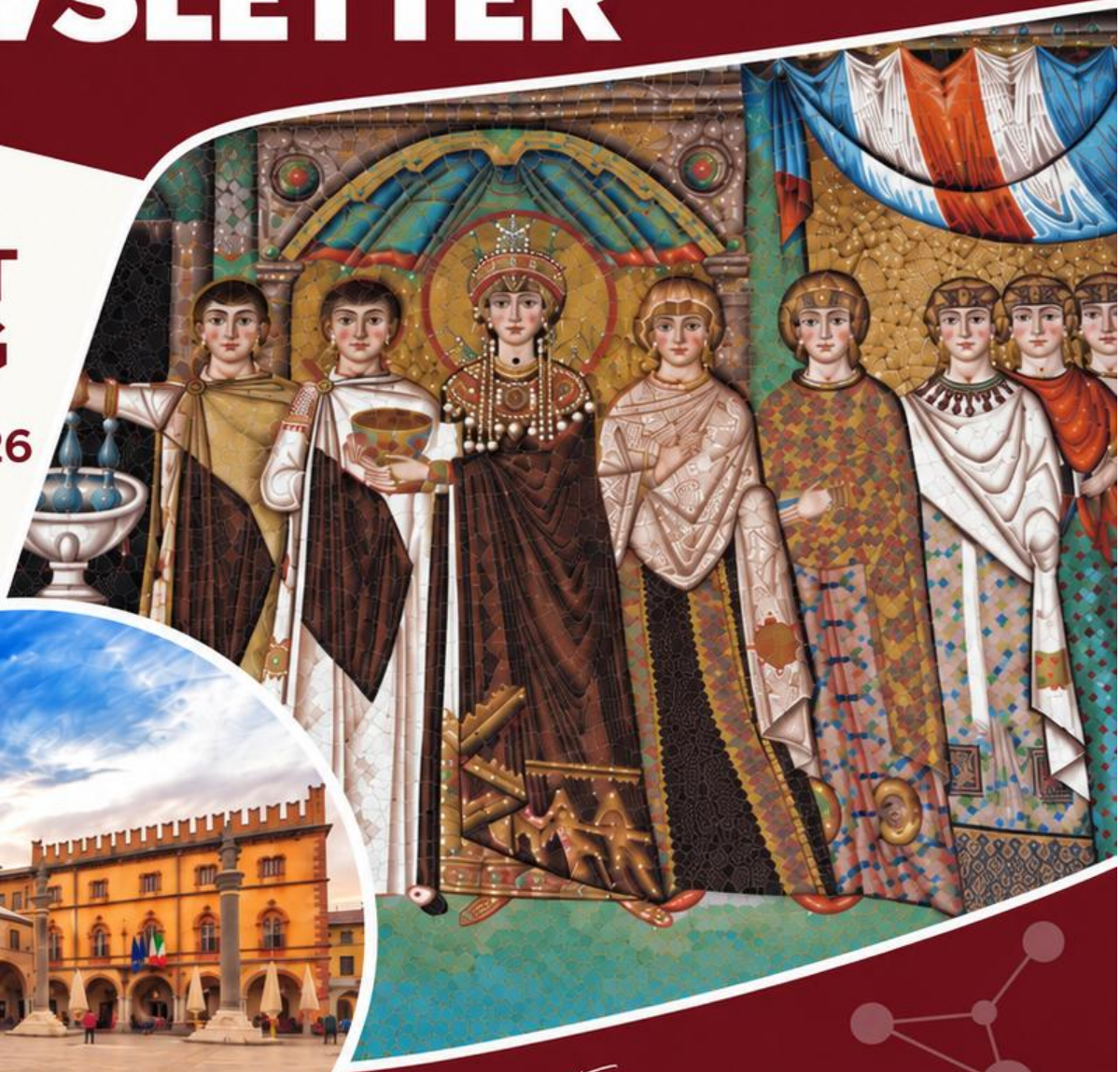
ReBond NEWSLETTER

FOURTH PROJECT MEETING

RAVENNA 2026



From Polymer Networks to a Sustainable Tomorrow

ReBond MSCA DOCTORAL NETWORK

Funded by the European Union

MARIE CURIE ACTIONS

CONTACT INFORMATION

GET IN TOUCH WITH THE REBOND TEAM AT UCLOUVAIN

Evelyne van Ruymbeke
Project coordinator
evelyne.vanruymbeke@uclouvain.be

Anne-Christine Baudouin
Project Manager
rebond-manager@uclouvain.be

Christine Hambursin
Project Manager
rebond-manager@uclouvain.be

STAY CONNECTED

FOLLOW OUR NEWS, ACTIVITIES AND IMPACT

ReBond Project
www.rebondproject.eu

Horizon-MSCA-2022 – ReBond
www.linkedin.com/groups/9581351/

@Rebond_project
www.instagram.com/rebond_project/

ReBond
MSCA DOCTORAL NETWORK

Day 1 – Versalis visit

On 9 June 2026, the ReBond Doctoral Candidates took part in an industrial workshop hosted by Versalis as part of the fourth ReBond project meeting in Ravenna. The visit focused on exposing the researchers to the way industrial R&D projects are conceived, developed and managed in practice. Working in small groups under the guidance of Christian Coppola, the participants explored four different project scenarios: generating a new project idea, responding to an issue arising in an industrial plant, developing a product driven by market needs, and designing a project to ensure compliance with a ministerial directive. Through these interactive case studies, the workshop highlighted how scientific expertise is combined with technical constraints, market requirements, regulatory considerations and project-management decisions in an industrial environment. The experience provided the Doctoral Candidates with valuable insight into industrial problem-solving and strengthened the connection between the scientific objectives of ReBond and real-world applications in the polymer industry.

Day 2 – Lectures

Prof. F. Doghieri

Thermodynamics, Phase Behavior and Free Volume in Polymeric Materials

Prof. F. Doghieri introduced the fundamental thermodynamic principles governing equilibrium, stability and miscibility in polymer systems, with particular emphasis on the Flory–Huggins theory, mixing entropy, interaction parameters and phase behavior in polymer solutions and blends. The concepts of UCST and LCST behavior, as well as the thermodynamic conditions for phase equilibrium in binary and ternary systems, were also discussed. In the second part of his talk, he extended these concepts by introducing the role of free volume and compressible lattice models, highlighting their importance in the description of polymer thermodynamics, glass transition and non-equilibrium glassy states. The discussion was further connected to practical applications such as gas and vapor solubility and mass transport in glassy polymeric materials.

