REVIEW

Naturally Functionalized Triglyceride Oils in Interpenetrating Polymer Networks

L.W. Barrett[a,1], L.H. Sperling[a,b,*] and C.J. Murphy[c]
[a]Department of Chemical Engineering and [b]Department of Materials Science and Engineering, Center for Polymer Science and Engineering, Materials Research Center, Whitaker Laboratory #5, Lehigh University, Bethlehem, Pennsylvania 18015 and [c]Department of Chemistry, East Stroudsburg University, East Stroudsburg, Pennsylvania 18301

The use of naturally functionalized triglyceride oils in interpenetrating polymer networks (IPNs) is reviewed. An oil bearing either hydroxyl or epoxide functionality may be crosslinked to form a soft elastomer in the presence of another monomer or network to form an IPN, or in the presence of a linear polymer, to form a semi-IPN. Polymerization and characterization of naturally functionalized triglyceride oils are mentioned, with emphasis on the distribution and effect of nontrifunctional triglycerides on elastomer properties. The simultaneous synthesis of polystyrene/functional triglyceride oil IPNs is reviewed, and several factors influencing IPN morphology and mechanical properties are discussed. The synthesis and properties of poly(ethylene terephthalate)/functional triglyceride oil semi-IPNs are emphasized, with the importance of ester interchange in the synthetic procedure, and factors influencing crystallinity and morphology are introduced.

KEY WORDS: **Castor oil, interpenetrating polymer network, poly(ethylene terephthalate), polystyrene, triglyceride oil, vernonia oil.**

NATURALLY FUNCTIONALIZED TRIGLYCERIDE OILS

While most triglyceride oils contain only double-bond functionality, a few special oils contain hydroxyl, epoxide or other chemical groups. Triglycerides are also triesters, being triacylglycerols, the combination of glycerol and various acid residues. In work carried out at Lehigh University over the last twenty years (1–9), numerous oils were studied, including castor oil and lesquerella oil, both containing hydroxyl functionality, and vernonia oil, containing epoxide functionality. The structures of the major trifunctional component of castor and vernonia oil are shown in Figure 1. Due to the special functional groups and the trifunctional nature of these oils they may be polymerized with an appropriate difunctional reactant to form elastomers. When combined with another polymer in network form, an interpenetrating polymer network (IPN) is created. IPNs may have much greater toughness and other mechanical properties than their constituent materials, a result of a synergism arising from the phase morphology developed during synthesis.

As these oils are prepared by nature with multiple chemical functionality, they are a renewable resource, providing an alternative to petroleum as a chemical feedstock, and may thus be of interest to developing nations. Since these oils are derived from crops rather than petrochemical based, all nations should be interested because, sooner or later, the large quantities of petroleum now consumed may run low or be curtailed due to environmental restrictions.

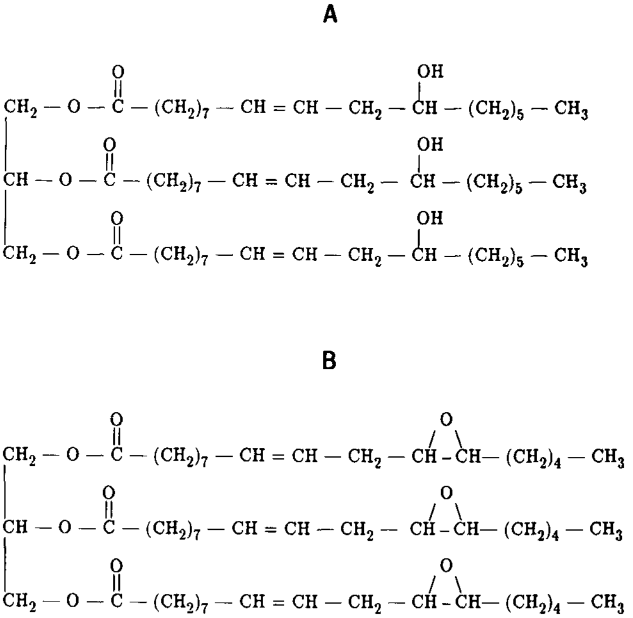

FIG. 1. Chemical structures of triricinolein (A) and trivernolin (B), the major constituents of castor oil and vernonia oil, respectively.

Castor oil in particular has received much attention, primarily because of its status as a large-scale commercial product (1,2). Castor oil from castor beans is basically the triglyceride of ricinoleic acid, with 83.6 to 90% of all acid residues being ricinoleic acid (10). Castor oil is routinely used in paints, adhesives and urethane foams. Through alkali pyrolysis, castor oil is also a major source of dibasic acids (11) such as decanedioic acid (sebacic acid), a major component of nylon. Other functionalized triglyceride oils are produced, but none in the same quantities as castor oil. Some of these oils, such as vernonia oil, show commercial promise, owing to their high functionality and the ability to cultivate economically the precursor oilseed plants in arid climates (12,13). Lesquerella oil, a hydroxyl-bearing oil similar to castor oil, has two additional $-CH_2-$ groups per acid residue beyond that of castor oil. Lesquerella oil is obtained from a wild plant native to Arizona and New Mexico and is thus a domestic source of functional triglyceride oil, as opposed to castor and vernonia oil, grown primarily in South America and Africa, respectively. Castor beans were grown successfully in Texas during the 1950s through the early 1970s, and efforts are currently under way to reestablish castor beans as a commercial crop in Texas (14).

The presence of epoxy acids as a natural constituent of certain seed oils has been known since the 1950s, and over 60 species of plants that produce epoxy fatty acids

---

[1] Current address: 3M Company, St. Paul, MN 55144.

*To whom correspondence should be addressed.

were identified by 1970 (15,16). The oil from *Vernonia galamensis*, or simply vernonia oil, represents the most promising of these epoxy oils, due to its ease of production (17), seed oil content and concentration of epoxy triglyceride in the oil [75–80% vernolic acid triglycerides (17–19)], and high epoxide concentration (typically about 400 g/eq. epoxide). Similar in structure to castor oil (see Fig. 1), vernonia is a rich natural source of epoxidized acids (20,21), as well as dibasic acids (22,23). Octanedioic and nonanedioic acids (subaric and azelaic acids, respectively) may be derived from vernonia oil in greater yields than from castor oil (22). The potential uses of vernonia oil by itself are many. The oil has a relatively low viscosity for its high epoxide concentration, making it a prospective reactive diluent for coatings applications (13,24). The rubbery nature of the polymerized oil may also find utility in toughening rigid epoxy materials, as it phase-separates into spherical domains when mixed and cured together with *bis*-phenol-A-based epoxy compounds (25). Vernonia oil may compete with and someday replace synthetically epoxidized triglyceride oils now used in large quantities as poly(vinyl chloride) plasticizers and stabilizers (13,26–30).

Infrared and nuclear magnetic resonance (NMR) spectra of selected oils. The infrared and NMR spectra of a number of triglyceride oils of possible use in the synthesis of polymers have been determined on specially purified samples of oils for the purpose of providing characterization standards. The major fatty acid components of several of these oils are shown in Table 1 (31).

