Renewable Resource-derived Elastomer Vitrimer and Its Sustainable Manufacturing and Application in Extreme Environmental Conditions

Jinlong Zhang, a,b,* Weiguo Li, c and Qinglin Wu d

The development of biomass (e.g., lignin, cellulose or vegetable oil)-based reversibly dynamic covalent cross-linked elastomer vitrimer materials is a novel approach to address issues related to the recycling of waste cross-linked elastomer material. The primary questions discussed are about how to design chemically recycled biomass-derived cross-linked elastomer vitrimer materials, what are the potential challenges in sustainable manufacturing of cross-linked renewable resources derived elastomer vitrimer materials, and what are their potential advanced applications under extreme environmental conditions, such as extreme low or high temperature and irradiated environments.

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Contact information: a: State Key Lab of Metastable Materials Science and Technology, College of Materials Science and Engineering, Yanshan University, Qinhuangdao, 066004, China; b: School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA; c: College of Aerospace Engineering, Chongqing University, Chongqing, 400044, China; d: School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA, 70803, USA; Corresponding authors: jzhan620@asu.edu

How to achieve chemical recycling of renewable resources derived cross-linked network elastomer vitrimer materials?

Cross-linked elastomer materials that have become widely used in our daily lives include rubber tires, polyurethane foams, and polydimethylsiloxane (PDMS) coatings. However, this increasing production, combined with poor recycling mechanisms, has led to a pandemic of waste elastomer materials (Clarke et al. 2023). Thermoplastic elastomer materials are easy to recycle and reused via a melting process, while cross-linked network elastomer materials are much more difficult to recycle or reprocess for the second time. They are normally cured to form covalent cross-linking structures before utilization. However, the incineration treatment as the conventional way to deal with cross-linked elastomer wastes adds to the release of carbon dioxide and thereby increases global warming impact. Considering the challenges of waste cross-linked elastomer treatment, a feasible and sustainable mechanical recycling approach was proposed 10 years ago to deal with waste tires by using their derived rubber powders to design high-performance elastomer toughed polystyrene composites (Zhang et al. 2013). However, its inherent limitations in mechanical recycling demand new techniques for the recycling of cross-linked network elastomer material. US Prof. Bowman at the University of Colorado, Boulder put forward a new concept in 2010, named “covalent adaptable networks,” which can be regarded as a breakthrough in the cross-linked network polymer recycling (Kloxin et al. 2010). Based on Bowman’s work, French Prof. Leibler from ESPCI Paris Tech put

forth a new concept in 2011, named “vitrimer,” thereby achieving cross-linked network material suitable for reprocessing and recycling (Montarnal et al. 2011). Therefore, research on reversibly dynamic covalent cross-linked vitrimer materials offers a new avenue for the recycling and reprocessing. This approach can make a significant contribution to address the plastic pollution crisis and achieve a goal of carbon emission peak reduction and carbon neutrality. Vitrimer is a cutting-edge research topic in the world now and even for the next 5 to 10 years. To address the high processing temperature issues at 200 °C of polyurethane (PU) cross-linked elastomer vitrimer material, a new concept is proposed here of an electronic donating effect to mediate the dynamic covalent bond exchange reaction under mild temperatures. Thus, PU elastomer is enabled to be easily recycled, with reprocessing at 100 °C for multiple times without decomposition (Zhang et al. 2020). The study is in terms of cross-linked network elastomer vitrimer is still in its infancy now. Thus, this work gives a new clue for design of PU vitrimers with mild processing temperatures. Given the depletion of fossil fuels, e.g., petroleum and coal, the development of source compounds from biomass or renewable resources for cross-linked network elastomer vitrimer materials (e.g., vegetable oil, natural rubber, cellulose, and lignin) is an exciting area currently for the purpose of cross-linked elastomer material chemical recycling and sustainable development. The challenge will be to tailor molecular chain structure and sequences via the molecular structure design, using approaches such as controlled radical polymerization and organic catalysis mediated ring open polymerization, to achieve fast stress relaxation under the catalyst-free conditions, thereby achieving chemical recycling dynamic covalent cross-linked biomass derived polyvinyl or polyolefin elastomer vitrimer materials. PU foam and PDMS elastomer materials are also commonly used polymer materials in our daily life. They are giving rise to large amounts of wastes at the end of their lifetime. Therefore, how to design renewable resources or biomass-derived PU or PDMS elastomer vitrimer materials achieving repeated chemical recycling is currently attracting significant attention. Moreover, carbon fiber reinforced cross-linked network polymer composites (e.g., carbon fiber reinforced epoxy resin composites for wind turbine blade) are widely used in aerospace and military field, but it is difficult to recycle carbon fiber at the end of their service lifetime. Therefore, the development of high-performance and easily chemically recycled carbon fiber reinforced biomass derived elastomer vitrimer materials should be receiving more priority.

