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Review

From landfilling to vitrimer chemistry in rubber life cycle

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ABSTRACT

Cross-linked rubbers used in everyday life, thermoset by nature, represent a major environmental problem at their end of life. The European Union has introduced a hierarchy in waste management from the least to the most favourable solution: landfill disposal, energy recovery, recycling, re-use and prevention. In the case of rubber waste, energy recovery and recycling are the two more widely used methods while prevention still needs to be developed. Recent progresses in organic and polymer chemistry offer new possibilities that may help to improve the end-of-life management of rubbers. Classical recycling methods consist in breaking more or less indifferently bridges and chains, impeding the elastomeric properties of recycled materials. New strategies deal with the design of dynamic bridges making the resulting rubber recyclable and even self-healing in some cases. Playing with the chemistry of rubbers thus appears as a "Cradle to Cradle" approach to get recyclability and prevention of rubber waste. Thermoplastic elastomers, recyclable owing to physical cross-links (supramolecular interactions as phase-separated or crystallized bonds, hydrogen bonds, ionic bonds, fillers) are insufficiently heat- or solvent-resistant. Reversible covalent chemistry as Diels-Alder reaction or better, exchangeable covalent chemistry (vitrimers, transesterification in particular) combine recyclability and solvent insolubility, but often fail in providing elastomers with high mechanical properties. As do so far dual networks, based on supramolecular interactions or reversible covalent chemistry in synthetic rubbers. To get a recyclable rubber exhibiting strong elastomeric properties, an interesting challenge would be providing natural rubber with vitrimer properties.

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0. Introduction

Polymers, commonly addressed as "plastics", are the material of the 21st century. They find their use at every step of our day-to-day life in a very broad range of applications such as automotive, building, aerospace or pharmacy. From a material scientist's point of view, they are historically divided in two main classes: thermoplastics and thermosets. On the one hand, thermoplastics are long, entangled polymeric chains, able to diffuse at high temperature by a phenomenon called reptation [1,2]. Without considering their potential degradation during recycling processes, thermoplastics are in theory fully recyclable by simple injection or moulding methods. At the industrial scale, this recyclability explains that thermoplastics represent about 90% of the total use of polymers nowadays. On the other hand, thermoset materials differ by the existence of chemical cross-links between the polymer chains. The polymer chains can no longer diffuse because of the formation of a polymer network that is however at the origin of a new set of interesting properties (thermal stability, solvent resistance and very good mechanical properties like hardness or elasticity in particular).

Elastomers are a special class of thermoset materials that present additional exceptional properties of elasticity and resilience. They are widely used in the industry when flexibility is required, to make gaskets and seals, or used as noise reduction and damping materials for example. Elastomers are some of the most versatile engineering materials available. However, thermosets by nature, they present a major recycling problem: cross-linking is necessary to obtain the excellent mechanical properties, but it also implies the existence of irreversible chemical bonds between polymer chains that prevent reprocessing or recycling of the material. Because of the scarcity and increasing prices of natural resources, and of the growing environmental awareness, waste management has become a crucial issue in today's society. It is necessary and industrially relevant to find efficient methods for recycling elastomers, reprocessing them, or even just extending their life cycle [3].

The scope of this review is to look at the end-of-life strategies of rubber. We adopted a general approach consisting in reviewing both the history of rubber use and waste management, together with the more recent and perhaps more efficient use of dynamic chemistries for elastomer recycling or life cycle extending. These new formulations show some potential to become the industrial rubbers of tomorrow. The end-of-life and recycling of currently used rubbery objects is a today's relevant problem, which will be tackled in the second part of this review after a brief introduction on what is a rubber. Up to now, the recycling of used objects stays limited because of the associated loss of mechanical properties. Another strategy relies on the chemical modification of the materials to design recycling ability. The aim in this case is to confer thermoplastic's processability to elastomers while maintaining their high elasticity and minimizing the loss of their thermoset characteristics. This represents many chemical and physical challenges that will be exposed in the third part of the review. A new kind of elastomers has been designed and is already used industrially. These so-called thermoplastic elastomers (TPEs) are cross-linked through the use of phase separation and physical interactions but are not fully heat or solvent resistant. Dynamic covalent chemistry is now envisioned as a better solution to produce eco-friendly elastomers. The design of