The infrared spectra of the unsaturated oils from crambe, limnanthes and lunaria, the hydroxy oils from castor and lesquerella and the epoxy oil from vernonia were determined as capillary films between silver chloride plates with a Beckman 1200 Fourier-transform infrared spectrometer (Fullerton, CA). Samples of the oils were prepared by dissolving in hexane, then chilling the solution to precipitate waxes, and filtering from Fuller's earth. The purified oil was then recovered by evaporation of the hexane in a rotary evaporator. Samples of the oils were stored at 0°C until the spectra were determined.

The infrared spectra of castor, lesquerella, vernonia and crambe oils are shown in Figure 2. The spectra of the oils studied have many features in common but also differences due to the particular functional groups present. They all show three absorptions between 3000 and 2800 cm^{-1} characteristic of C–H stretching modes. In saturated oils or synthetically epoxidized oils, the highest frequency absorption of this group, attributed to the vinyl C–H, is absent. Common to all oils are the carbonyl absorption at 1730 cm^{-1}, the characteristic triglyceride ester triplet at 1259, 1170 and 1100 cm^{-1}, and the sharp absorption at 730 cm^{-1}, which has been assigned to the bending of a saturated carbon chain more than seven carbon atoms long. Vernonia oil, in addition, shows the distinctive doublet at 848 cm^{-1} correlated to the epoxy (or oxirane) group (32). The presence of an absorption at 3300 cm^{-1} in the spectrum of vernonia oil indicates partial hydrolysis of the epoxide. Unless vernonia oil is carefully dried and stored hermetically, the epoxy group may slowly hydrolyze, resulting in the presence of both hydroxyl and epoxy absorptions. The hydroxy oils, castor and lesquerella, display the characteristic broad hydroxyl absorption centered at about 3300 cm^{-1}. The spectra of castor and lesquerella oils can be readily distinguished, however, by the stronger absorption at the 730 cm^{-1} band in lesquerella oil, which may be correlated with the longer chain of carbon atoms following the double bond compared to castor oil.

The NMR spectra of the unsaturated oils (crambe, limnanthes and lunaria), the hydroxy oils (castor and lesquerella) and the epoxy oils (vernonia, epoxidized linseed and epoxidized crambe) were determined as 15-wt% solutions in carbon tetrachloride, CCl_4. The NMR spectra of the unsaturated oils are essentially identical, differing only slightly in the relative intensities of some resonances. A composite spectrum is shown in Figure 3, and the various proton resonances in this spectrum and in the following spectra may be assigned as indicated on the figures by using the criteria of Wolff and Miwa (33). The NMR spectra of castor and lesquerella oils are also essentially identical, and their composite spectrum is shown in Figure 3. A composite spectrum of the epoxy oils is also shown in Figure 3. The spectra of the epoxy oils are essentially identical, with the exception of a strong resonance at about 5.3 ppm (labelled as D in Fig. 3) in the spectrum of vernonia oil, which is attributed to the vinyl protons on the double-bonded carbons. In synthetically epoxidized unsaturated oils, double bonds are converted to epoxy groups; thus resonance D at 5.3 ppm decreases in area as the degree of epoxidation increases. Conversely, the area of resonance E at 2.7 ppm, attributed to the epoxide protons, increases proportionally as the degree of epoxidation increases. The area of the 2.7-ppm resonance (epoxy), normalized to the area of the resonance at 4.2 ppm (F, attributed to glycerol protons) has been correlated to the degree of epoxidation determined by chemical methods (34).

Polymerization of functionalized triglyceride oils. With these oils, it is possible to make a completely natural-material-derived elastomer. For example, sebacic acid, itself derived from castor oil, may be used to crosslink castor oil to form a polyester elastomer with glass transition around −50°C. Similarly, vernonia oil has been used to create polyester elastomers through polymerization with suberic acid, a product obtained from that oil (22,35). While most of these elastomers are rather soft and weak as homopolymers, in combination with various plastics they serve to increase impact resistance, and in general they form tough plastics or reinforced elastomers. A good

TABLE 1

Principle Fatty Acid Components of Selected Oils (Ref. 31)

Castor oil	C_{18}	12-hydroxy-*cis*-9-octadecenoic acid (ricinoleic acid)
Vernonia oil	C_{18}	12,13-epoxy-*cis*-9-octadecenoic acid (vernolic acid)
Lesquerella oil	C_{20}	14-hydroxy-*cis*-11-eicosenoic acid (lesquerolic acid)
Limnanthes oil	C_{20}	*cis*-5-eicosenoic acid
Crambe oil	C_{22}	*cis*-13-docosenoic acid (erucic acid)
Lunaria oil	C_{22}	*cis*-13-docosenoic acid (erucic acid)
	C_{24}	*cis*-15-tetracosenoic acid (nervonic acid)

