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Biomimetic antioxidant cure: Silicones loaded with phenols including vitamins

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PURPOSE OF THE ABSTRACT

A range of natural antioxidant moieties ?including vitamins A and E ? provide protection for organisms against degradative oxidation processes. Many other natural materials, particularly those based on phenols including eugenol from cloves, quercetin from many vegetables, and catechol derived from flavonoids, also act as antioxidants. Release of (synthetic) antioxidants from synthetic polymers is often used to extend their lifetimes.

Silicones are synthetic polymers that, in oil form, readily degrade in the environment to sand, water and CO2. Their synthesis has a high energy toll. Silicones are known for water repellency, low surface energy, and high electrical resistance. They would not, therefore, immediately be considered as media for redox chemistry. One strategy to make silicones more sustainable involves diluting them with natural materials to both reduce their energy content and develop materials with new properties. We show that the inclusion of antioxidant molecules that can perform redox chemistry fulfills these requirements and provides a new biomimetic, catalyst-free method for silicone crosslinking.

Commercial silicone polymers were modified by hydrosilylation using a few ppm of Karstedt's platinum catalyst or a Piers-Rubinsztajn reaction [1] using a few ppt of B(C6F5)3; both telechelic and pendent polymers were available (Figure 1). The materials slightly increased in viscosity. Vitamin E derivatives, blocked at the phenolic position, were weak antioxidants, as judged by a DPPH assay. Retinoate silicone derivatives (Vitamin A) exhibited stronger, but unimpressive antioxidant behavior.

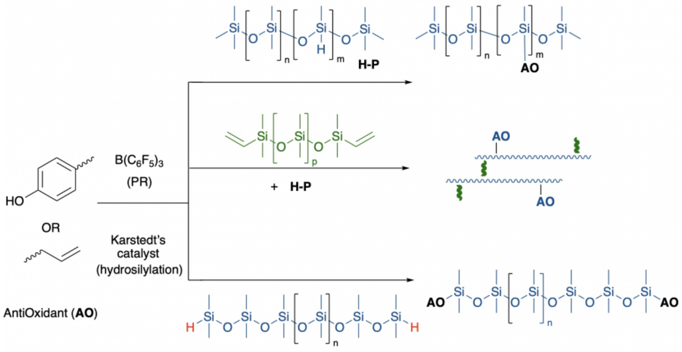
Exposure of eugenol derivatives to various peroxides at elevated temperatures led, depending on temperature and ratio of peroxide/eugenol, to gels, elastomers and eventually brittle elastomers as a consequence first of phenoxy radical formation and then formation of the biphenyl (Figure 2A). Even less chemistry was required to form robust elastomers from catechol or pyrogallol (Figure 2B). Simply mixing aminoalkysilicones with the phenol led to robust elastomers whose crosslink density was simply tuned by the ArOH/NH2 ratio. IR studies showed that both H- and ionic bonding are involved in crosslinking.

Both eugenol and catechol/pyrogallol silicone elastomers were powerful antioxidants, as measured by DPPH assays. If run in water, the external layer of the silicone reacted to form radicals that, only under vigorous conditions, led to hardening of the external layer. If better solvents for silicone were used, like isopropanol, the entire elastomer body could decolorize DPPH. The antioxidant activity tracked with the density of free ArOHs in the elastomer.

Phenolic oxidative coupling is one method nature uses to assemble complex polymers of which lignin is exemplary [2]. H-bonding is also well known to arise with biological phenols like tyrosine. However, the resilience of the phenol/amine bond in the silicone/phenol elastomers was surprising. The non-covalent interactions could be overcome, but only with difficulty. The materials were thermoplastic at about 80 °C, depending on the concentration of ArOH/NH2 groups. The elastomers could also be dissolved by adding chaotropic solvents or strong base, in which case the silicone backbone itself could be compromised.

The benefits of silicones in these materials are augmented by the inclusion of natural phenols. The materials can be crosslinked into elastomeric objects, including films, using a biomimetic redox process or simply by mixing to make robust, thermoplastic elastomers that exhibit protective antioxidant activity. We propose to show, in biological media, the available degradation pathways of the elastomers prepared by these different bonding modes.

FIGURES



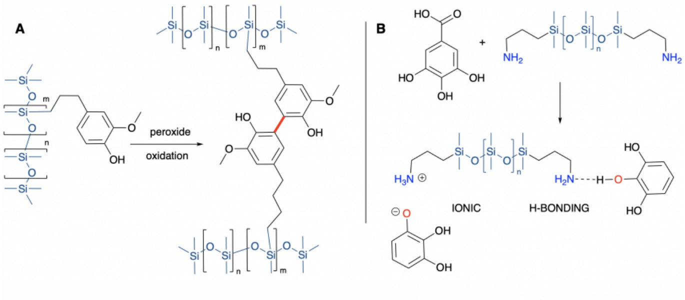


FIGURE 1

Figure 1

Antioxidants linked to HSi-silicones using hydrosilylation and Piers-Rubinsztajn.

FIGURE 2

Figure 2

A) Oxidative coupling and B) ionic + H-bond crosslinking of phenols.

KEYWORDS

Silicone | Natural Antioxidants | Phenolic coupling | H- and Ionic bonding

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