SHORT COMMUNICATION

Synthesis of Toughened Elastomer from *Vernonia galamensis* Seed Oil

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This paper examines the synthesis of a toughened elastomer from *Vernonia galamensis* seed oil by reacting vernonia oil with vernonia oil-derived suberic acid (octanedioic acid), and cross-linking the pre-polymer in the immediate presence of cross-linked polystyrene prepared *in situ*. The paper also demonstrates that the progress of reaction can be followed by monitoring the generation of hydroxyl groups using infrared spectroscopy. Analysis of some crystalline material on the cooler parts of the reaction vessels revealed the presence of component fatty acids of vernonia oil. Transmission electron microscopy characterization of the synthesized toughened elastomer suggests that vernonia oil-suberic acid polyester and polystyrene polymer are interpenetrating.

Various workers (1–4) have identified *Vernonia galamensis* seed oil (VO) as a rich source of epoxytriglycerides which have a number of potential industrial applciations (5,6). One of such applications, developed in Sperling's laboratory (4), was the synthesis of monomers from VO and sebacic acid used in the preparation of toughened elastomers. At present, sebacic acid and other dibasic acids are commercially available from sources other than VO. However, as part of our program on the utilization of VO as a source of industrially important dibasic acids, we recently reported the synthesis of a series of dibasic acids from VO, including suberic (octanedioic) acid (3).

Therefore, in order to improve the efficient utilization of VO in the synthesis of toughened elastomers, this study has examined the synthesis of a toughened elastomer from VO and VO-derived suberic acid. In addition, the study demonstrates that the progress of the reaction between VO and suberic acid can be monitored using infrared spectroscopy.

EXPERIMENTAL

Synthesis. Vernonia oil (VO)-suberic acid (SU)/polystyrene (P) simultaneous interpenetrating networks (VOSU-P-SIN) was prepared, essentially as described by Sperling and his group (7) for vernonia oil-sebacic acid/polystyrene simultaneous interpenetrating networks.

To prepare the vernonia oil-suberic acid prepolymer (VOSUPP), degummed vernonia oil obtained from K. D. Carlson, USDA, Peoria, was mixed with suberic acid at a ratio of 1 (epoxy group):1 (carboxyl group), assuming that the oil contains 80% epoxy acid, resulting in an average of 2.4 epoxy functionality per molecule of VO. The mixture was heated and stirred in a paraffin bath at 140°C under argon atmosphere, and after seven hours prepolymer (PPP) was prepared by rapidly mixing styrene with divinyl benzene and benzoyl peroxide at 1% and 0.4% concentrations, respectively. This was mixed at room temperature. PPP (equal amount by weight of VOSUPP) was immediately charged to the VOSUPP flask, and the reaction continued for 25 min, before pouring the mixture into molds that had been pre-heated at 80°C. The reaction was then continued at 80°C in a vacuum oven for 24 hr. Subsequently, the temperature of the oven was raised to 140°C for an additional 36 hr to complete the VOSU-P-SIN reaction.

Suberic acid was prepared from vernonia oil as previously described (3).

Infrared spectroscopy. The preparation of VOSUPP was followed by an hourly monitoring of the infrared spectrum of 0.7 mg of reaction mixture (neat), using a Perkin-Elmer 983 spectrophotometer.

Gas chromatography-mass spectrometry (GC/MS). After 7 hr of reaction of VO-SU mixture, crystalline sublimates were found to be deposited on the air condenser. This crystalline material was subjected to total fatty acid analysis by the room temperature transesterification technique previously described (2).

Ultrastructural studies. Small pieces of the polymer were cut into slices less than 1 mm in diameter and then immersed for 3 hr in 2% OsO_4 solution at room temperature. The slices were then washed in distilled water, dehydrated in a graded alcohol/water series, and embedded in Epon. Thin sections, approximately 500–600Å thick, were cut with a diamond knife using a Dupont 6000 ultramicrotome and then counterstained with uranyl acetate and lead citrate. Thin sections were examined in a Zeiss EM10 transmission electron microscope, and photographs were taken at original magnifications from 20–220,000.

RESULTS AND DISCUSSION

At 140°C, the reaction between vernonia oil and suberic acid is primarily that between the hydroxyl groups of suberic acid and the epoxy groups of vernonia oil (7) (Figs. 1 and 2). Cross-linking by the suberic acid can occur intramolecularly as well as intermolecularly.

It is therefore expected that as the disappearance of the epoxy group progresses, the generated hydroxyl groups should increase in concentration, provided they do not immediately participate in the reaction (8). This was confirmed by infrared spectroscopy (Table 1). A plot of the log absorbance of the -OH stretching frequency (ca. 3479 cm^{-1}) against time (Fig. 3, $r = 0.998$) reveals that generation of -OH is exponential with time. As the log [epoxy] plotted against time by Sperling and his group (7) also showed a linear relationship with time, the -OH

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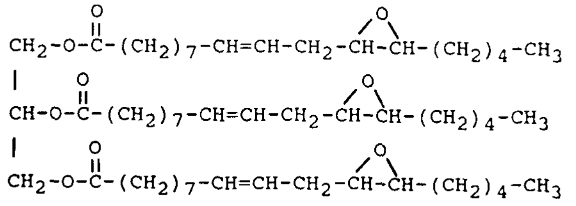

FIG. 1. Trivernolin (major component triglyceride of vernonia oil).

