Phosphate esters dynamic chemistry enables flame retardant vitrimers

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What is the outcome or accomplishment?

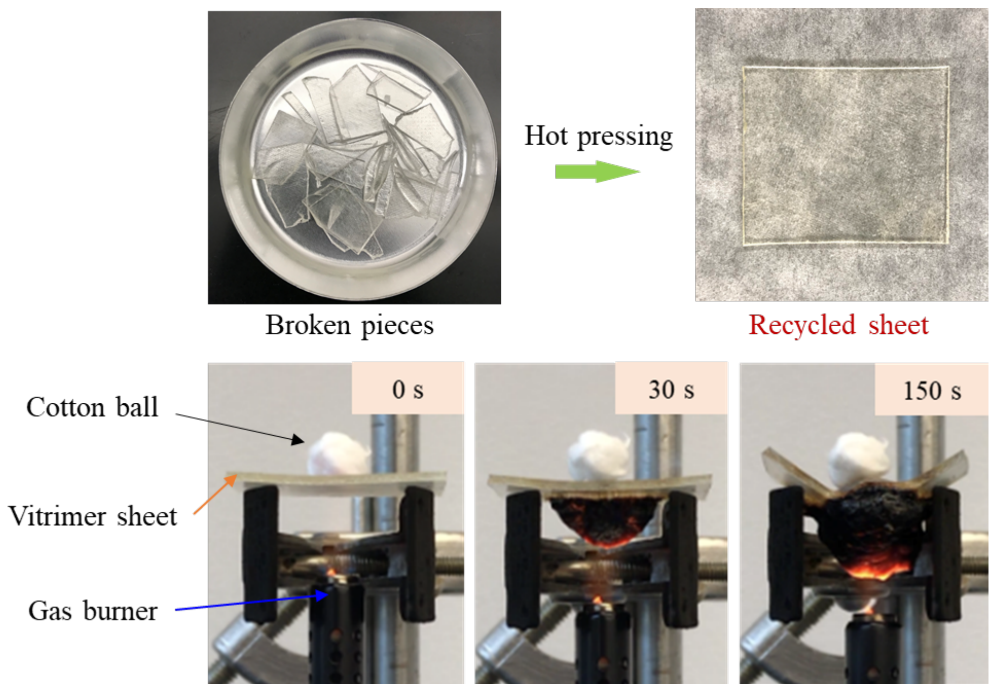
Researchers with the Louisiana Materials Design Alliance (LAMDA) report the first phosphate esters based thermoset polymers that are mechanically strong, completely malleable and recyclable, and significantly safe under fire. These promising properties rely on the unique behaviors of β-hydroxy phosphate esters at low, medium, and high temperatures, respectively. At room temperature, the abundant hydrogen bonds in the network contribute to outstanding toughness (5.44 MJ/m^3). Around 100 ^{o}C, the catalyst-free rapid exchange reaction between phosphate esters and neighboring β-hydroxyls endows the polymer with almost 100% recycling efficiency. Above 250 ^{o}C, a cellular layer of charred phosphoric acid generated from β-hydroxy phosphate esters could separate/insulate the heat effectively, providing fire protection. In addition, by combining phosphate diesters and acrylates, a new polymer integrated with ultraviolet (UV) curability, recyclability, and flame retardancy are also developed. This highly crosslinked network exhibited attractive recyclability even at the temperature lower than glass transition temperature. The fast exchange reactions via catalyst-free mixed transesterification between phosphate diesters and carboxylate esters of acylate structures are validated.

What is the impact?

The phosphate dynamic chemistry proposed here is a fantastic drop-in technology that can be easily used to develop a broad range of high-performance vitrimers while possessing intrinsic flame retardancy. Coupled with the high transparency, these self-healing fire-safe vitrimers can serve as multifunctional coatings for metallic structures or components with a high risk of fire and corrosion, such as in construction fields and electronics. The UV curability of the combination of phosphate diesters and acrylates enables the printing of customized and complicated structures in these advanced fields, such as robotics and aerospace, using digital light processing (DLP) technology. We believe that this work could expand the scope of dynamic covalent chemistry and create new directions in developing multifunctional thermoset polymers.

What explanation/background does the lay reader need to understand the significance of this outcome?

Fire hazards are a well-known limitation for polymers. Thermoset polymers, while they have high mechanical strength and thermal stability, are usually not recyclable, which causes a significant waste disposal issue. Therefore, sustainability and safety have been one of the key issues in polymer science and engineering due to the shortage of natural resources, the crisis in waste disposal, and fire hazards caused by flammable polymers. Recyclable thermosets or vitrimers and fire-retardant polymers have been developed separately for years to address these challenges partially. To our knowledge, no other vitrimer has demonstrated fire-retardant capability without adding extra flame-retardant structures. Therefore, integrating robust mechanical performance, recyclability, and flame-retardancy into one polymer using the new facile dynamic covalent chemistry initiated in this study is of significant value to both academia and industry.



(Top row) The broken thermoset vitrimer pieces after service can be reshaped into a new transparent sheet by a simple hot pressing for reuse. (Bottom row) The vitrimer sheet under the cotton ball generates an expanded char layer upon external fire to protect the cotton ball from temperature rising and burning for a couple of minutes.