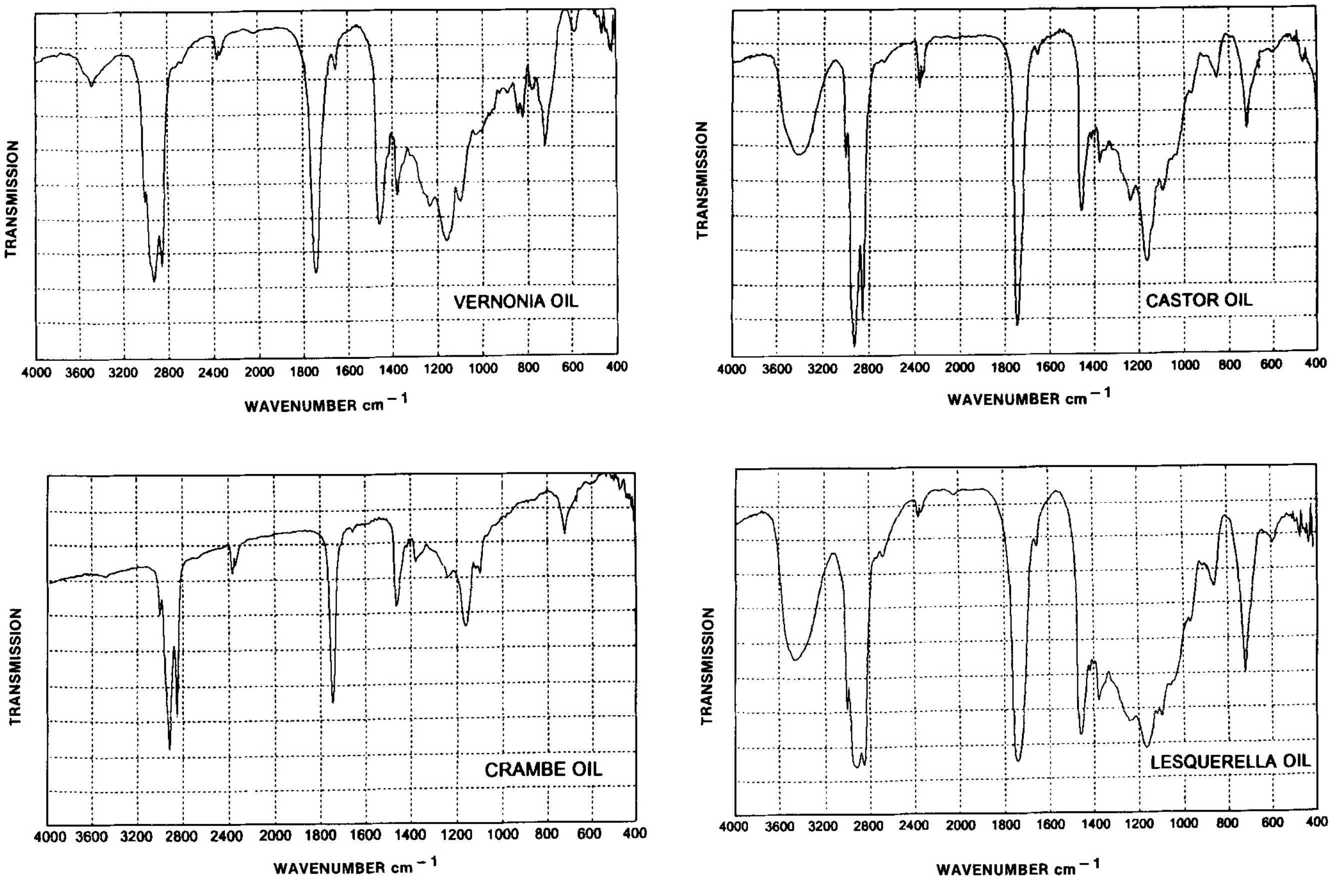

FIG. 2. Infrared absorption spectra of selected oils.

way to combine these elastomers with plastics is through the formation of interpenetrating polymer networks.

Castor oil polyurethane networks may be polymerized through reaction with diisocyanates (36), a reacton used industrially for some years. Diisocyanates used for this purpose have included tolylene diisocyanate and hydrogenated methylene diphenyldiisocyanate (HMDI). While these diisocyanates are not derived from natural sources, the diisocyanate of dimer acid is a commercial product (tradename DDI, Henkel, Fort Lee, NJ) derived from beef tallow, which could be used to maintain a renewable-resource product. Castor oil polyester networks may be produced by reaction with dibasic acids, such as sebacic acid, or diacyl chlorides, such as sebacoyl chloride (37). In the case of the polyester reactions, either water or hydrochloric acid is relased as a condensation by-product, which makes the formation of a void-free network material difficult. For this reason, the urethane reaction, which releases no condensation by-product, is preferred for network formation. Diisocyanate may be used to complete a polyester/urethane network started with castor oil prepolyesters polymerized to just below the gel point.

Vernonia oil polyester elastomers may be made by polymerization with dibasic acids, such as sebacic acid or suberic acid, both of which may be naturally derived. Being an epoxide-bearing compound, vernonia oil could also be reacted with the wide variety of polyamine curing agents developed for epoxy resins, to form polyether networks. Furthermore, the epoxides of vernonia oil may be polymerized through ionic ring-opening polymerization, forming a polyether network composed entirely of vernonia oil segments. Vernonia grease was formed in the author's laboratory through the latter method, initiated by sodium benzoate.

Although the oils are said to be 75 or 90% pure, this purity refers to the percentage of characteristic acid residues on the triglycerides found in the oil and does not imply, for instance, that castor oil is 90% triricinolein. The composition of the fatty acids making up the triglycerides in castor and vernonia oil is given in Table 2 (13,38). In general, most naturally occurring triglycerides are thought to have the acid residues placed randomly among the glycerol backbone sites available (39). In Table 3, the measured distribution of the characteristic acid residues of vernonia and castor oil (13,40) is compared with what would be expected by random distribution, calculated by a computer simulation, and the measured distributions are not completely random. For example, vernonia oil contains two standard deviations (2σ) more divernolin than random and 2σ less trivernolin than random, while castor oil contains 3σ less monoricinolein than random and 1σ more diricinolein than random.

The type and amount of nonfunctional triglyceride present in castor oil or vernonia oil can have an effect on numerous properties of the oil and the resulting networks. The polymerization kinetics of vernonia oil and sebacic

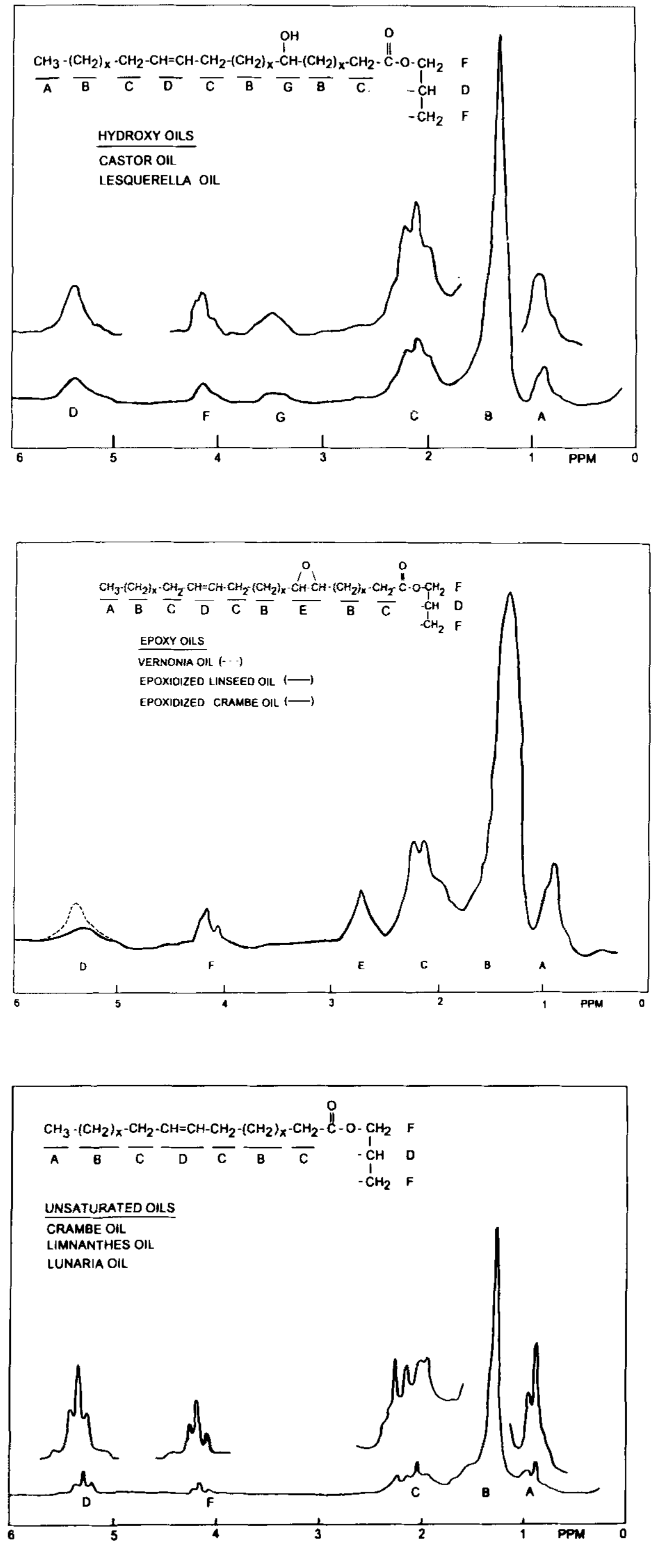

FIG. 3. Proton nuclear magnetic resonance spectra of selected oils.

