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Biomimetic crosslinking of silicones by phenolic coupling: Learning from the trees.

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PURPOSE OF THE ABSTRACT

Phenols are excellent antioxidants that intercept reactive radicals to give neutral molecules and much more stable phenoxy radicals. Nature uses such molecules not only to stabilize radical derivatives but as a means to create structural entities through phenolic coupling of two phenoxy radicals, a thermodynamically favorable process. Enzymes often help mediate these processes, as is the case with peroxidases and laccases in the formation of lignin, [1] the 3 dimensional network polymer that is intrinsic to the structural strength of, for example, wood. Lignin contains many biphenolic moieties.

Silicones are totally synthetic polymers that possess very different properties than organic analogues and are exploited for their thermostability, oxygen permeability, biocompatibility and, in the case of personal care products, a nice aesthetic comfortable feel. [2] Silicone polymers undergo facile decomposition in the environment to yield sand water and CO2; the rate of elastomer decomposition is less well understood. However, their synthesis has a high energy toll. One strategy to exploit the benefits of the materials, but mitigate the energy costs, is to dilute silicones with natural materials. We report the preparation of eugenol-modified silicone oils that have intrinsic antioxidant properties and that can be crosslinked using phenolic coupling to give antioxidant silicone elastomers.

Eugenol, isolated from clove oil, was chemically tethered to silicones using hydrosilylation. Libraries of compounds were made, including pendent and telechelic compounds in which both molar mass and quantity of eugenol were varied (up to 50% of silicone monomers could bear eugenol). The product polymers were all transparent oils that differed in viscosity depending on the variables just noted. All the compounds exhibited antioxidant activity using a DPPH assay, which converts purple DPPH radicals into yellow products. The antioxidant activity correlated directly with eugenol concentration in the polymer. There was no evidence that the phenoxy radicals formed underwent condensation - no changes in viscosity were observed.

More vigorous oxidants were explored to elicit phenolic coupling. Initial studies with benzoyl peroxide at 90 °C in solvent were encouraging as, for a given oil, the gels formed with product hardnesses that correlated with both quantity of eugenol groups and quantity of peroxide added. However, once the solvent was removed by evaporation crystalline benzoic acid remained trapped in the product and proved difficult to remove. Di-t-butyl peroxide requires a higher offset temperature - 130 °C - but clearly led to elastomers with t-butanol as the volatile byproduct.

It was possible to tune physical properties of elastomers simply by changing the amount of peroxide until the maximum was reached near the stoichiometric requirement of ½ peroxide/phenol. The elastomeric products were also antioxidants but, at very high crosslink densities, not all the phenols are able to participate in DPPH reactions.

FIGURES

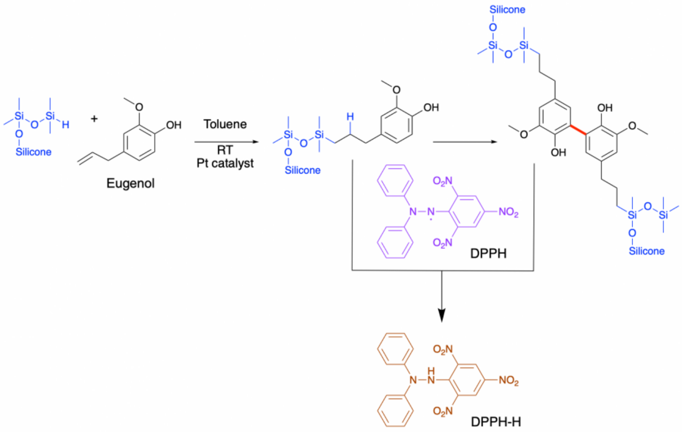

FIGURE 1

Oxidative coupling of eugenol silicones

Synthetic pathway to the curing of eugenol silicones with antioxidant properties.

FIGURE 2

KEYWORDS

antioxidant | silicone | biomimetic chemistry | eugenol

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