): a) structure and b) thermoresponsive behavior with the snapshots observed during molecular dynamics simulations

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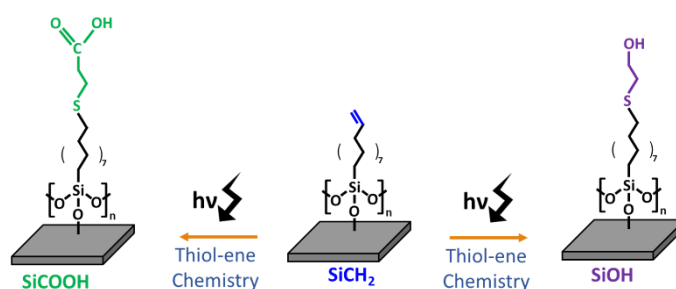
Photoinitiated thiol-ene reaction as a functionalization strategy of self-assembled monolayers

Paul Covin¹, Aissam Airoudj¹, Philippe Fioux¹, Florence Bally-Le Gall¹, Vincent Roucoules¹, Jamerson C. de Oliveira¹

¹ Université de Haute-Alsace, Université de Strasbourg, CNRS, IS2M UMR 7361, 68100, Mulhouse, France

Résumé

The use of self-assembled monolayers for modifying the interfacial properties of a material is quite well-established [1]. Furthermore, self-assembled monolayers can be used as an intermediary reactive layer that allows the grafting of a polymer or influences its deposition [2]. An example of the latter is the influence of self-assembled monolayers on the growth and morphology of plasma polymers [3]. It is in that context that the photoinitiated functionalization of alkene-terminated self-assembled monolayers with thiols containing different termination groups are explored. A careful characterization of the functionalized surface was performed, indicating that the chemistry (XPS, PMIRRAS) and the morphology (AFM, ellipsometry) are in accordance with self-assembled monolayers. Further work is now exploring the influence of those surfaces on the growth of plasma polymers.



Scheme. Functionalization of self-assembled monolayers via photoinitiated thiol-ene reaction

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Functionalization by plasma polymerization of carbon materials with hierarchical porosity

Fatima BEN YOUSSEF, Florence BALLY-LE-GALL, Julien PARMENTIER

Adresse ; Université de Haute Alsace, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, 15 rue Jean Starcky 68057 Mulhouse cedex, Mulhouse, France.

Résumé

The functionalization of materials by plasma polymerization is a useful process for adjusting the properties of materials to a targeted application by depositing a thin layer of appropriate polymer on the surface. This process is mainly used with non-porous substrates or in a lower extent with porous materials but with lack of evidence that internal surface of the material is functionalized. Moreover, the influence of the electrical conductive nature of the substrate (e.g. insulating Si (or SiO₂) versus conductive carbon material) on plasma polymerization mechanisms is hardly investigated. Therefore, functionalization of porous monoliths by this process appears as a challenge. Critical parameters such as pore size and electrical conductivity of substrate need to be addressed for fully understanding plasma polymerization mechanism within such materials. In our case, carbon materials with controlled pore size and electrical conductivity were used to investigate the diffusion of plasmagenic species and growth mechanism of the polymer within the porous and conductive nature of the material. A focus is given on the pore range that can be functionalized.

Our strategy is to develop carbon monoliths with hierarchical and controlled porosity.¹ Materials with an average macropore size ranging from 50 nm to 250 nm were prepared by the sol-gel process combining phenolic resin formation with spinodal decomposition. The xerogel was carbonized up to 950°C before surface functionalization by plasma polymerization. Perfluorooctyl acrylate (PFAC) was chosen as polymer precursor due to the ease of fluorine detection by spectroscopy techniques (EDX for instance). The deposition process was carried in an inductively coupled RF plasma reactor, operating at low pressure (typically at 0.2 mbar), in pulsed and continuous mode. Fluorine content, related to the polymer deposition, was followed with mapping techniques such as SEM-EDX as a function of the characteristic size of the porosity of the monolith. In addition, comparison of the polymer deposition on carbon monoliths and model planar substrates, either with insulating (Si wafers) or conducting (pyrolytic graphite sheets) properties, was investigated, and discussed.

