

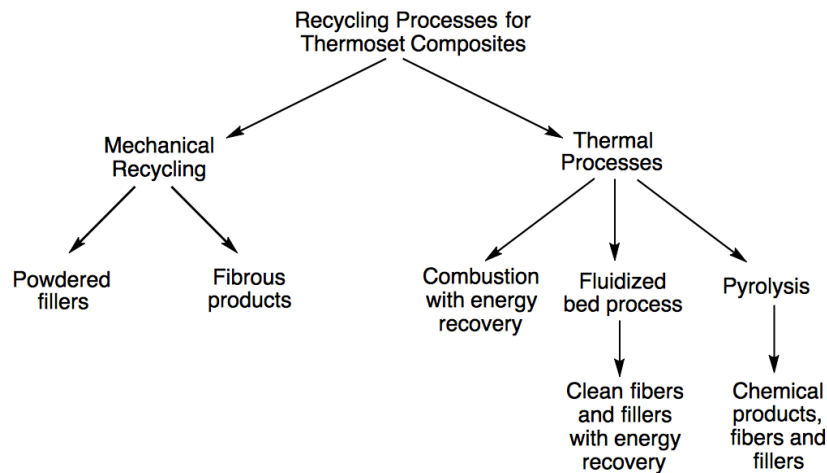
# Recent Advances in Recyclable Thermoset Polymers

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Literature Seminar

October 30, 2014

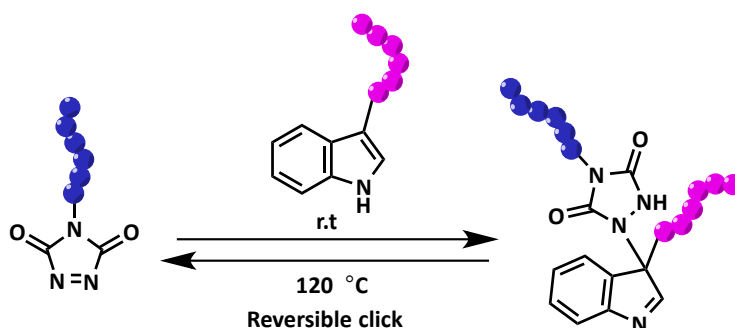
Thermoset polymers have attracted considerable attention over the past few decades and significant advances have been made within the last five years towards the development of new thermoset polymers with facile recycling properties.<sup>1</sup> Linear polymers, commonly called thermoplastics, typically have easily accessible melting points and can be reprocessed and recycled using heat, but are not durable enough for many high performance applications. One example of this type of thermoplastic polymer is polyethylene terephthalate (PET), the material used to make Coke<sup>®</sup> bottles. Covalently cross-linked polymers, commonly called thermosets, typically have superior dimensional stability, high-temperature mechanical, thermal, and environmental resistance. Thus, they do not have melting points and therefore are not easily processed using conventional thermoplastic recycling methods. One example of this type of thermoset polymer is polyimide (PI), which is used in printed circuit boards and in modern aircraft body parts. Consequently, it is often more cost-effective to discard these thermosetting polymers and composites in landfills than it is to attempt to recycle them through the thermal or mechanical routes shown in Figure 1.<sup>2</sup> Furthermore, thermosetting polymers are mainly derived from petrochemicals, which are finite resources.



**Figure 1.** Current ways to recycle composite thermoset polymers.<sup>2</sup>

In an effort to protect the environment by limiting the use of finite resources and avoiding the accumulation of persistent polymers in landfills and unregulated areas, legislation and tax incentives have been introduced to encourage the recycling of thermoset polymers.<sup>3</sup> Through the use of reversible covalent bonds to form cross-links in high-density network polymers, several research groups have designed novel polymer systems that can not only maintain the high performance properties consistent with thermosets under a wide range of conditions, but also be welded,<sup>4</sup> mended, reshaped,<sup>5</sup> or completely degraded to their constituent monomers upon a specific stimulus.<sup>6</sup> Their work has fundamentally changed the way in which thermoset polymers can be recycled.

In 2010, the Bowman research group first reported the synthesis of a new polymer system based on covalent adaptable networks and coined the term “CANs” to describe them.<sup>5</sup> They synthesized polymers that rely on the triggerable crosslinking and de-crosslinking of C-C bonds within a polymer network to create viscous and malleable thermoset polymers only when stimulated. Specifically, one system they investigated combined Diels-Alder and Reverse Diels-Alder triggered crosslinking and decrosslinking to afford thermo-responsive recycling properties to thermoset polymers. Their research presents an interesting paradigm for polymer/materials science because CANs inherently have the ability to incorporate other chemical functionality post-polymerization, providing an adjustable scaffold that is readily modified to incorporate new and important mechanical and chemical properties. The Du Prez research group further expanded the available CANs triggers to include recyclable thermoset polymers based on a reversible click reaction as shown in Figure 2.<sup>7</sup>

