ABSTRACT

The growing demand for sustainable polymeric materials has driven significant interest in adaptive elastomeric networks capable of combining mechanical durability with reprocessability, recyclability, and self-healing functionality. Dynamic covalent chemistry has emerged as a powerful strategy to design vitrimeric elastomers that bridge the gap between thermosets and thermoplastics by enabling network rearrangement without loss of structural integrity. In this context, the present thesis explores different design strategies to develop next-generation functional elastomers exhibiting vitrimer-like behaviour through the integration of dynamic covalent and supramolecular interactions.

A dual dynamic crosslinking strategy based on disulfide exchange and transesterification reaction was employed to construct vitrimer-like networks in epoxy-functionalized EVA-GMA elastomer, yielding materials with excellent mechanical performance, high extensibility, efficient bond exchange kinetics, and notable self-healing capability. The presence of conjugated moieties within the crosslinker further imparted fluorescence, demonstrating the possibility of integrating optoelectronic functionality into adaptive elastomeric systems.

In another approach, a multifunctional HXNBR-based vitrimers were developed, by incorporating dynamic imine, disulfide, and π–π interactions, resulting in elastomers with enhanced mechanical behaviour, rapid stress relaxation at elevated temperatures following the Arrhenius trend, and exceptional healing performance. The dynamic nature of imine bonds and weak π–π interactions enabled partial solubility in polar solvents, highlighting their potential as recyclable elastomeric adhesives.

Sustainability was further addressed through the development of a fully bio-based vitrimeric elastomer derived from epoxidized natural rubber functionalized with protocatechualdehyde derivatives. Dynamic imine and acetal exchange reactions imparted rapid stress relaxation, stimulus-responsive degradability, and efficient healing behaviour, demonstrating an effective route toward chemically recyclable elastomeric materials.

In addition, a self-healable SBR/PSR blend system based on polysulfide crossover reactions catalyzed by metal chloride was engineered to achieve improved mechanical integrity, efficient healing, and recyclability. The influence of silica reinforcement revealed a critical balance between mechanical reinforcement and dynamic healing behaviour.

Overall, this thesis establishes comprehensive structure–property–function relationships for dynamic elastomeric networks and presents versatile molecular design principles for developing mechanically robust, multifunctional, and sustainable vitrimeric materials suitable for advanced engineering applications.