TABLE 2

Fatty Acid Composition of Castor and Vernonia Oil (Refs. 13,38)

Fatty acid	wt%
Vernonia oil (Ref. 13)	
Vernolic acid (C_{18}, 1 C=C, 1 epoxide)	76.8
Linoleic or linolenic acids (C_{18}, 2 or 3 C=C)	16.5
Oleic acid (C_{18}, 1 C=C)	3.2
Stearic acid (C_{18}, saturated)	3.1
Other	0.4
Castor oil (Ref. 38)	
Ricinoleic acid (C_{18}, 1 C=C, 1 OH)	87
Oleic acid (C_{18}, 1 C=C)	7
Linoleic acid (C_{18}, 2 C=C)	3
Palmitic acid (C_{16}, saturated)	2
Stearic acid (C_{18}, saturated)	1

TABLE 3

Placement of Characteristic Acid Residues on Castor and Vernonia Oil: Measured *vs.* Random Distributions (Refs. 13,40)

	Measured %	Random % ± SD
Vernonia oil (Ref. 13)		
Trivernolin	59	63 ± 2
Divernolin	28	21. ± 4
Monovernolin	10	12 ± 2
Nonfunctional	3	4 ± 2
Castor oil (Ref. 40)		
Triricinolein	66	66 ± 2
Diricinolein	23	20 ± 4
Monoricinolein	5	11 ± 2
Nonfunctional	6	3 ± 2

acid was investigated previously by Fernandez *et al.* (41), in which the gel point of a stoichiometric mixture was reached after 4 h at 160°C, and 7 h at 140°C. In the earlier study, the critical extent of reaction was measured and compared with that calculated from Flory-Stockmayer gelation theory (42), with the conclusion that vernonia oil behaved as if it were 80% pure trivernolin, with 20% nonfunctional triglyceride. In light of the data for vernonia oil composition given in Table 3, it is useful to calculate exactly what the consequences of functional group placement has on the critical extent of reaction, by using the Flory-Stockmayer relations (42). Table 4 gives the results of some of these calculations for a theoretical naturally functionalized oil of 80 and 90% functional acid residue purity. At 90% purity (similar to castor oil), the lowest critical extent of reaction (0.707) occurs when the mixture contains 90% trifunctional glycerides and 10% nonfunctional diluent. The highest critical extent of reaction (0.750) has 70% trifunctional and 30% difunctional glycerides. For 80% purity (similar to vernonia oil), the range of critical extent of reaction is greater, from 0.707 to 0.816, due to the lower purity. Thus, the critical extent of reaction is only slightly affected by the presence of the impurities and their placement on the triglycerides. Based on the actual analysis of castor and vernonia oil, the difference in their calculated critical extent of reaction is small (0.746 and 0.761, respectively). It is doubtful that the critical extent of reaction, the gel point, can be measured with enough accuracy to draw structural conclusions.

Because the vast majority of the impurities in castor oil are similar in structure to triricinolein, only lacking

TABLE 4

Critical Extent of Reaction P_c as a Function of Placement of Functional Groups, Calculated from Flory-Stockmayer Gelation Theory[a]

90% functional acid content (castor oil)					80% functional acid content (vernonia oil)				
%Tri	%Di	%Mono	%Non	P_c	%Tri	%Di	%Mono	%Non	P_c
100	0	0	0	0.707	80	0	0	20	0.707
90	0	0	10	0.707	75	0	30	0	0.718
85	0	15	0	0.717	60	20	20	0	0.756
80	10	10	0	0.727	50	40	10	0	0.784
70	30	0	0	0.750	40	60	0	0	0.816
66	23	5	6	0.746	59	28	10	3	0.761

[a]Abbreviations: Tri, trifunctional; Di, difunctional; Mono, monofunctional; Non, nonfunctional.

one or more hydroxyl group(s), their physical effect on the network may reduce crosslink density and plasticize it somewhat, lowering the glass transition, modulus and tensile strength. Because pure triricinolein was not available, the complementary effect of addition of extra nonfunctional triglyceride oil was investigated. In Table 5, physical properties of castor oil-HMDI networks synthesized with additional amounts of safflower oil are tabulated. The additional safflower oil, being primarily linoleic acid triglycerides and without hydroxyl or epoxide functionality, simulates the effect of a less pure castor oil. As expected, the nonfunctional diluent acts as a plasticizer, which lowers the glass transition (closely following Fox equation predictions) and the modulus and reduces other mechanical properties. Thus, if the castor oil could be purified to obtain 100% triricinoein, stronger materials with higher glass transition temperatures would be expected. Along the same lines of reasoning, vernonia oil, at the 75% purity level, would be expected to form correspondingly weaker elastomers than castor oil of 90% purity.

TABLE 5

Effect of Additional Nonfunctional Oil on Castor Oil Networks

	Castor		
Property	100%	91.7%	82.9%
% Functional acid residues	90	82	73
Measured T_g (°C)	−5	−16	−24
Fox eqn. T_g calc. (°C)	−5	−17	−28
Gehman modulus (MPa)	2.7	2.4	2.0
Tensile strength (KPa)	1735	1185	795
% Elongation	126	79	69
Energy absorbed (J/m^3)	1260	600	320

The crosslink densities of vernonia polyester and castor oil polyurethane and polyurethane/polyester networks were determined through swelling and modulus measurements, and the results are given in Table 6. These two sets of results give different values of M_c (chain segment molecular weight); probably the swelling results are the more reliable. Out of twenty-one solvents tested, dichloromethane (CH_2Cl_2) was determined to swell castor oil network the greatest and was therefore assumed to have a polymer-solvent interaction parameter close to zero. By means of the zero interaction parameter assumption and the Flory-Rehner equation (43), crosslink density (n)

TABLE 6

Crosslink Density Parameters Calculated from Swelling and Modulus for Several Castor or Vernonia Oil Networks

Network	V_2 (CH_2Cl_2)	n ($\chi = 0$) (mole/cm^3)	$M_c = \varrho/n$ (g/mole)	$M_c/M_{c\ theio.}$
Swelling of networks				
VO/SA[a]	0.20	0.74×10^{-4}	1350	1.7
CO/TDI	0.27	1.36×10^{-4}	735	0.9
CO/HMDI	0.27	1.36×10^{-4}	735	0.9
CO/SA/TDI	0.22	0.90×10^{-4}	1110	1.4

Network	3G (dyne/cm^2)	n = G/RT (mole/cm^3)	$M_c = \varrho/n$ (g/mole)	$M_c/M_{c\ theio.}$
Modulus of networks				
VO/SA	2.4×10^7	0.33×10^{-4}	3030	3.8
CO/TDI	3.1×10^7	0.42×10^{-4}	2380	3.0
CO/HMDI	2.7×10^7	0.37×10^{-4}	2700	3.1
CO/SA/TDI	1.8×10^7	0.24×10^{-4}	4170	5.3

