Antioxidative activity on soybean oil. By the POV changes (Fig. 4b) after oxidation products I-V, TBHQ and BHA were added, each at 0.01%, to soybean oil, all of these oxidation products, except III, were confirmed to have antioxidative activity on soybean oil, too. The order of the antioxidative activity was: TBHQ > IV > V > BHA > II > I > III.

Antioxidative activity on lard. By the changes in POV (Fig. 4c) after adding oxidation products I-V, TBHQ and

BHA, each at 0.01%, to lard, all of these oxidation products were confirmed to have antioxidative activity on lard, too. The order of antioxidative activity was: V > IV > TBHQ > II > BHA > III > I.

From the results mentioned above, it was confirmed that these oxidation products increased the stability of three base oils over AOM, and that all of these five had antioxidative activity. However, this activity depended on the kinds of base oils. Table I shows the induction periods and the antioxidation ratios calculated from the relative ratios of the induction periods over that of TBHQ. It is notable that these oxidation products, except I, developed significant antioxidative activity stronger than that of the base compound TBHQ when methyl oleate was used as the base oil. Both IV and V developed remarkable antioxidative activity on soybean oil, whereas the activities of I, II and III were almost the same as that of BHA and comparatively low. The antioxidative activity of both IV and V on lard were the highest.

TABLE I

Antioxidative Activity of Oxidation Products of TBHQ on Methyl Oleate, Soybean Oil and Lard

Compound[a]	Methyl oleate		Soybean oil		Lard	
	IP[b]	AR[c]	IP	AR	IP	AR
None	7.0 hr		10.3 hr		5.1 hr	
I	8.0	0.05	10.8	0.02	10.8	0.10
II	45.8	2.53	11.8	0.06	56.5	0.87
III	33.5	1.73	9.6	−0.03	35.1	0.51
IV	27.1	1.31	27.3	0.68	67.0	1.05
V	27.0	1.31	24.3	0.56	86.8	1.39
TBHQ	22.3	1.00	35.1	1.00	64.0	1.00
BHA	38.8	2.08	12.5	0.09	47.8	0.72

[a]Concentration : 0.01%.
[b]IP : induction period.

$$^{c}AR : \text{antioxidation ratio} = \frac{IP_{sample} - IP_{control}}{IP_{TBHQ} - IP_{control}}.$$

Antioxidative activity

Methyl oleate: II > BHA > III > IV = V > TBHQ > I
Soybean oil: TBHQ > IV > V > BHA > II > I > III
Lard: V > IV > TBHQ > II > BHA > III > I

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☆Interpenetrating Polymer Networks from Triglyceride Oils Containing Special Functional Groups: A Brief Review[1]

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ABSTRACT

Although most triglyceride oils contain only double bond functionality, a few oils such as castor oil, vernonia oil, lesquerella oil, etc., contain other functional groups. These functional groups include hydroxy and epoxy groups, permitting the easy formation of polyesters and/or polyurethanes. In addition to the natural formation of epoxy-bearing oils, the double bond functionality in ordinary triglyceride oils can be epoxidized. When these oils are polymerized to form polyesters or polyurethanes in the presence of polystyrene to synthesize interpenetrating polymer networks (IPN), a new class of tough plastics is formed.

INTRODUCTION

Although most triglyceride oils contain only double bonds as functional groups in the fatty acid hydrocarbon chains, a few of these oils are endowed with special functionalities (1,2). Some of these functionalities include hydroxyl groups and epoxy (or oxirane) groups. These oils can react with many chemical reagents yielding polyurethane or polyester polymer networks. When such polymer networks are combined with a second polymer in network form, an inter-

¹Presented at the symposium on Nonfood Applications for Whole Plant Oils, 72nd annual AOCS meeting, 1982.

penetrating polymer network (IPN) is produced. Such IPN form impact-resistant plastics or reinforced elastomers depending on overall composition and phase continuity.

The present research program began in 1974 as an international program with Colombia, South America. The original intent was to develop castor oil-based interpenetrating polymer networks as castor beans now grow wild in Colombia. It was intended to develop a domestic crop at a suitable time. This research resulted in several publications (3-16) and a patent (17).