Day 2 – Lectures

Prof. G. Ianniruberto

Molecular Models for the Nonlinear Rheology of Polymeric Networks

The lecture examined molecular models used to describe the nonlinear rheology of permanent, transient and entangled polymer networks. Starting from rubber elasticity and polymer chain statistics, it introduced finite extensibility, constitutive equations and the tube/Doi–Edwards model. More advanced nonlinear effects, including chain stretching, convective constraint release, friction reduction and molecular tumbling, were discussed in relation to shear and elongational flow experiments.

Prof. D. Vlassopoulos

Nonlinear Phenomena and "Molecular" Rheometry

The lecture presented the main rheological behavior of polymeric liquids, solids and networks under shear and extensional deformation. It covered rheometric techniques and key nonlinear phenomena such as shear thinning, nonlinear elasticity, flow instabilities and the influence of molecular architecture and polydispersity. Several empirical relationships and experimental challenges in polymer rheology were illustrated through representative data.

Day 3 – DC Presentations

During the meeting, we also had the opportunity to present our work and share what we have been working on with the group. It was a good moment to discuss our results, exchange ideas, and hear different perspectives. These discussions are always useful, not only for the work itself, but also for getting a better idea of where we can go next.

Reproducing stress relaxation and bond-exchange kinetics in vitrimers via coarse-grained MD

B. Magyari

Experimental work has reported a non-monotonic dependence of the terminal relaxation time on vitrimer functionality f (the number of stickers per chain). Molecular dynamics simulations were performed to test whether this behaviour could be reproduced. Three formulations were studied: $f = 2$, 4, and 8 stickers per chain. The stress relaxation modulus $G(t)$ was obtained from the stress autocorrelation function via the Green–Kubo relation, and the dynamic moduli $G'(\omega)$ and $G''(\omega)$ were recovered by Fourier transformation. The non-monotonic trend was not reproduced. The discrepancy is attributed to the simulated $f = 2$ system failing to percolate, evidenced by the absence of a rubbery plateau that is present in the experimental data. The most likely origin is the polydispersity of the real samples, in which a fraction of chains carries more than two stickers and is therefore sufficient to sustain a percolated network.

