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Feature Article

Aromatic disulfide crosslinks in polymer systems: Self-healing, reprocessability, recyclability and more

Itxaso Azcune*, Ibon Odriozola[1]

Polymers & Composites Unit, IK4-CIDETEC Research Center, Paseo Miramón 196, 20014 Donostia-San Sebastián, Spain

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ABSTRACT

This featured article brings together recent advances in the field of smart polymers systems which incorporate reversible crosslinks based on aromatic disulfides. The reversibility of aromatic disulfides has been extensively exploited in dynamic combinatorial chemistry, but until recently it has had limited echo in polymer chemistry. Very recently, the incorporation of aromatic disulfide bridges in polymer networks has endowed the development of materials with unprecedented functionalities. Examples of this are self-healing elastomers or epoxy vitrimer composites which show mechanochromic activity. This article provides the reader with a snapshot of our own journey from the roots of sulfur chemistry to the development of new materials.

Contents

1. Introduction

Throughout the history of technology, new materials have set milestones and opened up new possibilities to overcome the existing environmental, technological and economic challenges with increasing sophistication and efficiency. Polymers,

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* Corresponding author.
E-mail address: iazcune@cidetec.es (I. Azcune).
[1] Current address: Constantia Flexibles, Av. de Burgos 67, 26007 Logroño, Spain.

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acknowledged by their light-weight, ease of industrial processing and a broad spectrum of physical properties, have become ubiquitous in the 21st century. They are progressively gaining and adding value in advanced applications, *e.g.* high-performance adhesives, structural composites, medical devices, etc. Historically, polymers have been classified into two main groups: thermoplastics and thermosets. The great advantage of a thermoplastic polymer is that it becomes liquid when heated above a given temperature and solid when cooled below. This property has a tremendous impact in the production of plastic products, since rapid, high volume and economic industrial manufacturing processes, such as injection and extrusion molding, can be used. Importantly, the materials can be reheated, reshaped and recycled closing the loop of their life cycle. However, when it comes to the production of permanent parts with excellent mechanical and thermal properties, thermosets win the game. Thermosets undergo a chemical crosslinking or "curing" step during the manufacturing process, which is responsible for the aforementioned properties. Unfortunately, they can no longer be remolded, reshaped or dissolved, and therefore, their recycling or repair is extremely difficult. Moreover, their associated component manufacturing processes require long-curing times to form the polymer network, and thus are mostly limited to low-medium volume productions. It is nonetheless true that, as the consumption of thermoset systems increases, their weaknesses and drawbacks, such as the lack of reparability, reprocessability and recyclability need to be addressed urgently for the sake of the sustainable development. In the wake of the dynamism shown by living nature, materials that can inherently repair internal and external damages during service life [1–4], as well as thermosets that allow (re)processing and recycling while keeping their functional properties, are actively pursued. This has recently been addressed by the introduction of reversible chemical bonds in polymer networks.

1.1. Reversible chemical bonds in polymers

Reversible chemical bonds, extensively investigated in the frame of dynamic combinatorial chemistry (DCC) [5], have attracted much attention of materials scientists. A reversible bond is defined as a class of chemical linkage that can break and re-form reversibly under equilibrium conditions. It can either be non-covalent (*e.g.* hydrogen bond, electrostatic interactions, etc.) or covalent [6]. Recently, the outstanding properties that could be gained by introducing reversible or dynamic bonds in a polymer network were noticed [4], and the field has blossomed into a myriad of new materials and concepts. Starting from dynamers [4,7], term coined by Skene and Lehn to refer to "*constitutional dynamic polymers of either supramolecular or molecular nature whose monomeric components are linked through reversible connections, which can be either non-covalent interaction or reversible covalent bonds*", to Bowman's covalent adaptable networks (CANs) [8] or Leibler's vitrimers [9].

CANs relate to polymer networks that are connected by reversible or dynamic covalent bonds [8,10,11]. Reversible covalent bonds can be divided into two groups, depending on their exchange mechanism: (a) dissociative CANs, where an existing bond is broken before a new bond is formed, and (b) associative CANs, where the cleavage of the exiting bond and the formation of a new one are concerted. A typical example for a dissociative CAN bond is given by Diels-Alder based polymers. On the other side, the pioneering work in associative CAN systems was based on a photo-mediated free radical addition fragmentation chain transfer reaction using groups as allyl sulfides [12]. The term vitrimer refers only to the second type of CANs, *i.e.* associative CANs, and it has its origin on their "vitreous-like" thermal behavior observed by Leibler and co-workers for epoxy systems containing β-hydroxyester reversible moieties [13].

Vitrimers constitute a new generation of polymer networks that can inherently be healable/repairable, reprocessable and recyclable. Vitrimers can flow when reaching a given temperature, since the exchange reaction is triggered by temperature, but in a different way to thermoplastics and dissociative CANs [13,14]. The latter type of networks show a drastic viscosity drop once a critic temperature is exceeded, whereas vitrimers show a restrained fall. This is because this kind of material retains a fixed crosslinking density throughout the thermal processing, even if the covalent bonds are in a constant exchange. Vitrimers are characterized by a second critic temperature defined as topology freezing temperature (T_v). T_v is the temperature at which the material changes from viscoelastic solid to viscoelastic liquid. Therefore, in the range of its T_v the material can be processed as well as it loses the resistance to creep. Below this temperature, the material shows typical properties of thermosets, but above it, the material gains the aforementioned new functionalities that open new groundbreaking opportunities for material processing. Depending on the equilibrium energy of the dynamic covalent bond and the nature of the chemical structure of the polymer network, a range of T_g and T_v values has been reported. Excellent reviews have been published dealing with the chemical origins, the existing chemistries and the properties of vitrimers [9]. The most common dynamic or reversible chemistries used in the creation of vitrimers or vitrimer-like materials are carboxylate transesterification [13,15], transamination of vinylogous urethanes [16], transalkylation of triazolium salts [17], transcarbamoylation [18], siloxane silanol exchange [19], olefin metathesis [20], imine amine exchange [21] and disulfides, which will be further mentioned in this Feature Article.

1.2. Disulfide bridges in polymer systems

The potential of sulfur chemistry has been acknowledged for the preparation of dynamic polymers and it has been accordingly reviewed recently [22]. The most commonly explored sulfur-based chemistries in this sense are: (i) thiol/disulfide exchange, promoted by the presence of thiolates [23], and (ii) disulfide exchange which undergoes through radical-mediated mechanism [24].