Beginning in 1978, the program was broadened to include polymers containing oxirane groups. Two types of materials were examined: (a) vernonia oil, which is a triglyceride oil that naturally contains 80% epoxy groups on an acid residue basis, and (b) ordinary triglyceride oils, such as linseed oil, whose double bonds were deliberately epoxidized. These oxirane groups can be polymerized with materials such as sebacic acid, which itself is derived from castor oil, to produce polyester networks. In addition, the hydroxyl groups on lesquerella oil have been esterified with sebacic acid, leading to new elastomers and IPN.

This paper will review the research to date, and also describe new oils now under examination.

DEFINITIONS

Interpenetrating polymer networks are a type of graft copolymer. In Figure 1, the solid line indicates polymer I, and the dotted line is polymer II. In the case of a polymer blend, structure A, the two molecules are not joined, but lie near one another in juxtaposition. Such a material can be prepared by mixing two polymers in an extruder, for example.

Structure B is a graft copolymer where polymer I forms the backbone and polymer II forms the side chain. The graft copolymers are widely used as impact-resistant plastics such as high impact polystyrene and ABS materials. Such products include the white opaque plastic used to make refrigerator ice trays.

Structure C represents a triblock copolymer. A block copolymer differs from a graft copolymer in that the chain segments are linked end to end. The triblock copolymers are widely used as thermoplastic elastomers. Common commercial products include sneaker soles and electrical wire insulation.

Structures D and E represent a semi-IPN and a full IPN, respectively, where either one or both of the polymers are crosslinked. Whereas structure E requires two polymers to make two networks, structure F uses two polymers to make one network. The type of grafting encountered in structure F, known as AB crosslinked polymers, is called conterminous grafting. In the discussion that follows, structure E will be emphasized.

An interpenetrating polymer network as described in structure E is defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other.

The synthesis of an IPN is illustrated in Figure 2, which shows two types of interpenetrating polymer syntheses. First, the reaction for a sequential IPN is shown, where monomer I is polymerized together with crosslinker I to produce a network. Then monomer II and crosslinker II are swollen in and then polymerized in a sequential mode to make the IPN.

In the simultaneous interpenetrating networks (SIN), the two reactions are run simultaneously. This reaction will be emphasized in the present paper. One reaction, for example, can be a polyesterification or a polyurethane stepwise reaction, while the other is an addition reaction using styrene to make polystyrene via free radical chemistry.

CASTOR OIL IPN

Castor oil is a special monomer for polymerization because it contains essentially three hydroxyl groups per molecule, one on each ricinoleic acid residue. The presence of the three hydroxyl groups permits reactions with sebacic acid to form a polyester, or with a diisocyanate to form a polyurethane. In both reactions, in the proper concentration ranges, a crosslinked network will be formed because the castor oil is trifunctional. It should be especially noted that the reaction between castor oil and sebacic acid yields a material in which every carbon atom originates from a renewable resource, because sebacic acid itself is commercially derived from castor oil.

The reaction scheme to produce castor oil-based simultaneous interpenetrating networks is illustrated in Figure 3. The castor oil is reacted with sebacic acid in Figure 3 to form a prepolymer at 180 C (upper left). The temperature is then lowered to 80 C, styrene, crosslinker (divinyl benzene) and initiator (benzoyl peroxide) are added and the reaction continued at 80 C (lower left). Under these conditions the styrene and divinyl benzene polymerize, but the castor oil prepolymer reaction has substantially stopped. As
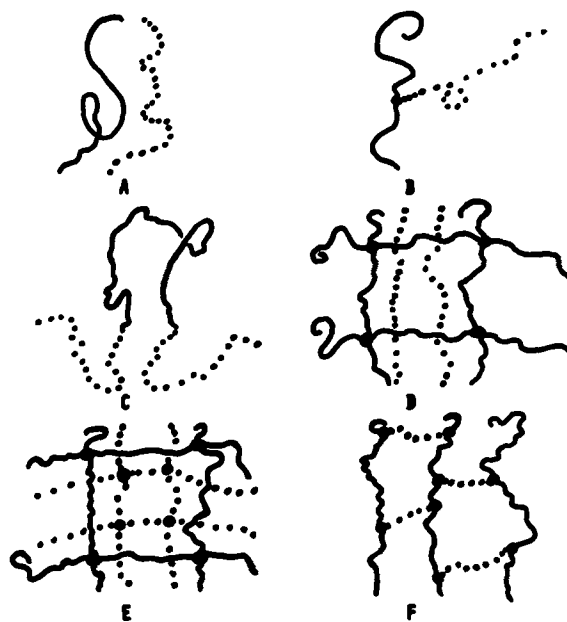

