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Natural Phenolic Crosslinkers for Sustainable Silicones

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PURPOSE OF THE ABSTRACT

Silicone elastomers are widely used in applications ranging from adhesives and film formers to implanted biomaterials. They are entirely synthetic and require a large energy input for their synthesis; degradation of silicone oils in the environment to water, sand and CO2 is efficient.

How little silicone is necessary in a composite to exhibit silicone properties? One strategy to enjoy the benefits of silicones but use much less of them to fulfill the desired application, is to dilute them with natural organic materials. Silicones have exceptionally low surface energy and will bloom to air interfaces where their hydrophobic, thermal, and electrical stability and biocompatibility properties manifest.

Previously, we have examined the ability to disperse/graft proteins [1] vegetable oils [2] and saccharides [3] in silicone elastomer. We were interested in developing silicone-based materials that could act as antioxidants. Natural oligo/polymeric antioxidants ranging from lignin [4] humic acid, green tea extracts, to tannins are readily available. There is a report on the use of tannic acid as an H-bonding silicone crosslinker [5].

Model studies with catechol and pyrogallol demonstrated that even these small phenols are capable of crosslinking aminoalkylsilicones into elastomers. While with the polyphenolic crosslinker tannic acid, pendent aminoalkylsilicones performed well, it was much easier to design the crosslinking - the network structure - and to tune physical properties by judicious use of different molar mass telechelic polymers. It was possible to make elastomers with useful physical properties with loadings from only about ~ 0.5% by weight, which gave soft elastomers, to ~ 4% by weight, above which the materials were brittle and readily cracked with mechanical stress. Subtle variations were observed with the different polymeric phenols, but specific structures were less important than the loading in the silicone. By varying the molecular weight of the silicone, the [NH2] could also be altered, both of which had effects on the mechanical properties of elastomers. Shorter chain length silicones resulted in materials that were strong yet brittle, while longer chain length silicones exhibited great elongation. The materials were thermoplastic - melting around 160-180 °C, depending on the crosslink density. IR data demonstrated that both ionic and H-bonding were involved. The elastomers required chaotropic solvents - a mixture trifluoroacetic acid and guanidine - to break the interactions and release the silicone oil starting material [6].

These data indicated that tannic acid was too efficient a crosslinker; only low levels of dilutions in silicones were possible. Higher molar mass natural polyphenols that could be expected only to interact/react at the external interface were therefore examined. These included tannins used in wine making, green tea extracts, two types of lignin and humic acid. In all cases, it was possible to prepare silicone elastomers/foams in loadings of the natural material up to about 50% by weight, above which the materials were brittle and friable.

Polyphenol antioxidants act as both molecular crosslinkers and reinforcing fillers for silicone elastomers up to

about 50% by weight; only small quantities of the small multifunctional crosslinker tannic acid could be incorporated. The resulting materials possess desirable silicone properties, antioxidant activity and, we hope to show, accelerated degradation at the end of life.

FIGURES

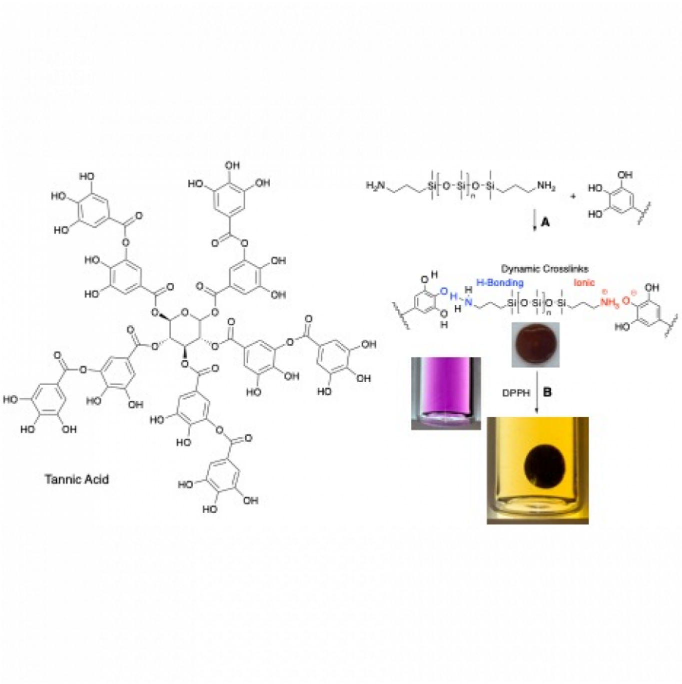

FIGURE 1

Polyphenolic Silicone Elastomers

A) Silicone elastomers crosslinked with polyphenolic compounds and B) decolorization of DPPH.

FIGURE 2

KEYWORDS

Sustainable | Antioxidant | Silicones | Polyphenols

BIBLIOGRAPHY

[1] Zelisko, P. M.; Aguilar, A. L.; Brook, M. A., Delivery of Both Active Enzyme and Bleach from Water-in-Silicone Oil (D4) Emulsions. Langmuir 2007, 23 (7), 3620-3625, DOI 10.1021/la063340s.
[2] Gale, C. B.; Chin, B.; Tambe, C.; Graiver, D.; Brook, M. A., Silicone Structurants for Soybean Oil: Foams, Elastomers, and Candles. ACS Sustainable Chemistry & Engineering 2019, 7 (1), 1347-1352, DOI 10.1021/acssuschemeng.8b05047.
[3] Faiczak, K.; Brook, M. A.; Feinle, A., Energy-Dissipating Polymeric Silicone Surfactants. Macromolecular Rapid Communications 2020, 41 (11), 2000161, DOI 10.1002/marc.202000161.
[4] Zhang, J.; Brook, M. A., Exploiting Lignin: A Green Resource. In Mobilizing Chemistry Expertise To Solve Humanitarian Problems Volume 2, American Chemical Society: 2017; Vol. 1268, pp 91-116.
[5] Kong, S.; Wang, R.; Feng, S.; Wang, D., Tannic Acid as a Natural Crosslinker for Catalyst-Free Silicone Elastomers From Hydrogen Bonding to Covalent Bonding. Frontiers in chemistry 2021, 9, 778896-778896, DOI 10.3389/fchem.2021.778896.
[6] Rambarran, T.; Bertrand, A.; Gonzaga, F.; Boisson, F.; Bernard, J.; Fleury, E.; Ganachaud, F.; Brook, M. A., Sweet supramolecular elastomers from [small alpha],[small omega]-([small beta]-cyclodextrin terminated) PDMS. Chemical Communications 2016, 52 (40), 6681-6684, DOI 10.1039/C6CC02632J.