Design, Synthesis and Characterization of Recyclable polymeric network for high-technology applications

Polymeric materials are designed to meet a wide range of applications in end-use products and are essential to modern life. Their production has increased by many millions of tons in recent decades and is expected to triple by 2050. Many of these polymeric materials were developed for long-term durability and not for being degradable and recyclable [1]. In particular, thermoset polymers are highly crosslinked networks with equally high durability, chemical and mechanical strength. They find several applications in various industries, such as microelectronics, automotive, building materials, ships, and sporting goods, due to their strength, ease of molding, and lightweight compared to metals and ceramics [2]. The main problem with these materials is their poor reworkability and recyclability precisely because of their high crosslink density.

The use of adaptive covalent networks (CANs) has attracted growing interest as a promising solution to this problem. These are cross-linked networks that, unlike thermosets, when thermally treated, can reorganize the connectivity between chains making reprocessing possible [3]. CANs can be divided into associative and dissociative subclasses, according to their exchange mechanism, each of which has its own advantages and applications. In dissociative CANs, upon heating, there is a loss of network connectivity resulting in a decrease in viscosity, similar to that of thermoplastic materials [4]. Whereas associative CANs are permanently cross-linked polymeric materials that exhibit viscoelastic behavior similar to that of a liquid upon heating, while keeping a constant crosslink density, behaving like silica glass; for this reason, these materials are also called vitrimers [5]. While in general a dissociative mechanism results in ease of molding at the cost of lower chemical and mechanical resistance, the opposite can be said for vitrimers.

The goal of the project is to develop recyclable polymer networks through the use of CANs. The first step is to produce telechelic pre-polymers by ARGET-ATRP (Activators ReGenerated by Electron Transfer- Atom Transfer Radical Polymerization), a technique widely used to produce polymers with defined molecular weight and control over dispersion, composition, topology, and functionality. The telechelic polymers will then be post-functionalized to introduce different types of functionality into the final chain. Post-functionalization can be done by radical atomic addition (ATRA), nucleophilic substitution and thermal dehydrohalogenation followed by further functionalization of the produced double bond. The functionalized linear polymers will be cross-linked with an appropriate polymerization agent that will produce CANs with different types of labile bonds. Lastly, the evaluation of rheological, thermal, and mechanical properties will allow an iterative improvement of the tested design. Specifically, attention will be paid to polymer structure (IR, NMR, GPC, swelling), thermal stability (DSC, TGA), rheo-mechanical properties, exchange rate of dynamic bond [4], and number of reprocessing cycles that the material can undergo before properties begin to deteriorate significantly. The ultimate goal of the CANs produced is their use in high-tech applications, so it is important to achieve properties as similar as possible to those of materials already on the market.

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