

The Vitrimer Route to Recycling of Polymer Waste

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The fundamental issue underlining the difficulty of recycling polymers is that the free energy of polymerization is strongly favorable – thus, reversing this process to create monomers is energetically unfavorable, and hence economically not viable. We shall thus discuss different strategies that can facilitate this key process for families of polymers, and in particular, we shall consider an approach using vitrimers to compatibilize blends. Dynamic covalent polymer networks - polymer networks that can undergo bond association and dissociation reactions rearrange their structures while maintaining their overall integrity, thus resulting in unique properties such as self-healing, reprocessability, shape memory and adaptability. Here, we show that when immiscible blends are heated and processed together with dynamic crosslinkers added in small amounts, the immiscible mixed plastics are compatiblized by a new material, called a multiblock copolymer, that is formed in situ. Since these copolymers molecules can be formed where we need them most, i.e., where the two immiscible polymers meet, they continue to compatibilize these mixtures across multiple use cycles without degrading properties. This new method of upcycling, which does not involve deconstructing or reconstructing any of the original polymers, introduces a potential solution for recapturing materials and energy endowed in postconsumer mixed plastics that typically end up in landfills.

As a means of understanding these results we conduct simulations and show that the introduction of crosslinks whether reversible or permanent, directly impacts the equilibrium polymer density. For a limiting case where the bonds are the same size as the polymer chain bonds, simulations, Flory-like arguments and thermodynamic calculations show that the crosslinks induce an increased entropic cohesion in the liquid. The resulting density increase causes an enhancement of interfacial tension as has been found experimentally. These findings implicate density as a key variable in polymers with (dynamic) crosslinkers, one that can be used to facilely tune their properties. Additionally, we also consider the dynamics of these systems – while standard polymer theories (e.g., the Rouse model) can describe the chain motion between crosslinks, the larger scale motion is not described by the sticky Rouse model. The implications of this idea to mechanical reinforcement will be explored.