Cross-linking polyethylene through carbenes

de Zwart, F.J.; Bootsma, J.; de Bruin, B.

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A carbene-forming molecule can glue various polymers, even ones lacking functional groups

By Felix J. de Zwart, Johan Bootsma, Bas de Bruin

The development of universal methods for surface modification and cross-linking of polymeric materials is highly desirable. Mechanical properties of natural and synthetic materials rely on the ability of the polymeric chains to form a three-dimensional (3D) network, for example, through cross-linking (1, 2). On page 875 of this issue, Lepage et al. (3) show that a rationally designed bis-diazirine inspired by the well-known 3-aryl-3-(trifluoromethyl)-3H-diazirine motif can be used for the cross-linking of nonfunctionalized saturated hydrocarbon polymers.

In natural macromolecules such as chitin and synthetic materials such as Kevlar, hydrogen-bond formation between amide groups form noncovalent cross-links. Many oil-based polymer coatings used in paintings and to protect wooden structures derive their 3D structure and strength from covalent cross-links formed in radical-based processes. Other examples of covalent cross-linking, such as vulcanization of rubber and the strengthening of unfunctionalized polyethylene glycol, but efficient generic cross-linkers for the strengthening of unfunctionalized polyolefins have not been developed (8).

Lepage et al. now report a carbene cross-linker containing two diazirine motifs. Free carbenes can be generated upon photochemical or thermally induced nitrogen (N₂) loss (see the figure). A drawback of molecules containing N₂ expelling motifs (such as diazirines) is explosion risk, and the authors abandoned known bis-diazirine compounds because of their volatile and explosive nature. They rationally designed a bis-diazirine cross-linker that finely balances risk and reactivity and generates two free carbenes that insert into C–H bonds of the polymer. The tethered structure forms cross-links between different polymer chains, even those of PE and PP. The molecular weight of PP increased with the amount of cross-linker added, corroborating successful cross-linking of the substrate. The bis-diazirine also cross-linked several other polymers, such as poly(vinylalcohol) (PVA). For PVA, whether carbone insertion occurred through C–H or O–H bonds was not investigated, but the latter seems most likely (9). This cross-linking methodology could find applications in upgrading biopolymers in which O–H bonds are ubiquitous.

The authors also explored application of the cross-linker as an adhesive for high-density PE (HDPE). Adhesion to this low-surface-energy material is difficult—it failed for a control sample with a commercial adhesive (Super Glue). However, the bis-diazirine cross-linker showed high performance in adhesion tests, and analysis of ripped samples revealed a cohesive failure mechanism indicative of cross-linking to the HDPE surface. The cross-linker was also an effective synthetic fabric strengthener.

Lepage et al. assume that in their reactions, singlet carbenes are generated that insert in a concerted manner into C–H bonds, which makes sense given the relatively controlled reactivity toward cyclohexane. But formation of triplet carbenes that react through radical processes cannot be fully excluded (10). Radical-type pathways could damage polymer integrity, so examining the electronic structure of the formed carbenes is needed. This could also aid in developing carbenes that can be generated at lower temperatures, possibly through transition-metal catalysis (4).

The cross-linker developed by Lepage et al. not only has potential applications as an adhesive, but similar reagents could be used in paints and coatings. Prospective bio-based binders such as cellulose and lignin lack readily cross-linkable groups such as isocyanates, ketones, or alkenes. The cross-linking method of Lepage et al. may help turn biomass-based macromolecules into functional materials.

REFERENCES AND NOTES


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