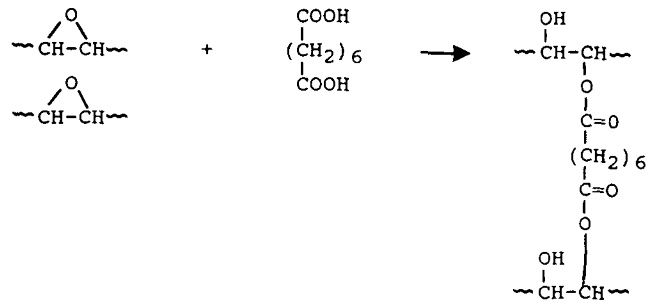

FIG. 2. Reaction scheme for vernonia oil-suberic acid prepolymer.

TABLE 1

Infrared Spectra of Vernonia Oil-Suberic Acid Reaction

Time (hr)	Absorbance 3479 cm^{-1} [hydroxyl]
0	22.04
1	27.54
2	33.11
3	44.22
4	45.42
5	51.61
6	66.34
7	71.50
Coefficient of correlation of log [A] vs time	0.9981

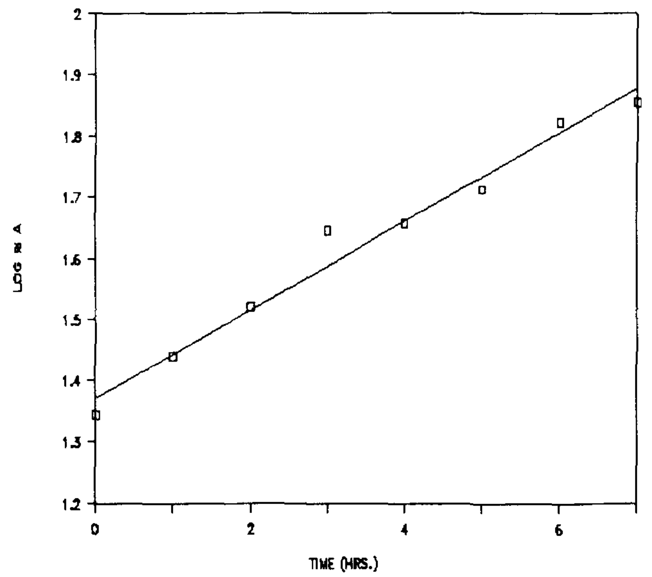

FIG. 3. A plot of log absorbance versus time.

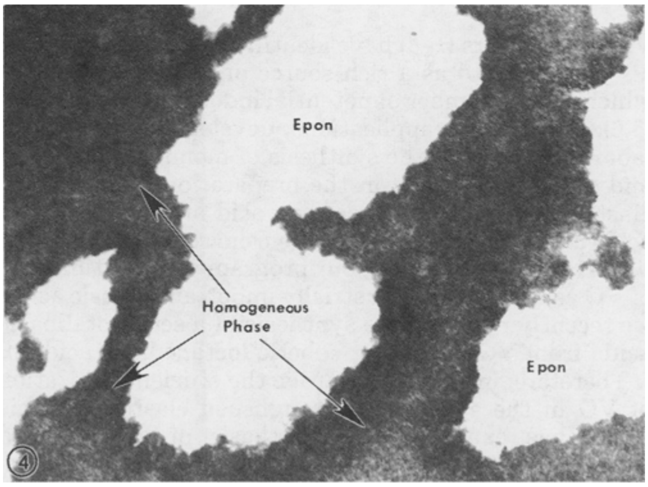

FIG. 4. Transmission electron micrograph showing the epon and the homogeneous phase of the elastomer ($\times 5 \times 10^3$).

stretching frequency could constitute a simple technique for monitoring the disappearance of the oxirane group, and indeed for similar reactions between vernonia oil and dibasic acids. It should be noted here that because of the weakness of the epoxy absorption frequency (ca. 825 cm^{-1}), it is impossible to monitor the reaction in a similar fashion using the disappearance of the epoxy group. Although Sperling and his group noted the possibility of an additional formation of -OH group due to allylic oxidation, we believe that such a contribution is insignificant. We came to this conclusion because of the absence of -OH absorption when VO was heated alone under conditions similar to those of the VOSUPP reaction.

Another observation in this study was the deposit of white crystalline material on the wall of the air condenser. A GC/MS analysis of methylated portions showed that this crystalline material contains no free acids; however, upon transesterification, fatty acids methyl esters were found, 49.98% of which were vernolic acid. This suggests that some triglycerides may be entrained in the argon stream under the reaction condition. However, we should note that the amount of material lost due to this deposit is insignificant (<0.1%).