[a]Abbreviations: VO, vernonia oil; SA, sebacic acid; CO, castor oil; TDI, tolylene diisocyanate; HMDI, hydrogenated methyldiphenyldiisocyanate.

and elastically active M_c were calculated and compared to the theoretical M_c expected for a perfect network (780 to 880 g/mole, depending on the crosslinking reactant used). In these swelling calculations, measured crosslink densities came close to that expected for a perfect network. The n may also be calculated with the classical rubber elasticity equation, $E = 3G = 3nRT$, in which the Young's modulus of elasticity, E, was measured *via* the shear modulus, G, with a Gehman apparatus (American Society for Testing Materials Standard Method D-1053). From the modulus measurements, crosslink densities three to five times lower than theoretical were calculated. Lower-than-theoretical crosslink densities could be caused by dangling network ends, inactive loops or internal structures, which act as chain extensions rather than crosslinks. If the swelling results are accepted as closer to reality, there is no good explanation for the modulus results, which ordinarily yield greater crosslink densities (modulus measurements are much more sensitive to entanglements than swelling measurements). If, instead, the modulus measurements are accepted as closer to reality, then the polymer-solvent interaction parameter may be recalculated, based on the crosslink density from modulus measurements and swelling results. The reverse calculation yields an interaction parameter of about 0.42 for the networks at room temperature (20–25°C). This value is close to other polymer-solvent systems in which the solvent is considered to be good, such as polystyrene/toluene (0.44 @ 27°C), poly(methyl methacrylate)/tetrahydrofuran (0.45 @ 25°C) and poly(isoprene)/chloroform (0.37 @ 20°C) (44).

TRIGLYCERIDE OIL INTERPENETRATING POLYMER NETWORKS

IPNs may in general be formed by two methods (45). In the sequential method, a crosslinked network is formed, then swelled with the monomer and crosslinker of the second component and polymerized to create the interpenetrating network. If the two components polymerize by noninterfering routes, then the IPN may be formed by the simultaneous method, where monomers and crosslinkers of both materials may be mixed and polymerized together simultaneously. Prior triglyceride oil IPN research has proceeded by polymerizing both components from their monomeric state. In this way, the components are initially miscible, either as monomers (simultaneous method) or as a swollen network (sequential method), and phase-separate as polymerization and crosslinking occur. It is the relationship between crosslinking and phase separation kinetics that controls the final IPN morphology (45,46).

IPN morphology may be controlled by either the kinetics of phase separation or the kinetics of gelation. Starting with a miscible blend of monomers in a simultaneous IPN synthesis, as polymerization of both components proceeds, the mixture will eventually phase-separate if the polymers are immiscible. If phase separation occurs more rapidly than gelation, the two components will separate into rather large phase domains. If, however, the two components in the mixture polymerize rapidly and/or are able to crosslink before they can phase-separate, the phase separation will be constrained to occur only at the microscopic level, creating a microheterogeneous morphology.

Microheterogeneous morphology, with phase domains on the order of 10 to 20 nm, generally leads to enhanced mechanical energy loss characteristics when the two components are an elastomer and a plastic. Toughened plastics or reinforced elastomers are produced when the phase domains are in the range between 50 to 200 nm, depending upon the relative amount of plastic and elastomer in the IPN. Castor oil polyurethane/polystyrene IPNs have been produced (2–9) that were tough enough to form shoe heels that have outlasted their mate leather soles.

Castor oil has been used extensively in IPN research, beginning in 1977 with sulfur-crosslinked castor oil, which was swelled with styrene and divinylbenzene (8) or methyl methacrylate and tetraethylene glycol dimethacrylate (9) and then polymerized. This form of crosslinked triglyceride, known as factice, makes use of the unsaturated bonds in the triglyceride oil and can be made with any unsaturated oil (47). The utility of castor oil does not lie in its ability to form factice, however, and subsequent to this early work, the hydroxyl functionality was exploited to form polyester or polyurethane networks. Castor oil polyester and polyurethane IPNs with polystyrene were studied at Lehigh University during the late 1970s and early 1980s (4–9), and today, research on castor oil polyurethane IPNs with acrylic and other polymers is active worldwide (48–55).

Polyester and polyurethane networks have two distinct advantages over factice. Because the step growth reaction does not interfere with radical chain polymerizations, simultaneous polymerization with monomers such as styrene and acrylics is possible. Thus, a wide range of potentially useful materials can be made. The other advantage is that the triglyceride oil double bonds remain intact in the polyester or polyurethane networks, which allows staining for electron microscopy imaging of the phase structure in the IPNs formed. These characteristics of triglyceride oils have made them invaluable in the study of morphology development in IPNs.

The vernonia oil polyester elastomer may also be prepared by reaction with dibasic acids, themselves derived from the oil, forming a natural product elastomer. Fernandez *et al.* (18,41) have produced vernonia/polystyrene IPNs by using sebacic acid as the vernonia oil crosslinker. These IPNs had properties ranging from reinforced elastomer to toughened plastic, depending on the overall composition. Ayorinde *et al.* (22), whose research group has previously reported preparing subaric acid from vernonia oil, made polystyrene IPNs with subaric acid as crosslinker (56).

Many other functionalized triglyceride oils, such as vernonia, lesquerella, crambe and linseed, as well as their epoxidized analogs, have also been used to form IPNs with chain-polymerizable monomers, such as styrene and acrylics (2,3,5,18,38,57). These functionalized triglyceride oils, while not yet commercial, offer characteristics different than castor oil, both in terms of the chemistry involved and the physical properties and morphology development of the IPNs.

Historical perspective. The Lehigh oils research program began in 1974, with an international program between Colombia, South America, and the United States, jointly funded by Colciencias and the National Science Foundation (NSF). The research went through several stages. First, sequential IPNs were studied by Godfrey Yenwo. Then, simultaneous interpenetrating networks

(SINs) were studied by Napoleon Devia. Both of these Ph.D. theses emphasized castor oil/polystyrene IPNs, studying the interrelationships among synthesis, morphology and mechanical behavior. During this time, several M.S. theses were awarded at the Universidad Industrial de Santander (UIS) in Bucaramanga, Columbia, and at Lehigh University. Dr. Alfonso Conde directed the UIS effort. Then, the research at Lehigh shifted to other oils. A third Ph.D. thesis at Lehigh, by Shahid Qureshi, emphasized IPNs based on a number of different oils, many of them "wild" oils. Qureshi's emphasis was on epoxidized oils.

Then NSF-funded research shifted to lesquerella oil, an oil based on *Lesquerella Willd.* plants of New Mexico and Arizona, known locally as Bladderpod or Popweed, because of their brittle seed pod. This research was undertaken by Marc Linné. Research on vernonia oil, emphasizing the species that comes from Northern India, was undertaken by Ana Maria Fernandez.