Annealing-driven network organization in model polyisoprene vitrimers

A. Russo

Well-defined polyisoprene vitrimers reveal a strong coupling between network structure and rheological response. Thermal annealing drives the metastable phase-separated morphology toward a pseudo-equilibrium state through dynamic imine exchange and cluster reorganization, resulting in significant mechanical reinforcement. Combined SAXS, microscopy, and rheology demonstrate that the extent of reinforcement depends strongly on crosslink density: highly crosslinked networks show the largest increase in elasticity, while loosely crosslinked systems exhibit distinct contributions from entanglements. These findings highlight how dynamic bond chemistry, mesoscale organization, and network connectivity collectively govern vitrimer mechanics.

Day 3 – DC Presentations

S. Chiani

Structure and dynamics of HDPE cross-linked by an azidotriazine via reactive extrusion

In this presentation, I discussed the incorporation of azidotriazine-based covalent adaptable networks into high-density polyethylene (HDPE) and their effect on its semicrystalline morphology and molecular dynamics. The results show that the dynamic crosslinks act as interfacial plasticizers, preferentially located in the amorphous regions near the crystalline lamellae. Increasing the crosslinker content reduces the degree of crystallinity and equilibrium melting temperature, while also modifying the crystallization kinetics and lamellar structure. In addition, dielectric spectroscopy revealed enhanced segmental mobility and a decrease in the liquid-to-glass transition temperature. Overall, these findings demonstrate that azidotriazine crosslinks can effectively modify both the crystalline structure and molecular mobility of HDPE.

G. Merola

Reprocessable Elastomers

The presentation gives an update on the development of a reprocessable vitrimer elastomer. After successfully introducing a boronic ester crosslinker into the polymer matrix, some preliminary characterizations were performed on a laboratory scale. The formulation was then scaled up to be further analized in an industrial setting. The curing kinetics were investigated, and different strategies were explored to reduce the curing time and better understand the factors controlling the curing process.

Day 3 – DC Presentations

T. Guarino

Equi-biaxial extensional rheology of crosslinked polymer networks

Extensional flows are among the dominant deformation modes encountered in polymer processing operations. While uniaxial extension is routinely characterized using standardized protocols and commercial extensional rheometers, equi-biaxial extension remains comparatively less explored. In this work, the extensional response of permanently crosslinked elastomers is investigated under both uniaxial and equi-biaxial deformation. Uniaxial measurements were performed using a Sentmanat Extensional Rheometer (SER), whereas equi-biaxial measurements were obtained using four custom-built techniques: bubble inflation, lubricated squeeze flow (LSF), continuous lubricated squeeze flow (CLSF), and membrane stretching. The different methods are compared in terms of the strain fields they generate and the deformation conditions they can access, providing the basis for an operating diagram of equi-biaxial testing techniques.

A.R. Constantinou

Entropic Phase Separation in Polymer–Vitrimer Melts: What We've Learnt and What's Next

Vitrimers have been proposed as a potential additive to improve the thermomechanical properties of thermoplastics without losing recyclability. In my presentation, I sketched a thermodynamic model of such mixes and compared its predictions to simulations run by my collaborators. We found that, independently from the miscibility of the chosen materials, entropy works to drive the vitrimer away from its polymeric matrix as soon as its degree of conversion exceeds a low threshold, on the order of a few crosslinks per chain. The work this presentation was based on has since been accepted for publication in *Macromolecules*.