FIG. 1. Some structures of two polymer materials. Structure A, a polymer blend; structure B, graft copolymer; structure C, a block copolymer; structure D, a semi-IPN; structure E, an IPN; and structure F, an AB crosslinked polymer (ref. 18, Vol. 2).
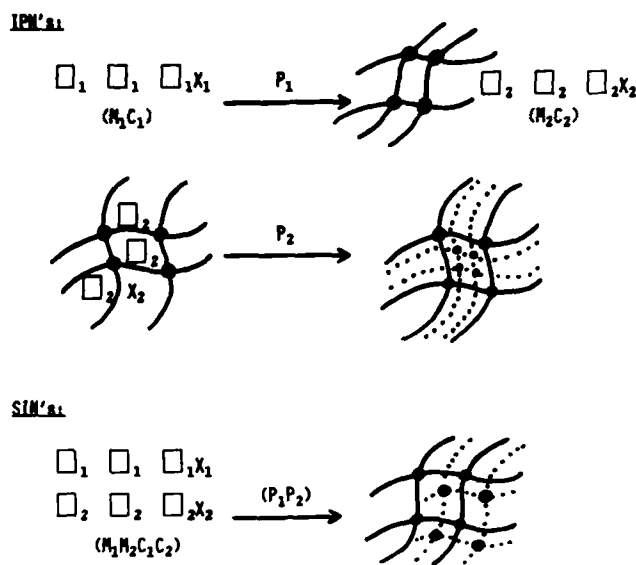

FIG. 2. The synthesis of sequential IPN above and simultaneous interpenetrating networks, SIN, below. For the synthesis of SIN, two different reactions operate simultaneously such as condensation polymerization and addition polymerization (19).

illustrated in Figure 3, the material first phase separates and then phase inverts on continued reaction. After the phase inversion is complete, the material is poured into the mold and the reaction continued until the polystyrene gels and finally reacts completely. Then the temperature is again raised to 180 C with the castor oil prepolymer continuing to react, finally gelling. Then the material is postcured to produce the finished SIN.

The phase inversion process will now be reviewed. A series of samples were taken as a function of reaction time and put in test tubes (see Fig. 4). In each of the test tubes the material layered into a soft material on top and a hard material on the bottom. The amount of soft material on the top decreased with increasing reaction time.
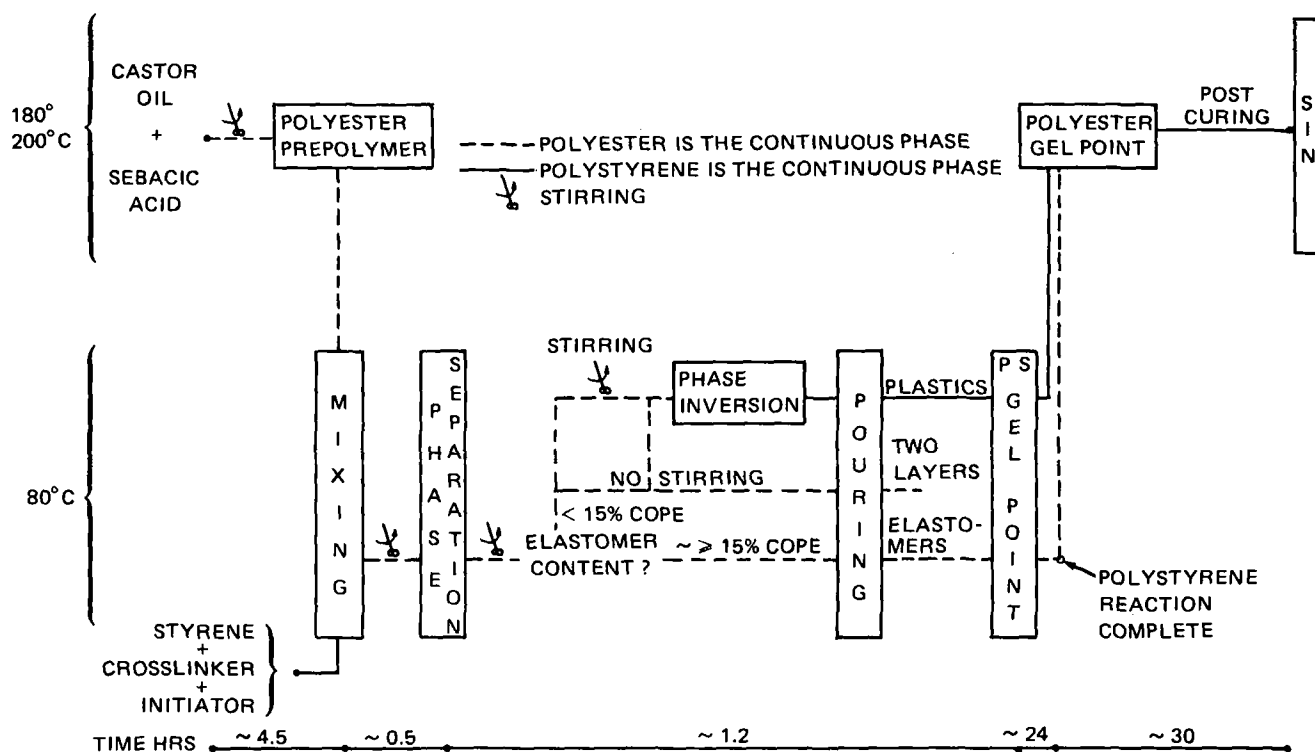
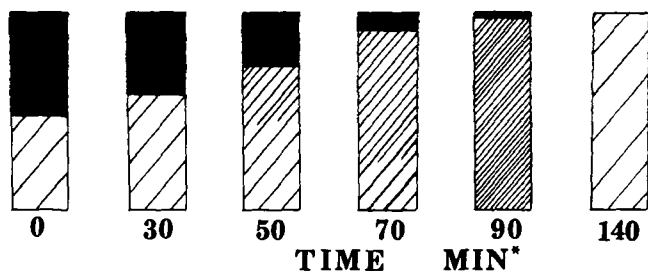FIG. 3. The reaction scheme for synthesizing castor oil/polystyrene-based SIN (11).

