

FRAMEWORK PROGRAMME OF EARLY STAGE RESEARCHER TRAINING¹

1. BASIC DATA

Mentor's name and surname	Klementina Pušnik Črešnar	Mentor's register number at <u>ARIS</u> (<u>SICRIS):</u>	34450
Mentor's e-mail:	klementina.pusnik@um.si	Mentor's tel. no.:	02 220-7607
Research programme (RP) leader's name and surname:	Lidija Fras Zemljič	RP leader's register number at <u>ARIS</u> (<u>SICRIS)</u> :	19753
Title of research programme:	Textile Chemistry and Advanced Textile Materials	RP's Register number at <u>ARIS</u> (SICRIS):	P2-0118
Research organisation (RO) of University of Maribor, where training shall be conducted:	FS UM	RO Register number at <u>ARIS</u> (SICRIS):	0795
Research field according to <u>ARIS classification</u> :	2.04 Materials 2.04.03 Polymeric materials	Research field according to Ortelius classification (EURAXESS)	180 Materials engineering 421 Materials technology

2. DEFINITION OF RESEARCH PROBLEM AND GOALS OF DOCTORAL RESEARCH²

Starting point of research task of the early stage researcher and its position in the research programme, where the mentor is included, work hypothesis, research goals and foreseen result with emphasis on an original contribution to science:

Scientific Background

Plastics, as one of the most essential polymeric materials—including both thermoplastics and thermosets—play a crucial role in the EU economy and daily life due to their lightweight nature, durability, and cost-effectiveness. Their high versatility has led to widespread adoption across various commercial sectors, including civil engineering, transportation, packaging, energy storage, and biomedicine. According to recent statistics published by Plastics Europe in 2022, global plastic production reached 400.3 million tonnes (Mt), with Europe contributing 58.7 Mt. This industry

¹ Term early stage researcher (ESR) is written in male form and used as neutral for women and men.

² Research and study programme of training have to harmonise with contents of the research programme, where the mentor is a member.

encompasses approximately 53,150 companies, employs over 1.5 million people, and holds significant economic value, generating a trade balance of 9.2 billion euros and an annual turnover exceeding 400 billion euros. However, due to their long lifespan, plastics can become environmentally hazardous waste if not managed properly at the end of their life cycle.

Addressing this challenge is of paramount importance, driving both academic and industrial sectors to advance knowledge in the development of innovative methodologies and the synthesis of novel plastic-based composite materials.

These materials must be engineered to facilitate efficient upcycling or recycling, thereby contributing to sustainable resource management and aligning with the principles of a circular economy.

Polymer materials based on Covalent Adaptable Networks (CANs), often referred to as vitrimers, are emerging as a new class of innovative materials that bridge the gap between thermosets and thermoplastics, providing a viable solution for polymer upcycling and recycling. The functionality of CANs is largely attributed to dynamic covalent chemistry (DCC), which enables bond rearrangement within the polymer network, facilitating stress relaxation and structural reconfiguration. Furthermore, nanoparticle-driven CANs represent a novel advancement in this field, as various nanoparticles can serve as specific stimuli to trigger dynamic bond formation, thereby enhancing the material's adaptability including:

Self-healing materials: The ability to rearrange covalent bonds allows CANs to recover from mechanical damage.

Recyclable polymers: CANs can be processed multiple times without losing their structural integrity, making them environmentally sustainable.

Smart materials: These networks respond to environmental stimuli, making them ideal for applications in sensors and actuators.

Problem identification and motivation

Covalent Adaptable Networks (CANs) are crosslinked polymer networks in which the crosslinking strands can undergo reversible rearrangement reactions. These molecular restructurings provide a microscopic mechanism that enables macroscopic flow and stress relaxation in thermoset materials, a property that was previously unattainable. Consequently, CANs serve as an intermediary between thermoplastics and thermosets. While they exhibit the crosslinked structure characteristic of thermosets, they can be reprocessed similarly to thermoplastics. CANs retain all the mechanical advantages of conventional thermosets, yet their unique chemical bonding structures allow them to selectively respond to external stimuli, leading to modifications in structure, properties, and even shape.

Traditionally, CAN crosslinks are dissociative, meaning they break before reforming within the network. However, in 2011, a new class of CANs, known as vitrimers, was introduced. These materials exhibit a viscosity-temperature relationship similar to that of glassy silica, following an Arrhenius-like dependence. This behaviour results from their dynamic associative crosslinking mechanism, where covalent bonds break only when new bonds simultaneously form. Consequently, the crosslink density in associative CANs remains nearly constant, regardless of external stimuli.

This characteristic has two major implications:

The dynamic bond exchange process in CANs can be triggered by various stimuli, leading to stress relaxation and structural reconfiguration. For instance, upon exposure to light or heat, the covalent bonds can break and reform, enabling the material to adapt its shape or relieve internal stresses without sustaining permanent damage. Additionally, the activation of these reversible structures can be controlled by external environmental stimuli such as radiation or temperature changes, classifying CANs as smart and responsive materials.

The defining feature of all CANs is the presence of exchangeable covalent bonds within their organic structures, allowing them to undergo substantial shape transformation while maintaining or altering the overall level of crosslinking. This unique ability to dynamically reorganize their network structure through reversible bond exchange reactions sets vitrimers apart from traditional thermosetting polymers, which are typically static and resistant to reshaping or reprocessing.

Furthermore, the incorporation of nanoparticles (NPs) such as iron oxide, titanium, and silica into CANs introduces an additional level of tunability. These nanoparticles can influence the reversibility of the polymer network in response to external stimuli, allowing for enhanced adaptability.