Day 3 – DC Presentations

Will it adhere? Enhancing adhesion between immiscible polymers with vitrimer

C. Spina

The presentation focused on the latest results regarding the adhesion between PS and PMMA vitrimers with two different percentages of functionalized monomer (10% and 3%), each cross-linked at 1%. After a brief overview of the methodology used to prepare the bilayer polymer assembly for the adhesion tests, I presented some interesting insights into the weakest interface expected within the bilayered samples. The results showed that the vitrimer-vitrimer interface between VPS and VPMMA could potentially lead to high adhesion, while, surprisingly, the adhesion between the commercial PMMA and the VPMMA turned out to be weaker than expected, likely due to poor compatibility between the two.

From Flow to Structure: Exploring Flow-Induced Effects in Dynamic PE Networks

A. Karimi

This presentation explored how dynamic covalent bonds and network composition influence the flow behaviour of dynamic polyethylene (PE) networks. Rheological results showed that bond-exchange kinetics strongly affect long-time relaxation, while the networks remain highly sensitive to shear history. Because flow during melt processing can orient and stretch polymer chains before crystallization, the next question is whether this deformation history can influence how structure develops during cooling, particularly in dynamic networks, where bond exchange provides an additional mechanism for molecular relaxation.The second part therefore focused on flow-induced crystallization. Initial experiments on neat PE showed that even short shear pulses can significantly accelerate crystallization, with both shear rate and shear duration affecting the response. Strain alone did not fully describe the observed behaviour, while specific mechanical work emerged as a promising parameter for relating flow history to crystallization. Initial Raman measurements showed only modest changes in local chain ordering after shear, highlighting the need for further structural studies and future investigation of flow-induced crystallization in dynamic PE networks.

Day 3 – DC Presentations

Rheology and structure of polystyrene based vitrimers and their blends in thermoplastic matrix

L. Santori

Vitrimers are a promising class of polymers that combine the durability of crosslinked materials with the processability of thermoplastics. Their dynamic chemical bonds allow the network to rearrange when heated, giving these materials a unique combination of properties. In this work, we investigated polystyrene-based dioxaborolane vitrimers, both on their own and as additives in conventional polystyrene. We found that their structure and rheological behavior evolve significantly during prolonged thermal exposure, reflecting the interplay between reversible bonds, polymer entanglements, and the formation of a secondary network. We also explored the use of vitrimers as additives in polystyrene. Encouragingly, blends containing up to 40 wt% vitrimer retained good processability while providing tunable dynamics. At higher vitrimer concentrations, the blends exhibited more pronounced structural changes, including thermal annealing and, eventually, phase separation. Overall, these findings provide new insight into the time-dependent behavior and structural complexity of vitrimers, while highlighting their potential as functional additives for conventional thermoplastic materials. Understanding how vitrimer content influences structure, rheology, processability, and mechanical performance can help guide their use in the development of next-generation polymer systems.

Day 4 – DC Presentations

Synthesis and Characterization of Polyolefin Vitrimers from High Vinyl Polybutadiene

A. Genio

The presentation features synthesis and characterization of polyolefin vitrimers from high vinyl polybutadiene. The research focused on synthesizing polyolefin-based vitrimer from a hydrogenated polybutadiene functionalized with dioxaborolane exchange chemistry. Each step of the synthesis included characterizations such as structural and thermo-rheological techniques. From the optimized synthesis pathway, it is planned to study structure-property relationships of the materials through varying the number of grafts and crosslinking density of the final vitrimer. Preliminary mastercurves of the materials were also shown during the presentation to superficially follow the evolution of the linear rheological properties corresponding to the structural changes in the synthesis. Future work of this research briefly includes study of the extensional rheology of the materials and its application as an additive or compatibilizer of commercial polyolefins.

Synthesis and properties of PS-PMMA copolymers containing reversible covalent crosslinks as compatibilizers in blends

A. Vijayan

Random PS-PMMA copolymers (20-120 kDa) were synthesized by RAFT polymerization, along with PS and PMMA vitrimer precursors and a PS-r-PMMA-based crosslinker, each of the vitrimer components containing boronic ester groups. These materials were evaluated as compatibilizers in PS/PMMA (30/70) blends prepared by twin-screw extrusion and compression molded into discs. Four systems were compared: an uncompatibilized reference, a blend with the random copolymer, a blend with the vitrimer precursors and the copolymer-based crosslinker, and a blend with the vitrimer precursors and a small-molecule crosslinker. SEM, AFM, and optical microscopy indicated that the small-molecule crosslinker system achieved the most effective compatibilization, yielding smaller and more uniformly dispersed PS domains. Further optimization is needed. Future work will explore solution blending and characterize the blends by dielectric spectroscopy, rheology, and mechanical testing.