The present effort, the Ph.D. thesis of Leonard Barrett, emphasizes vernonia oil- and castor oil-based semi-IPNs with poly(ethylene terephthalate) (PET), a semicrystalline polymer. This research is being funded by EniChem America (Princeton, NJ). The basic effort is to improve the crystallization rate of PET and to toughen engineering compositions with the addition of castor oil or vernonia oil, which could then be subsequently polymerized.

While the present review emphasizes functional group-based triglyceride oils and their IPNs, there is a continuing broader field of IPN research both at Lehigh University and around the world (58). These developments have yielded a significant number of industrial products, ranging from false teeth to sound- and vibration-damping materials. It is hoped that the international effort now under way in oils IPN research will soon yield additional commercial products.

Polystyrene and acrylic IPNs. Polystyrene and poly(methyl methacrylate) are two of the most common plastics in use today. Although for many purposes they have adequate performance, for more demanding applications these plastics are rubber-toughened. In fact, much of the polystyrene in use is a combination of polybutadiene rubber and polystyrene, called hi-impact polystyrene (HIPS). HIPS has a complicated phase morphology, which leads to a great toughening effect, and could be considered a semi-IPN, as the polybutadiene is crosslinked in the presence of linear polystyrene chains (59). (A semi-IPN has one crosslinked polymer and one linear polymer.) Since triglyceride oil elastomer is quite capable of providing toughening similar to polybutadiene, polystyrene/triglyceride oil IPNs have been created with properties comparable to HIPS.

Because styrene or acrylic monomer and triglyceride oils are miscible and polymerize by noninterfering mechanisms, IPNs may be produced by the simultaneous method. A schematic of the simultaneous synthesis process for polystyrene/castor IPNs is shown in Figure 4. Styrene monomer, divinyl benzene as crosslinker, and initiator are simply mixed and heated with castor oil prepolyester, made from castor oil and sebacic acid, and a diisocyanate crosslinker. As polystyrene forms and castor oil polymerizes, phase separation occurs and the final phase morphology is influenced by many factors, including how long the mixture is stirred during the process (7) and the sequence of polystyrene and castor oil polyester gelation (1,60). Stirring or shear mixing during the synthesis process can affect which phase becomes continuous, as the less viscous phase tends to be the more continuous one (7). Polystyrene/vernonia oil IPNs may be made in a manner similar to that used for polystyrene/castor oil (18,35,41). Because the reaction of vernonia with dibasic acid does not release any condensation by-product, prepolymerization of vernonia oil is not necessary.

Extensive research on polyacrylate/castor oil IPNs has been undertaken by Patel *et al.* (61–64). In this work, several diisocyanates used at varying NCO/OH ratios were polymerized along with numerous different acrylate

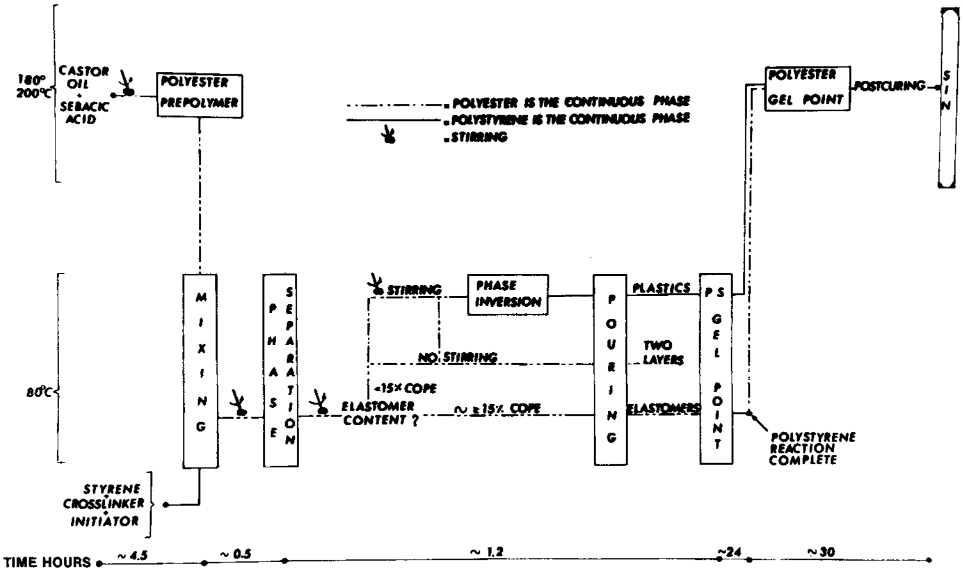

FIG. 4. Schematic depicting the process by which polystyrene/castor oil (polyester-based SINs) simultaneous interpenetrating networks are synthesized (7).

monomers to make a plethora of IPNs, which were characterized by an equally diverse set of measurements. Besides mechanical properties, many electrical properties were found to be synergistically improved, such as dielectric constant, dielectric loss and electrical conductivity.

As a result of the polystyrene/triglyceride oil IPN research, much has been learned about the effects of crosslinking and phase separation kinetics on morphology. In general, if the two components reach their gel point at about the same time and before phase separation can occur, a fine morphology may result. A transmission electron micrograph showing the morphology of a 50:50 polystyrene/vernonia oil-sebacic acid polyester IPN made by simultaneous polymerization is shown in Figure 5. The dark phase in Figure 5 is the vernonia polyester, as stained by osmium tetroxide. Here, the vernonia polyester phase is continuous, and polystyrene domains are less than half a micrometer in diameter. Such a morphology would result in a toughened elastomer. Materials where polystyrene is the continuous phase and vernonia elastomer is dispersed in small domains would behave as a reinforced plastic.

Poly(ethylene terephthalate) semi-IPNs. In the prior triglyceride oil IPN literature, primarily amorphous plastics have been used. PET is a departure from that norm in that it is a semicrystalline thermoplastic. The use of castor and other triglyceride oils with other polymers has mostly been limited to that of a plasticizer or stabilizer (13,26–29). Because PET is semicrystalline, the morphology of the semi-IPN becomes more complicated, introducing crystallinity as a factor to be considered. Semicrystalline PET has outstanding material properties required for an engineering plastic; however, its crystallization rate is slow, forcing long cycle times in injection molding applications (65). Crystalline PET injection molding grades tend to have lower molecular weight, which increases the crystallization rate and improves melt flow, but the resulting material can be quite brittle and is nearly always sold as a composite with up to 40% chopped glass fiber for increased toughness (66). To address these drawbacks of PET, it was thought that by making semi-IPNs with functionalized triglyceride oils, toughness as well as crystallization rate could be improved.