FIG. 4. Layering effect during the synthesis of 10:90 castor oil polyester (COPE)/polystyrene network (PSN) simultaneous interpenetrating network (11).

Transmission electron microscopy was carried out on each of the samples, both top and bottom. The castor oil phase was stained with osmium tetroxide. The results are shown in Figure 5. In each case the bottom material had polystyrene as the continuous phase. Apparently, this is the final form of the material. The upper layer first showed the oil as the continuous phase shown as the dark material (upper left).

The top center figure illustrates the partly phase inverted material. The top right figure shows a morphology similar to the lower material, illustrating that phase inversion was completed and the material ready for pouring into the mold. It must be remarked that the final morphology of this material is strikingly similar to that found in high impact polystyrenes (18,20,21). In that case, of course, the rubber component is a polybutadiene instead of the castor oil-based elastomer of the present study.

The phase inversion phenomenon is modeled in Figure 6. Phase II (PS rich) forms the continuous material when the volume fraction of polymer II is the larger and/or the melt viscosity of polymer II is lower, as illustrated by being either above or to the right of the curve. Otherwise, phase I (oil rich) is continuous. Actually, the line is not sharp, there

being a range of dual-phase continuity (23). As the styrene is polymerizing, phase II increases in volume, probably following the dotted line in Figure 6.

The mechanical data are illustrated in Figure 7. Whereas the pure homopolymer castor oil elastomers are soft and weak, the IPN are tough and highly extensible. Especially interesting are curves 6 and 7, for chemically identical systems. Curve 6 represents the simultaneous interpenetrating mode of polymerization, and curve 7 represents the sequential IPN mode of synthesis. Note that in this case, curve 6 is that of a tough elastomer while curve 7 is that of a plastic, illustrated by the higher initial slope and a yield point (12).

EPOXY OIL IPN

Epoxy groups can be placed on unsaturated triglyceride oils by reactions involving hydrogen peroxide in the presence of glacial acetic acid and a cationic ion exchange catalyst (24). Alternatively, some oils, such as vernonia, are natural bearers of epoxy groups (25,26) (see structure 1). The chemistry of these oils has been reported recently (27,28).
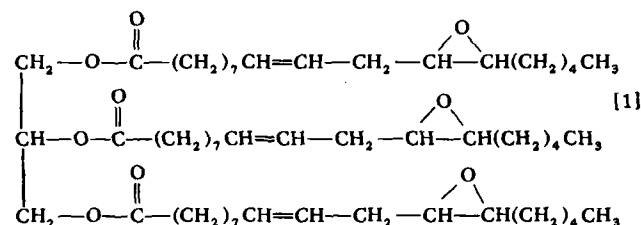
The morphology of a 50:50 vernonia oil/polystyrene simultaneous interpenetrating network is shown in Figure 8. The vernonia oil-sebacic acid polyester forms the continuous phase, forming a reinforced elastomer.