Day 4 – DC Presentations

A. Sapouna

Effect of degradation on the dynamics and crystallization of polyolefins

During the meeting in Ravenna, the effect of degradation on the dynamics and crystallization of HDPE was presented based on isothermal crystallization SAXS experiments. The results were used to investigate how degradation affects the crystallization kinetics and lamellar structure of HDPE. The results showed that the HDPE system characterized by lower M_w and PDI exhibited a decrease in the crystalline lamellar thickness (d_c), accompanied by an increase in the amorphous layer thickness (d_a) and a decrease in the degree of crystallinity (X_c). These observations support the previous conclusion that chain branching is the predominant degradation mechanism in this system. In contrast, for the HDPE system characterized by higher M_w and PDI, the d_c remained essentially constant, while the d_a increased and only a slight decrease in X_c was observed, supporting chain scission as the predominant degradation mechanism. Overall, the results show that different degradation mechanisms lead to district changes in the molecular architecture and affect crystallization behavior and lamellar organization of the different HDPE grades.

K. Lyroni

Unravelling spontaneous and driven mechanodynamics of gluten

In this presentation, we focused on the investigation of the gelation mechanism of gluten at rest, but also under shear conditions. By utilizing the home-built Rheo-DLS set-up, we were able to capture the mechanics and the dynamics of gluten at the same time. In more detail, at rest, the material exhibits a sol-gel transition. However, the first preliminary results of gluten under shear indicate that at the pre-gel state, the self-healing of the material after the shear is competing with its aging mechanism. More information was provided also by constructing the Dynamic Analysis Map of the various relaxation times of the different Regions of Interest, where some heterogeneities were observed.

Day 4 – DC Presentations

M. Conti

Synthesis of comb polymers with dynamic branching chains

The first part of the presentation demonstrated the thermal bulk oligomerization of an azo-compound (1,2-bis(4,6-diphenyl-1,3,5-triazin-2-yl) diazene) in the presence of its triazine azide derivative (2-azido-4,6-diphenyl-1,3,5-triazine), revealing new reactivity for this well-known class of molecules and providing insights into the bulk oligomerization mechanism of the triazine azide itself. The second part focused on the synthesis of a dynamic comb-like polymer system, where the arms can exchange upon heating via a dioxaborolane metathesis reaction. The backbone and the arms were precisely synthesized using RAFT polymerization.

M. Danikas

Segmental and Chain Dynamics in Poly(Propylene Oxide) Dynamic Networks

The presentation explored the molecular mechanisms governing dynamic bond exchange in vitrimers and their impact across different length scales. Dielectric spectroscopy was used to probe how dynamic bonds influence segmental polymer dynamics, while pressure-dependent measurements provided insight into the thermodynamic origins of bond exchange. The discussion also highlighted how polymer architecture affects macroscopic viscoelastic behavior, comparing pendant-network vitrimers with telechelic PPG-based systems. In the latter, the molecular-weight dependence of segmental and normal-mode relaxation offered a way to distinguish between Rouse and reptation dynamics and to better understand how bond exchange couples with polymer motion.

Dinner time!

Before heading to dinner, we took some time to enjoy the seaside and spend a few moments together on the beach. It was a nice break after the activities of the day, with some time for photos, conversation, and simply enjoying the atmosphere of Ravenna. Later in the evening, we continued to the Circolo Marinai d'Italia for dinner. Away from the meeting room, the evening was a chance to relax, share stories, and enjoy each other's company in a more informal setting. It was a simple and enjoyable way to end the day, combining a little bit of sea, good conversation, and time together.

Next meeting: Montpellier

And now, we already have the next meeting to look forward to: Montpellier! After Ravenna, we will meet again for another round of discussions, presentations, and, hopefully, some time to enjoy the city together. The location will change, but the recipe stays the same: good science, good company, and hopefully good food.

See you in Montpellier!