Cross-linking polyethylene through carbenes

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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 drying of glues, rely on reactive functional groups already present in the polymer.

Polymers such as polyethylene (PE) and polypropylene (PP) lack reactive cross-linkable groups, but cross-linking can be essential to tune mechanical properties. Copolymerization of ethylene or propylene with functionalized olefins can introduce reactive groups, but the scope of suitable comonomers is limited, and important material properties such as microstructure and molecular weight can become difficult to control (4, 5). It is especially challenging to synthesize high-molecular weight copolymers with tunable amounts of functional groups (5). Mildly efficient cross-linking strategies that break carbon-hydrogen (C–H) bonds by using high-energy radiation or peroxides exist for PE, but these methods degrade PP (6). High-energy reactants tend to react through hydrogen-atom abstraction (HAA) and related radical-type pathways that damage the polymer.

Free (singlet) carbenes and transition-metal carbene complexes can undergo direct C–H insertion instead of HAA to form covalent carbon-carbon bonds even from unactivated C–H bonds. Carbenes are used for polymer postfunctionalization, as polymerization catalysts and as polymer backbone

Methods developed by 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 pathways 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 alkynes. The cross-linking method of Lepage et al. may help turn biomass-based macromolecules into functional materials.

REFERENCES AND NOTES

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amount of cross-linker added, corroborating successful cross-linking of the substrate. The bis-diazirine also cross-linked several other polymers, such as polyvinylalcohol (PVA). For PVA, whether carbene 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.

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