The dynamic mechanical spectroscopy of this material is shown in Figure 9. Here, the storage modulus, E', and
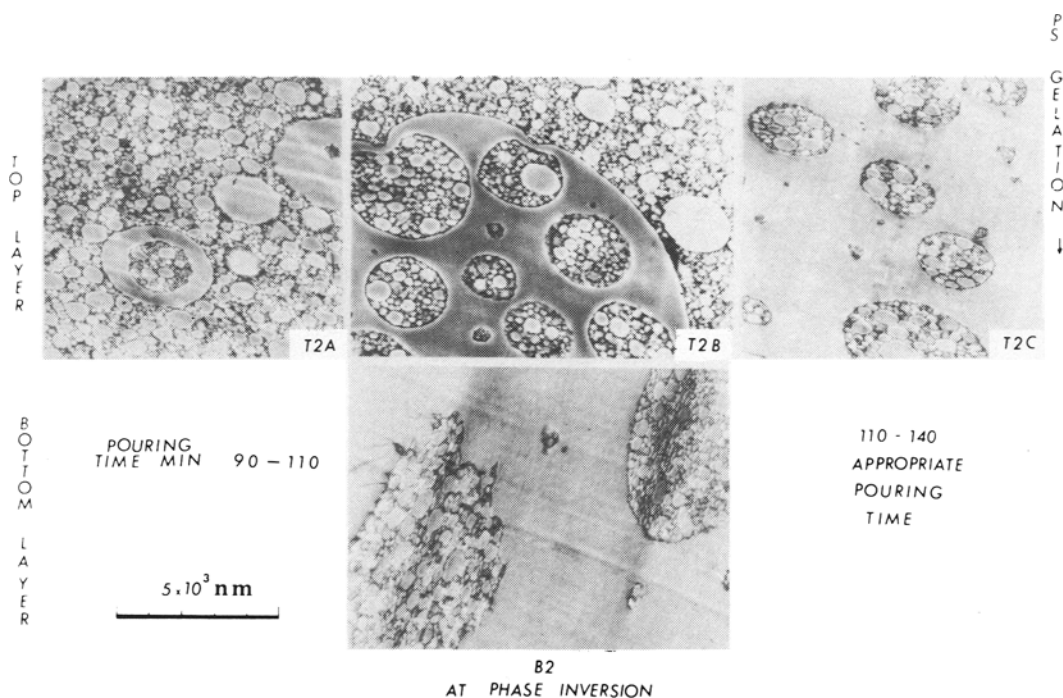
FIG. 5. Morphological changes induced by stirring for variable lengths of time during the synthesis of 10:90 castor oil polyester (COPE)/polystyrene network (PSN) SIN mix (11). * refers to reaction time with stirring prior to pouring. Shadowing is proportional to softness.
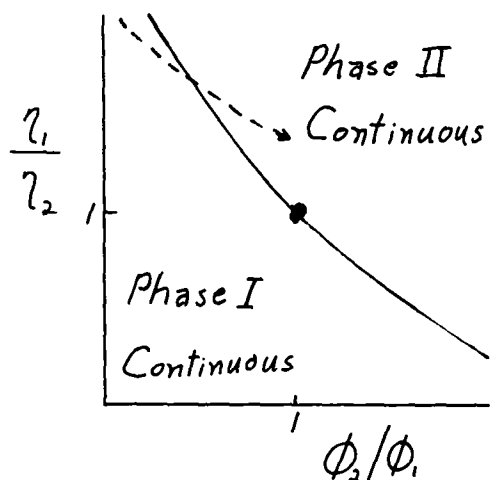