Is it possible to manufacture renewable resources derived cross-linked network elastomer vitrimer materials using repeated 3D printing?

3D printing has its own characteristics, such as high printing accuracy, complex structure design, and flexible printing methods. Natural rubbers, PDMS, and PU cross-linked elastomer materials are widely used in 3D printing of functional wearable electronic items, flexible sensors, and soft robots. However, due to the covalent cross-linked structure, these elastomer materials can’t be recycled, printed, and utilized in multiple times, thereby producing large amounts of electronic wastes and also resulting in severe environment pollution issues. Therefore, the research on the 3D printing cross-linked elastomer vitrimer material recycling and reprocessing makes it possible to address the challenging issues in term of the recycling of and reprocessing of wearable electronic products and flexible sensor materials. As vitrimer is a new type of dynamic covalent cross-linked materials, the dynamic covalent bonds can be easily broken and reformed at the appropriate temperature. Thus, single/twin screw extrusion, injection molding, and hot pressing as conventional
polymer compounding approaches have been explored for vitrimer material manufacturing to achieve its recycling and reprocessing. For instance, in the authors’ previous work, the usage of PU elastomer vitrimer via hot press compounding enabled the material to be recycled three times, and its mechanical properties still maintained a decent performance (Zhang et al. 2020). However, traditional polymer compounding has its own restrictions, as it is hard to tailor complexity in material internal structure to achieve its unique function. Digital light, direct ink writing and fuse-deposition molding 3D printing as advanced manufacturing techniques are emerging as sustainable strategies for elastomer vitrimer material manufacturing. The research in terms of renewable resources or biomass (lignin, cellulose or vegetable oil) derived elastomer vitrimer material 3D printing is still in its infancy. Therefore, underlying questions need to be further explored in the near future, such as how to tailor the rheological properties of renewable resources derived elastomer vitrimer material to maintain printed product integrity during direct ink writing or digital light 3D printing (Li et al. 2021) and how to perform fuse deposition molding 3D printing approach (Sun et al. 2021) to design conductive biomass elastomer vitrimer with the prerequisite of ultra-low conductive filler utilization.

**What are the potential applications in extreme environmental conditions of renewable resources derived cross-linked network elastomer vitrimer?**

Cross-linked network elastomer vitrimers have their unique characteristics in addition to recycling and reprocessing, such as self-healing and shape memory effect. These attributes make vitrimer material suitable for use in the aerospace, space exploration, and military areas under extreme environmental conditions, e.g., extreme low/high temperatures, ultra-high vacuum, and radiation-filled environments (Yang et al. 2021). For instance, the cross-linked renewable resources derived network elastomer vitrimer has its inherent characteristics such as ultra-fast self-healing capacity at room temperature. Thus, it is an ideal sealant material for space shuttles [e.g., National Aeronautics and Space Administration (NASA)] that enable to repair its damage automatically to avoid aerospace catastrophe. It is also promising to further develop sustainable renewable resources derived elastomer vitrimer hybrid coating protection materials for fighter aircraft and space aircraft the need to serve under extreme environmental conditions, e.g., ultra-low temperature below 200 °C, ultra-vacuum, and radiation conditions (Yang et al. 2021). Moreover, it is still challenging currently to develop biomass-derived PU or nitrite butadiene rubber vitrimer sealant materials for high speed railway bearings that work under heavy loads and ultra-low temperature extreme conditions. 2D transition metal carbides (MXene) as a new type of 2D material is a promising to address this question above, e.g., polyurethane-Mxene hybrid materials (Wyatt et al. 2021).

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