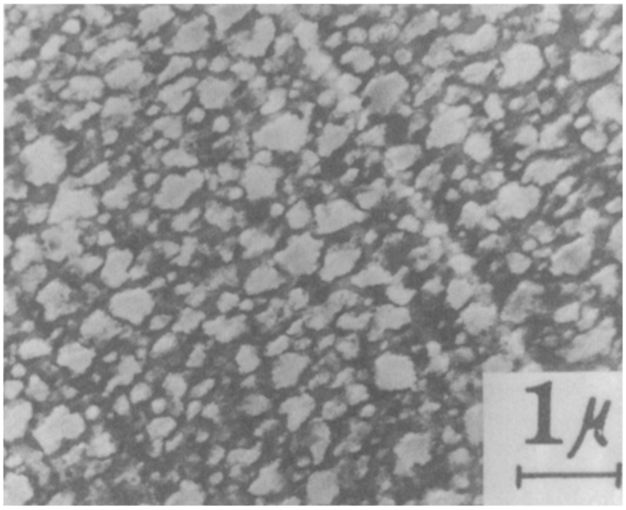

FIG. 5. Transmission electron micrograph of a 50:50 polystyrene/vernonia oil interpenetrating polymer network. The vernonia polyester phase was darkened by staining with osmium tetroxide (42).

Using fully polymerized PET as the starting material puts some constraints on the IPN formation process. PET may be considered as the condensation product of terephthalic acid and ethylene glycol. Because the castor oil would polymerize with terephthalic acid in competition with ethylene glycol, simultaneous semi-IPN formation from monomers is not possible because noninterfering polymerization routes are required. Although PET and castor oil polyester network are both polyesters, PET is aromatic and castor oil is aliphatic, and the two are immiscible. Thus, castor oil will not dissolve in PET, nor will PET swell a castor oil network, making sequential IPN formation impossible. To control the IPN morphology of PET and castor oil network, the two components must first be either miscible or well mixed, then be allowed to phase separate as the castor oil crosslinking occurs.

It was discovered that continued heating of castor oil and PET results in a miscible mixture, a consequence of bond interchange reactions that form a miscible copolymer mixture (67–69). Since PET contains ester groups and castor oil contains both ester and hydroxyl groups, ester interchange takes place (69). The resulting semi-IPN is a hybrid structure, in which the crosslinked and/or uncrosslinked materials may be copolymers and not pure components. Thus, the extent to which the bond interchange reactions take place affects many aspects of the resulting semi-IPN. This method, wherein miscibility between the two components is affected by bond interchange copolymer formation, is potentially applicable to many other systems where bond interchange takes place, to make interesting new IPNs and semi-IPNs.

To study the effects of these interchange reactions, experiments were carried out in which the PET and oil were carefully weighed into a differential scanning calorimeter (DSC) pan, and the thermal transitions of the mixture were monitored *vs.* the time held isothermally at 300°C. In these experiments, the PET and oil were cooled to −150°C, after which the first scan from −150°C to 300°C was taken, in which glass and melting transitions were recorded. The sample was then held at 300°C for twenty minutes, then rapidly cooled to −150°C, and the cycle was repeated until the DSC heating scans appeared to be constant.

The change in glass transition temperature of several PET/triglyceride oil mixtures studied *vs.* time held at 300°C is shown in Figure 6. As ester interchange leads to PET/triglyceride copolymer, the glass transition temperature of the oil-rich phase increases. It is interesting to note that the glass transition temperature of the PET/castor oil mixture first decreases before it increases. In heating pure castor oil, it was also noticed that the DSC-determined glass transition temperature decreased with time. Castor oil is able to undergo ester interchange with itself, forming glycerol, which has a glass transition temperature about 20°C lower than that of castor oil, so that in the PET/castor mixture, initially glycerol is created, which decreases the glass transition temperature, then as PET becomes copolymerized with the glycerol and castor oil, the glass transition temperature eventually increases (69). Synthetically epoxidized soybean oil has much greater epoxide content than vernonia and thus reacts

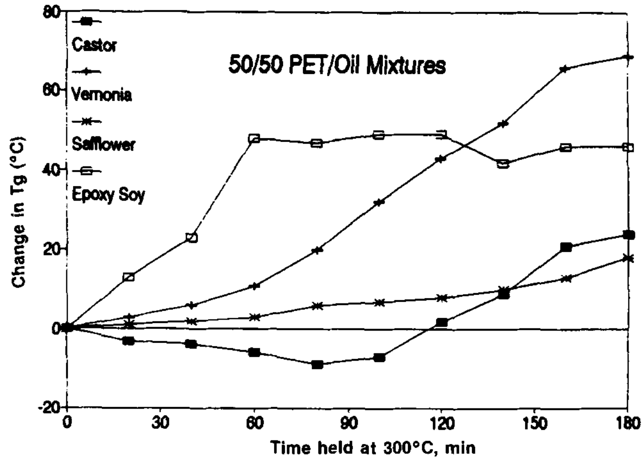

FIG. 6. The change in glass transition temperature *vs.* time held at 300°C for various triglyceride oils mixed with poly(ethylene terephthalate) (PET) 50:50 by weight. Abbreviation: T_g, glass transition temperature.

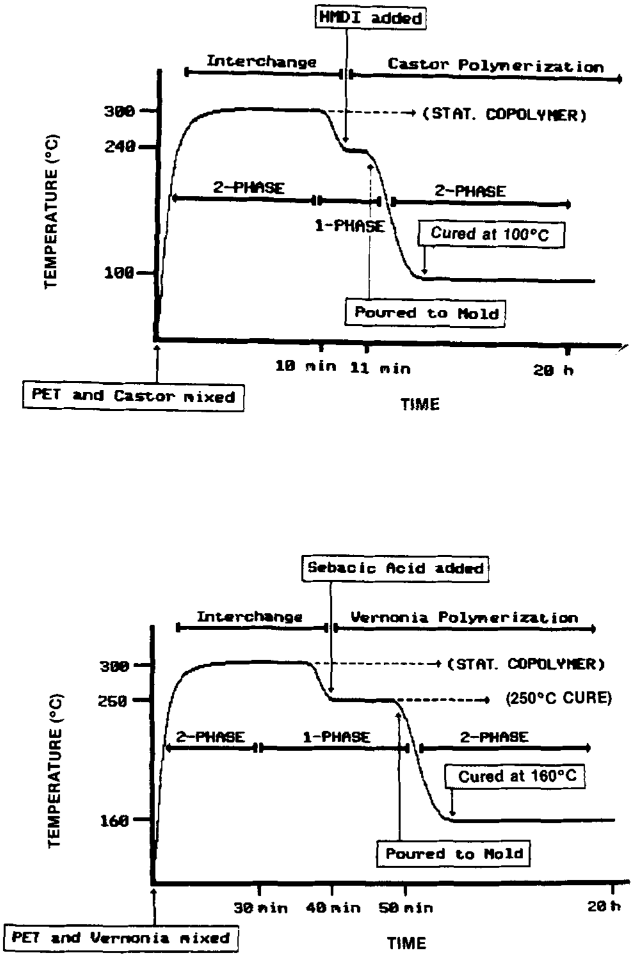

FIG. 7. Time-temperature schemes for production of poly(ethylene terephthalate) (PET)/castor oil (A) and PET/vernonia oil (B) semi-interpenetrating polymer networks (70). Axes are not drawn to scale. Phase changes determined by differential scanning calorimetry and electron microscopy.

with PET to form copolymer faster, while safflower oil, without any special functionality other than its ester groups, reacts slowly.