FIG. 6. A phase continuity diagram for polymer blends and reacting polymer-polymer systems. η_1 and η_2 represent the melt viscosities of the two polymers at the instant of time and ϕ_1/ϕ_2 represents the weight or volume fractions (22).
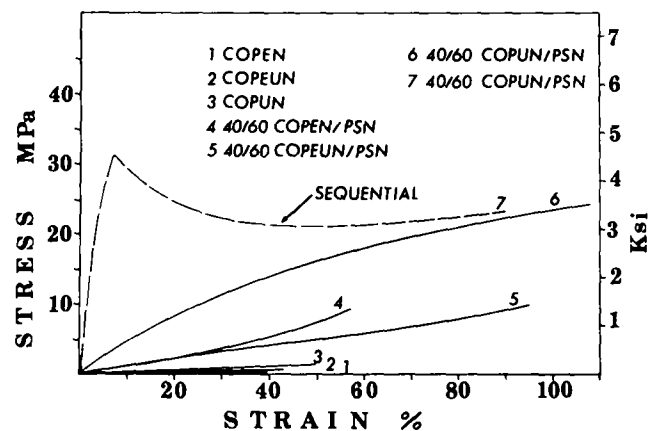

FIG. 7. Stress-strain behavior of castor oil/polystyrene SIN (13). COPEN, castor oil polyester network; COPEUN, castor oil polyester-urethane network; COPUN, castor oil polyurethane network; PSN, polystyrene network; KSI, thousands of pounds per square inch.

loss modulus, E'', are plotted against temperature. The glass transitions are illustrated by the sharp decline in E' or the maxima in E''. Tan δ, which is the ratio of E''/E', is also illustrated. A glass transition of the vernonia oil-sebacic acid polyester is seen to be ca. -50 C at 110 Hz. The room temperature modulus, illustrated by the E' curve, is ca. 5×10^8 dynes/cm^2 at room temperature, corresponding to a fairly stiff elastomer.

The glass transition of the vernonia oil-polyester at -50 C compares with the glass transition of an epoxidized linseed oil material at ca. -12 C. Part of the increase in the glass transition temperature of the epoxidized linseed oil elastomer is caused by the very dense crosslinking found in epoxidized linseed oil materials.

The mechanical behavior of several triglyceride oil SIN is shown in Table I. The homopolymer polystyrene network,

PSN, is shown as the control. Although the tensile strength of the materials is not especially altered by the presence of the triglyceride oil network, the impact strength improves significantly. For example, the polystyrene network has an impact strength of ca. 16 J/m, while that of the SIN goes from 34 to 59 J/m, an increase of a factor of 3-4.

Research in this area is now continuing with the use of *Lesquerella palmeri*. This wild plant grows in western Arizona and is known locally as Bladder-Pods or Pop Weeds, because of the hard shell around the seeds which can be popped or crushed by stepping on them. This particular lesquerella oil has an hydroxyl group on ca. 2/3 of the acid residues and makes a somewhat softer polyester elastomer than castor oil because of its lower reactivity. Since it has two more -CH$_2$- groups in each acid residue between the glycerine residue and the hydroxyl group than castor oil,
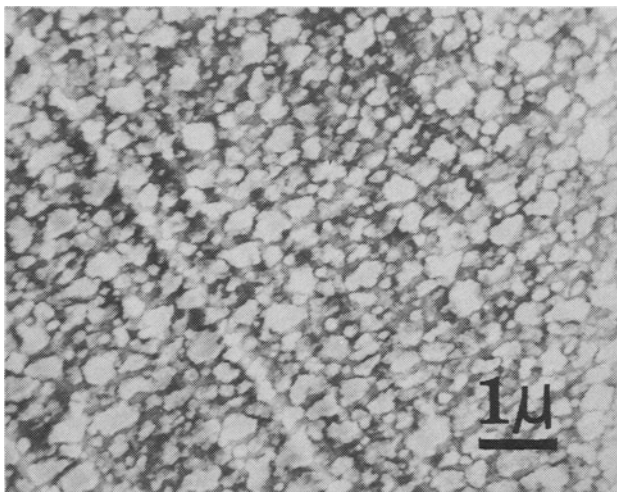
FIG. 8. A 50:50 SIN of vernonia oil-sebacic acid polyester/polystyrene. The vernonia oil component is stained with osmium tetroxide and forms the continuous phase (16).
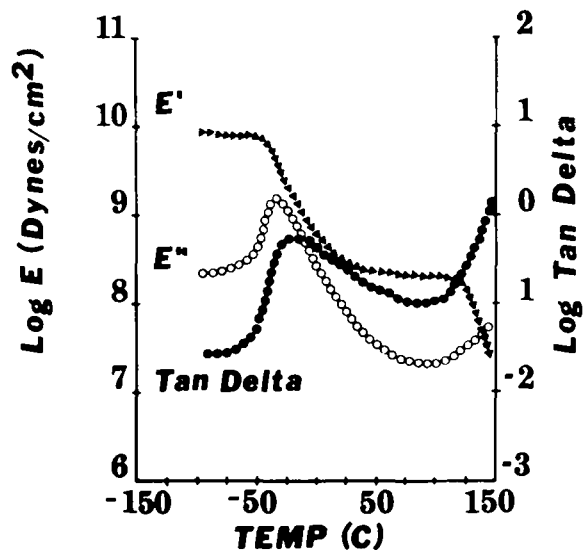