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SYNTHESIS AND STUDIES OF OLEOGELS AS SUBSTITUTES FOR STRUCTURAL FATS

Senem YILMAZER¹, Katia PINA CHAGAS¹, Philippe MESINI^{1*}.

¹ *University of Strasbourg, CNRS, Institut Charles Sadron, 23 rue du Loess, 67000
Strasbourg, France.*

*E-mail : Philippe.mesini@ics-cnrs.unistra.fr

Résumé

Trans-unsaturated fatty acids (TFA) in the diet represent a major public health problem because they increase the frequency of cardiovascular diseases. TFAs are present in many solid fats of animal origin or in margarines, resulting from the hydrogenation of vegetable oils. However, these solid fats are necessary to texture the lipid phases of food. In this context, many studies are being carried out to replace solid fats in foods. One of the most promising ways is to solidify cis-unsaturated oils (liquid at room temperature) by organogelators. These small molecules gel solvents at low concentrations, typically a few percent by weight ^[1] self-assembling into a solid 3D network in oil. Organogelators capable of gelling edible oils are called oleogelators. Examples of oil gelators are easily found in the literature, but for food applications, they must be without adverse effects when taken orally. In the present work we have synthesized *N*-acyl-amino acids because these compounds are endogenous i.e. naturally present in the body and we have tested it as gelators of triolein. We have studied the thermodynamic properties of the gels formed with it using micro differential calorimetry (μ -DSC), and their mechanical properties as a function of temperature. From these measurements, we mapped out the *c-T* phase diagram. The structures have been investigated by cryo-SEM, WAXS, and FTIR, and were correlated with thermal and mechanical behaviour.

These gels are also under investigation to understand the impact of gelation on pancreatic digestion.

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Consortium strasbourgeois sur l'électronique organique

- STELORG -

N. Leclerc¹, O. Bardagot¹, A. Hébraud¹, G. Ulrich¹

A. D'Aléo², B. Heinrich², L. Mager², S. Méry²

L. Biniek³, M. Brinkmann³

T. Heiser⁴, S. Fall⁴, P. Lévêque⁴, Y. Lin⁴, E. Martin⁴, E. Steveler⁴, M. Boero⁴

¹ Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES), Université de Strasbourg, CNRS UMR7515, 25 rue Becquerel, 67087 Strasbourg Cedex

² Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), Université de Strasbourg, CNRS UMR7504, 23 rue du Loess, 67034 Strasbourg Cedex

³ Institut Charles Sadron (ICS), CNRS UPR022, 23 rue du Loess, 67034 Strasbourg Cedex

⁴ Laboratoire des sciences de l'ingénieur, de l'informatique et de l'imagerie (ICUBE), Université de Strasbourg, INSA et CNRS UMR7337n 23 rue du Loess, 67034 Strasbourg Cedex

STELORG est un consortium de recherche interdisciplinaire strasbourgeois qui vise à rassembler les acteurs locaux impliqués dans l'électronique organique (<https://stelorg.unistra.fr/>). Plus de 15 chercheurs et enseignants permanents de 4 institutions de recherche situées sur le même campus de Cronenbourg (ICPEES, IPCMS, ICS et ICube) sont impliqués dans STELORG. Nos compétences vont de la chimie organique au développement de dispositifs opto-électroniques. La méthodologie générale est centrée sur des réunions/discussions régulières et des collaborations entre chercheurs aux compétences complémentaires afin d'améliorer la compréhension de l'**impact des modifications chimiques** sur les **propriétés structurales et optoélectroniques** des matériaux, et de construire des **dispositifs optoélectroniques organiques** avec des **performances améliorées ou de nouvelles fonctionnalités**. Les projets typiques comprennent la chimie (macro)moléculaire, l'étude des propriétés chimiques et physico-chimiques (thermiques, spectroscopiques, électrochimiques, etc.), les propriétés structurales à l'état solide et en couches minces, ainsi que l'élaboration et l'optimisation de dispositifs. Le champ d'application de notre recherche couvre la plupart des dispositifs optoélectroniques organiques, avec un accent sur les matériaux pour la conversion de l'énergie photovoltaïque et thermoélectrique.