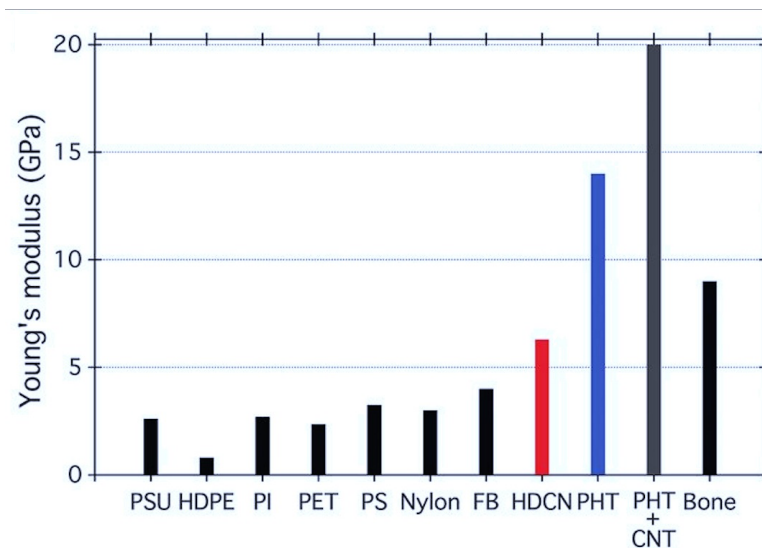


**Figure 2.** Novel CANs type polymer based on reversible click reaction forming an ene adduct.<sup>7</sup>

Congruent to Bowman *et. al.*'s discoveries, the Leibler research group discovered a novel network polymer system based on the chemical equilibrium between bond breaking and reforming reactions without irreversible side reactions in 2011.<sup>4,8</sup> In their system, heating has the dual effect of displacing the equilibrium toward depolymerization and accelerating the rate of bond breaking and bond reforming reactions. Leibler *et. al.* coined the term “vitriimer” to describe their novel recyclable polymer systems that rely on strong glass forming covalent networks. Organic strong glass formers can be shaped and reshaped in the same way as glass (silicon dioxide) because they exhibit melt to hardening characteristics that follows the Arrhenius equation. Leibler *et. al.* applied their polymer design to epoxy resins hardened with carboxylic acid or anhydride monomers and  $Zn(acac)_2$  catalyst. The catalyst enables the polymer to be molded after polymerization through rapid transesterification reactions under precise thermal conditions. The Williams research group has further developed vitriimer chemistry to eliminate the need for metal additives to affect fast and efficient transesterification reaction between monomers derived from renewable resources.<sup>9</sup> The Zhang research group has shown water triggered recycling of a network polymer based on polyimine bond exchange reactions.<sup>10</sup> Finally, the Hillmyer research group has expanded the transesterification functionality to produce polyactide vitrimers.<sup>11</sup>

Stemming from a serendipitous laboratory mistake, Garcia and coworkers at IBM discovered a novel covalent network polymers formed by the condensation of paraformaldehyde with bisanilines that form hard thermoset polymers or, when more oxygenated, produce self-healing gels.<sup>6</sup> The Young's modulus of a polymer is indicative of its ability to elastically deform under load. The higher the Young's modulus of a material, the stiffer it is. Garcia *et. al.*'s hard

thermoset polymers have Young's modulus comparable to or better than some composite, thermoset, thermoplastic polymers currently on the market as seen in Figure 3. Only strong acid digestion of their novel polymer allows for full depolymerization and recovery of the bisaniline monomers.



**Figure 3.** Young's Modulus comparison of Garcia *et. al.*'s recyclable thermoset polymers: (HDCN, hemiaminal dynamic covalent network), (PHT, poly(hexahydrotriazine), (PHT + CNT, poly(hexahydrotriazine with 5 wt% carbon nanotubes added) vs. traditional thermoset: (PI, poly imide), thermoplastics: (PSU, polysulfone),(HDPE, high-density polyethylene), (PET, polyethylene terephthalate), (PS, Polystyrene), Nylon and composite material: (FB, fiber board), bone.<sup>6</sup>

With the continued development of CANs, vitrimers, and other novel thermosetting polymer systems within academia and industry, the viability of these recyclable polymers will undoubtedly expand further into industrial and biological realms. While several new classes of recyclable thermoset polymers have been developed, additional research is needed to evaluate their chemical and recyclable compatibility with composite materials such as fiberglass and carbon nanotubes. The most obvious drawbacks to some of the thermoset recycling approaches discussed herein are the use of potentially dangerous acidic conditions to produce reusable monomers. Moreover, the use of a thermal triggers to enable post synthetic remolding of an otherwise thermosetting polymer somewhat relegates its use to a small portion of industries that require chemical and environmental stability without high-temperature stability. Because thermoplastics are easily recycled, reshaped, and reformed when heated, there is well-established infrastructure to recycle these types of polymers at the end of their useful life. In order for recyclable thermosets to take hold in the current market, researchers must make it a priority to design them in a way that facilitates their integration within this existing recycling infrastructure or with very low-cost recycling mechanisms. Additional research innovations will further facilitate the steady transition from the industrial utilization of non-recyclable thermosets to recyclable thermosets with comparable high performance characteristics. Continued investigation into alternative polymer network formation strategies will certainly obviate the current limitations associated with recycling thermoset polymers.

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