When VOSUPP and PPP were synthesized and crosslinked in the immediate presence of each other a creamy, white, tough, rubbery substance was formed. Ultrastructural studies reveal that the polymeric material was intensely stained with osmium tetroxide, uranyl, and lead stains. At low magnifications one structural phase was visible, in which a homogeneously stained material surrounded spaces filled with Epon (Fig. 4). At higher magnifications, the homogeneously phased material was composed of a network of rod-like structures (Figs. 5 and 6). These rods were approximately 20-30Å in length and less than 10 Å in diameter. They formed a complex

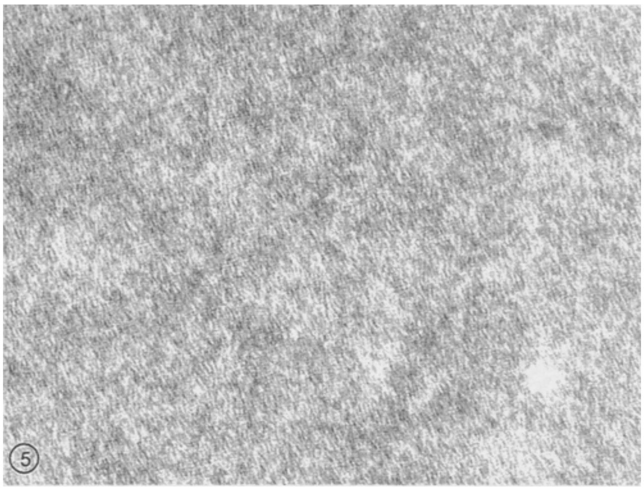

FIG. 5. Higher magnification of the homogeneous phase showing the fibrous substructure of the elastomer (× 104 × 10^3).

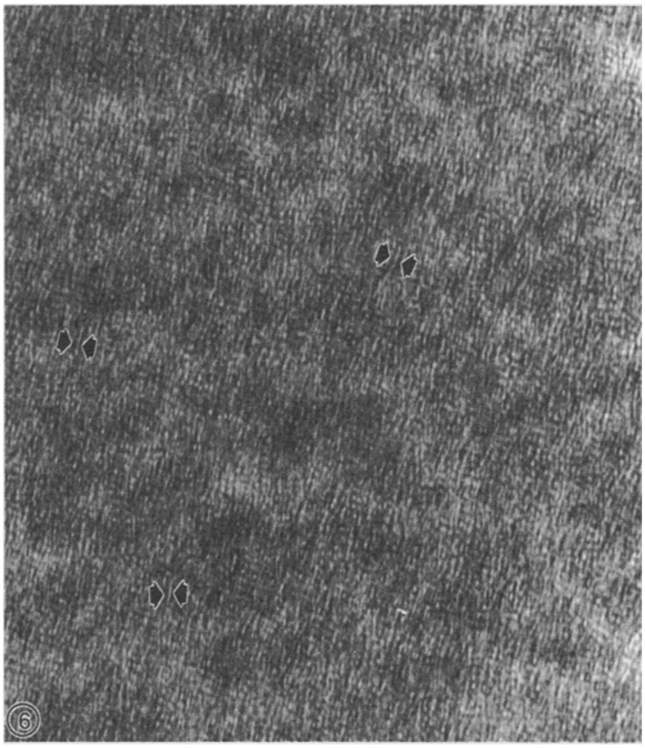

FIG. 6. At high magnification the lattice-like structure of the elastomer is revealed. Rod-like elastomer fibers (arrow head) result from osmiophillic Vernonia oil-suberic acid polyester (× 567 × 10^3).

intercalating lattice structure, where the interstices were totally obliterated. The ultrastructure of the lattice was apparent after osmium fixation and staining, and required no counterstaining with uranyl acetate and lead citrate for visualization.

The polymer was composed of a lattice network of small lipidic molecules that bound osmium tetroxide. They displayed a bimolecular "leaflet-type" structure, where the lipidic subunits were largely running parallel to each other and apparently cross-linked with adjacent molecules. The electron microscopic investigations did not reveal any cross-bridges between the lipidic molecules, however, they may indeed exist. We gained the impression that the molecules are slightly out of phase with each other and were constituted into a lattice network (Fig. 6).

The present preliminary studies further demonstrate the potential utilization of vernonia oil for the synthesis of toughened elastomers. Future studies will include the use of various dibasic acids and the material characterizations of the resulting polymers.

ACKNOWLEDGMENTS

This study was made possible, in part, as a result of funding from the United States Department of Agriculture, Office of International Cooperation and Development, International Research Division (USDA/OICD/IRD, #58-319R-8-020), and the Howard University Faculty Research Fund.

The authors thank J. B. Morris and F. E. Grissom of Howard University for their support, K. D. Carlson of USDA/ARS, Peoria, Illinois, for supplying the *V. galamensis* oil, and R. E. Perdue of USDA/ARS, Beltsville, Maryland for valuable information on the agronomic potential of *V. galamensis* oil.

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[Received September 26, 1988; accepted April 3, 1989]
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