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Acrylated soybean oil: a key intermediate for more sustainable elastomeric materials

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PURPOSE OF THE ABSTRACT

Use of renewable feedstocks is one of the twelve green chemistry principles and can be one of the hardest to follow in the polymeric area. However, the use of plant oils as a platform to generate functional materials might be the key to achieve this ideal.[1] The facile epoxidation of soybean and related vegetable oils has opened new paths for investigation in this field. While epoxide opening by amines and thiols have been reported, the need for catalysts to improve the rate of the ring opening and/or to avoid the cleavage of the ester bond has limited potential functionalization of the base structure with other interesting building blocks.

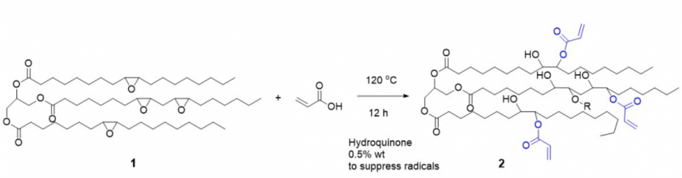
The opening of oxiranes in 1 using acrylic acid under mild conditions, generated the key acrylated soybean oil starting material 2.[2] The resulting beta-hydroxy acrylate moiety is more reactive than simple acrylates, particularly for the catalyst free aza Michael reaction.[3] The exposure of the acrylated soybean oil to telechelic aminopropylsilicones, which act as crosslinkers, led to soft (10-15% mol of amino silicone) or hard (> 25% mol) brownish elastomers; elastomers with better optical properties can be generated by reaction of 2 with pendent aminosilicones (transparency can be achieved in spite of the differences in RI between the 2 constituents). Thia-Michael additions are also possible with 2. Cysteamine, an odor-free sulfur compound, is an interesting building block due the two different functional groups that it possesses.[4] The internal amine can act as the base to generate thiolates that can then add-without the addition of catalyst or heat-to the acrylic groups to generate aminofunctional oil 3.[5]

These compounds serve as the bases of functional polymers. Amino-soybean oil 3 forms Schiff bases with terephthaldehyde to form dynamic covalent materials.[6] We were particularly interested in antioxidant materials that provide protective films on various substrates. Eugenol, extracted from cloves, was selected as the active antioxidant. Thiol-ene chemistry was used with cysteamine to generate amine-functional eugenol 4. The concentration of eugenol on the polymer can be tailored simply by choosing the fraction of acrylates to be used as crosslinkers and those to be used to bind eugenol. Crosslinking can be induced using telechelic amino silicones or via UV crosslinking using DMPA as initiator.

An alternative route also leads to eugenol-containing elastomers. The aza-Michael addition of 3-aminopropyltriethoxysilane to 2 leads to alkoxysilane materials 5 that are able to self-cure with hydrolysis. Eugenol was also modified with alkoxysilane groups by direct hydrosilylation with diethoxymethylsilane giving 6. The different alkoxysilanes were mixed and allowed to cure to generate orange elastomeric films. Both types of eugenol-containing films were potent antioxidants as shown by DPPH assays.

As described above, acrylated soybean oil 2 is a key molecule leading to functional materials that are largely based on a renewable feedstock. We hope to show that this and the derivatives described are easily degraded by natural processes at the end of normal use and will examine their antimicrobial properties.

FIGURES



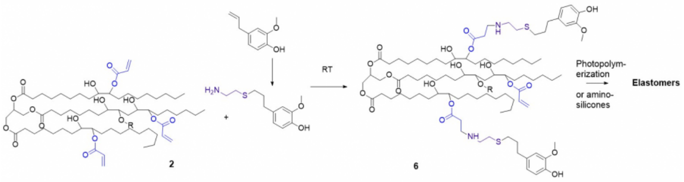


FIGURE 1

Acrylated soybean oil 2

Conditions of synthesis for the acrylated soybean oil

FIGURE 2

A route to eugenol-modified soy-based elastomers.

Synthesis of antioxidant soybean oil using a modified eugenol with cysteamine via thiol-ene chemistry

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KEYWORDS

Plant oils | Acrylated soybean oil | Aza-michael reaction | Thia-michael reaction

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