FIG. 9. Dynamic mechanical spectroscopy behavior of a 50:50 vernonia oil-sebacic acid polyester (VOSAN)/polystyrene (PSN) SIN, determined on a Rheovibron at 110 Hz (16).

the glass transition temperatures of lesquerella oil should be as low or slightly lower than the corresponding castor oil compostions (see Table II) (12,29). Because of their low glass transition temperatures, these elastomers have the potential of making excellent rubber-toughened plastics.

DISCUSSION

Although most triglyceride oils contain only double bond functional groups, a few oils naturally contain interesting other groups such as hydroxyl or oxirane. However, even those oils which contain only double bonds can be modified to insert other functional groups such as oxirane.

Both naturally occurring functional group oils such as castor oil and vernonia oil were employed in making elastomeric networks and simultaneous interpenetrating networks. A series of oils, including linseed and lesquerella oil, were reacted to insert oxirane groups and these were in turn polymerized to make elastomeric networks and SIN.

The elastomers formed from these special functional oils were shown to reinforce such brittle plastics as polystyrene. In this way they can replace the petrochemically formed elastomer, polybutadiene. Although the price structure today is still slightly in favor of the petrochemically derived polybutadiene, it may be seen that the prospects are excellent for a price inversion to take place, and the naturally occurring oils eventually to be cheaper.

It should be noted that several of the oils used in this investigation, with the exception of castor oil, are as yet noncommercial or only experimentally available. Some of these oils, such as lesquerella, can be grown in the western United States desert regions, thus improving land utilization. Since they would not compete with other crops and can be grown on low-priced land, it may be visualized that these will be eventually a low-priced commodity.

TABLE I

Mechanical Behavior of SIN (24)

Base oil	AV[a]	Specimen[b]	Tensile strength (MPa)	Strain ϵ_B (%)	Young's modulus, E (MPa)	Impact strength (J/m)
PSN Control	—	—	45	4	830	16
Linseed	47	10/90 ELODAN/PSN	42		689	34
Linseed	79	10/90 ELODAN/PSN[c]	40		746	
Crambe	47	10/90 ECrODAN/PSN	37	10	758	59
Lunaria	47	10/90 ELuODAN/PSN	35	5	726	43
Lesquerella	52	10/90 ELqODAN/PSN	36	6	778	45
Linseed	47	40/60 ELODAN/PSN	18	37	51	—
Crambe	47	40/60 ECrODAN/PSN	15	63	76	—
Lesquerella	52	40/60 ELqODAN/PSN	13	56	21	—

[a]Acid value; mg KOH/g sample. The higher the acid value, the lower the extent to which the oil is prepolymerized prior to mixing with the styrene.

[b]Nomenclature: ELO, epoxidized linseed oil; ECrO, epoxidized crambe oil; ELuO, epoxidized lunaria oil; ELqO, epoxidized lesquerella oil; DAN, dimer acid network; PSN, polystyrene network.

[c]In this case, the epoxidized linseed oil was not prepolymerized prior to mixing with the polymer.

TABLE II

Lesquerella palmeri and Castor Oil Transition Temperatures (12,29)

Designation	[−COOH] [−OH]	[−NCO] [−OH]	Elastomer phase T_g (C)	Polystyrene phase T_g (C)
Lesquerella palmeri-sebacic acid/urethane	0.75	0.25	−45	−
(*Lesquerella palmeri*-sebacic acid/urethane)/polystyrene SIN	0.40	0.60	−35	113
(*Lesquerella palmeri*-sebacic acid)/polystyrene SIN	1.00	−	−32	114
Castor oil-sebacic acid/urethane	0.60	0.40	−50	−
(Castor oil-sebacic acid/urethane)/polystyrene SIN	0.60	0.40	−30	−

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[Received May 17, 1983]