Studies have demonstrated that the incorporation of NPs significantly enhances CAN properties, improving their mechanical stability, recyclability, and responsiveness. The integration of

nanoparticles into covalent adaptable networks not only enhances their functionality but also broadens their applicability. As a result, CAN-NP composites hold great potential for use in self-healing materials, sustainable composites, and smart technologies.

The primary aim of this research is to develop Covalent Adaptable Networks (CANs) based on polypropylene and polyethylene, incorporating nanoparticles (NPs) (iron oxide, zinc oxide, titanium, and nanocellulose) to enhance either self-healing properties or recyclability. The NPs will serve as regulators of dynamic covalent bonds, influencing structural properties and examining their effects on thermal, mechanical, and surface characteristics. Furthermore, this study will investigate how variations in NP incorporation—such as differences in size, shape, and functional groups—affect CANs' performance, largely depending on the specific properties of CAN-NPs, including surface chemistry, morphology, and responsiveness to external stimuli. Nanoparticle-driven CANs further enhance adaptability, as nanoparticles act as stimuli to trigger dynamic bond formation. This enables key functionalities such as self-healing, recyclability, and smart responsiveness to external stimuli, making them ideal for applications in adaptive textiles, sensors, and actuators. Research Methodology:

1. Synthesis and Characterization of NPs

Nanoparticles will be synthesized, surface-functionalized, and characterized to optimize their interaction with CANs and assess their effects on final structural and thermal properties, ultimately improving self-healing and recyclability.

2. Synthesis of CAN-NPs: The development of associative and dissociative CANs by introducing various multifunctional crosslinkers, based on several crosslinking mechanisms, including ester, ether, disulfide, imine, amide, and epoxy bonds, during the extrusion reaction. CANs will be synthesized using thermoplastic-derived polymers with Diglycidyl Ether of Bisphenol A (DGEBA), which reacts with functional groups in the thermoplastic matrix to form crosslinked networks.

- i) To enhance reactivity, thermoplastic-based polymers will be chemically modified by grafting maleic anhydride (succinic) onto their chains, creating reactive sites for further crosslinking reactions.
- Under specific conditions, such as heating, the CAN-NP network can be reprocessed or reshaped without compromising its structural integrity.

CAN-NPs can undergo multiple processing cycles while maintaining structural integrity, making them an environmentally sustainable alternative to conventional polymers.

Hypothesis

The incorporation of specific NPs will trigger dynamic covalent bond exchange under controlled conditions, enhancing the self-healing capability and recyclability of CANs-NPs. The interaction between NPs (iron oxide, zinc oxide, titanium, and nanocellulose) and the CAN polymer matrix is expected to influence key structural, thermal, and mechanical properties, thereby improving adaptability and reprocess ability.

Analytical Techniques

To thoroughly investigate the synthesis and properties of CANs and NPs, the following analytical techniques will be employed:

- 1. Nanoparticle Characterization:
 - XRD (X-ray Diffraction)
 - ATR-FTIR
 - o TGA
 - Zeta Potential Analysis
- 2. CAN Characterization:
 - ATR-FTIR (Fourier Transform Infrared Spectroscopy)
 - TGA (Thermogravimetric Analysis)
 - DSC (Differential Scanning Calorimetry)
 - o DMA (Dynamic Mechanical Analysis)
 - o Rheology
 - Mechanical Testing
- 3. Interfacial Interactions Between NPs and CANs:

- o QCM-SPR (Quartz Crystal Microbalance with Surface Plasmon Resonance)
- Surface Zeta Potential Analysis
- 4. Surface Chemistry and Structural Properties:
 - XPS (X-ray Photoelectron Spectroscopy)
 - TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry)
 - AFM (Atomic Force Microscopy)
 - o Goniometry
 - o Zeta Potential Analysis
 - o XRD

3. STUDY PROGRAMME

Foreseen study programme, to which early stage researcher shall be enrolled in academic year 2025/2026:

Doctoral School of the Faculty of Mechanical Engineering, modul Design and Textile Materials

4. DESCRIPTION OF WORK AND TASKS

Implementing projects of scientific research. Taking part in the design of research programmes. Cooperating with research sponsors. Drawing up research and other reports. Monitoring and coordinating research work according to the grant agreement. Ensuring safety and health at work. Organising and instructing employees and students on using personal safety equipment and other safety measures. Performing other tasks at the behest of the superiors. Participating in ad-hoc and permanent committees of university or faculty bodies. Acting on behalf of colleagues and superiors during their absence (upon authorisation). Participating in annual and other inventories. Performing other related tasks delegated by superiors.

5. REQUESTED LEVEL OF EDUCATION

VII/2. tariff group

6. REQUESTED FIELD OF EDUCATION

Technical, Natural sciences

7. KLASIUS SRV

Seventh level: Second cycle of higher and similar education/Second cycle of higher and similar education

8. KLASIUS P

145 - Education of teachers of individual subjects

- 4 Natural science, mathematics and computing
- 5 Engineering, manufacturing and construction

9. REQUESTED KNOWLEDGE

Computer skills: MS Windows, Word, Excel, Internet, e-mail, e-commerce

10. REQUESTED SPECIAL REQUIREMENTS

1

11. REQUESTED LANGUAGES

Active knowledge of one world language

12. REQUESTED WORK EXPERIENCE

1

13. FORESEEN POSTDOCTORAL TRAINING

Kliknite ali tapnite tukaj, če želite vnesti besedilo.

Mentor's signature:

Research programme leader's signature:

Name and surname of Dean or authorised person³: Prof. Dr. Matej Vesenjak

Signature of dean or authorised person:

Place and date:

Maribor, 5.2.2025

Kliknite ali tapnite tukaj, če želite vnesti datum.

Stamp:

³ The training program is signed by the dean of the member where the ESR's employment and training will take place.