PET/castor oil (67,68) and PET/vernonia oil (70) semi-IPNs were produced by taking advantage of the bond interchange reactions. In these materials, bond interchange was allowed to occur to the point where a miscible mixture was obtained, then crosslinker for the triglyceride oil was added. A wide range of semi-IPN compositions was made by a method utilizing a flask and magnetic stirring. The procedures for PET/castor and PET/vernonia semi-IPNs are essentially the same, but with important differences. The time/temperature processes are shown schematically in Figure 7. For either semi-IPN, the requisite amount of PET was first melted in the triglyceride oil in a flask at about 280°C, under nitrogen atmosphere and with stirring, and then the temperature was raised to 300°C. With continued stirring and time at 300°C, the initially immiscible mixture becomes miscible, as evidenced by its clarity. From this point, the synthesis procedure differs depending upon whether castor or vernonia oil is used. For castor oil mixtures, the source of heat is removed, and the miscible mixture is allowed to cool to 240°C (cooling much further below this point results in crystallization and precipitation of the PET from solution). The required amount of diisocyanate crosslinker, HMDI, is then added by syringe, and the solution is quickly mixed and poured into molds. The hydroxyl-isocyanate reaction occurs rapidly at 240°C, so that the mixture must be poured into the mold within less than a minute, before the castor oil gel point has been reached. After pouring, the castor oil semi-IPN molds are placed in an air oven at 100°C for 18 h to complete the network formation.

For PET/vernonia oil, after a clear mixture was obtained, the mixture was held at 300°C for an additional 10 min, allowing the bond interchange reactions to occur to a greater extent. After 10 min at 300°C, the mixture was cooled to 280°C, and the required amount of sebacic acid was added, which reduced the temperature to about 250°C, where the mixture was held for another 5 min. During this time, the sebacic acid reacts with the vernonia epoxide groups to form a polyester network, with the gel point occurring after approximately 15 min under these conditions. After 5 min at 250°C, the mixture was poured into a preheated mold and allowed to cool, during which time the PET crystallizes. Finally, the material was placed in a vacuum oven at 160°C for 18 h to complete the vernonia polyester network formation reaction.

Tensile stress-strain data for several PET/castor polyurethane semi-IPNs are shown in Figure 8. While the original PET was rather brittle, and the castor oil polyurethane elastomer was rubbery but fairly weak, the semi-IPNs of intermediate composition were significantly tougher materials. The intermediate semi-IPNs had their glass transition broadened considerably, indicating a microheterogeneous and/or co-continuous morphology, which is able to enhance synergistically the toughness of the material. Toughness of the 50 wt% semi-IPN, as measured by the energy density required to break the specimen, was nearly 100 times greater than that of the PET from which it was made. Similar trends were observed in the PET/vernonia polyester semi-IPNs prepared, but these semi-IPNs were generally weaker, as the neat vernonia polyester elastomer is weaker than castor oil polyurethane.

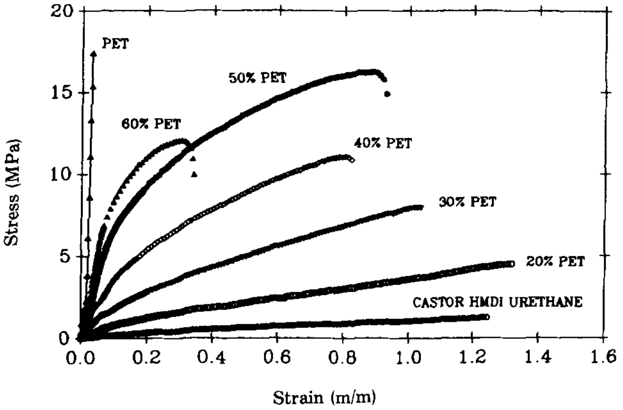

FIG. 8. Tensile stress-strain curves for poly(ethylene terephthalate) (PET)/castor polyurethane semi-interpenetrating polymer networks (68). Abbreviation: HMDI, hydrogenated methylene diphenyldiisocyanate.

Because of the difference in relative rate of polymerization between vernonia and castor, the sequence of PET crystallization and triglyceride network formation were different. Castor oil polyurethane network is synthesized rapidly at the high temperatures used and reaches its gel point concurrently with PET crystallization. Vernonia oil polyester network formation occurs more slowly, and for the synthesis procedure given above, the PET crystallizes prior to network formation. Because the PET crystallized before the vernonia polyester network could form, the PET/vernonia semi-IPNs displayed two glass transition temperatures as synthesized (one for PET and one for vernonia, in addition to the PET melting temperature), while the PET/castor semi-IPNs, in which crystallization and gelation occurred simultaneously, had a single, broad glass transition.

Alternatively, rather than allowing the PET/vernonia material to cool from 250°C in the mold, it may be placed in a 250°C oven under reduced nitrogen pressure, which keeps the PET from crystallizing while the vernonia polyester network forms. In this case, where the network is formed prior to crystallization of PET, a completely different material was obtained. Because the elastomeric network was formed before PET could crystallize, the material was much more rubbery, and was completely amorphous. Thus, if the triglyceride oil network is formed when the oil and molten PET are miscible, the PET is unable to crystallize when cooled, presumably due to a restraining effect of the network.

Four generalized factors were determined to play a crucial role in the development of morphology in the PET/triglyceride oil semi-IPN systems studied. The factors are bond interchange, phase separation, crystallization of PET and network formation or crosslinking. These factors and their influences on the system are summarized in Table 7. The factors are not wholly independent. The extent, sequence and kinetics of bond interchange affect phase separation, PET crystallization and crosslinking and thus have a major influence on the resulting semi-IPN properties. Similarly, the sequence and kinetics of crosslinking affects PET crystallinity as well as morphology. Although the numerous factors and their consequences can become complicated, they provide a means of control over the microstructure of the material.

One of the purposes of the work was to create PET materials that are not only tougher but also crystallize faster. As shown by DSC in Figure 9, small amounts of castor oil when blended with PET increase the crystallization onset temperature in cooling from the melt state and also decrease the crystallization onset temperature in heating from the quenched glassy state. The effectiveness of castor oil is comparable or better than the commonly used nucleating agents, calcium acetate or sodium

TABLE 7

Influence of Four Major Factors on PET/Triglyceride Oil Semi-IPNs[a]

Factor	Greater and/or faster application of the factor leads to:	Lesser and/or slower application of the factor leads to:
Bond interchange	Lesser phase separation More complex structure Lower PET melting point T_gs shifted inward Faster or slower crystallization (composition dependent) Faster or slower crosslinking (composition dependent)	Greater phase separation Less complex structure Higher PET melting point T_gs like neat materials
Phase separation	Larger phase domains Poor mechanical properties Two glass transitions	Microheterogeneous Good mechanical properties Single, broad T_g
PET crystallization	Greater crystallinity Higher modulus Less elongation Greater phase separation	Lesser crystallinity More rubbery Lesser phase separation
Crosslinking	Lesser crystallinity Lesser swelling Lower PET melting point Lesser phase separation	Greater crystallinity Greater swelling Higher PET melting point Greater phase separation

[a] Abbreviations: PET, poly(ethylene terephthalate); IPN, interpenetrating polymer network.

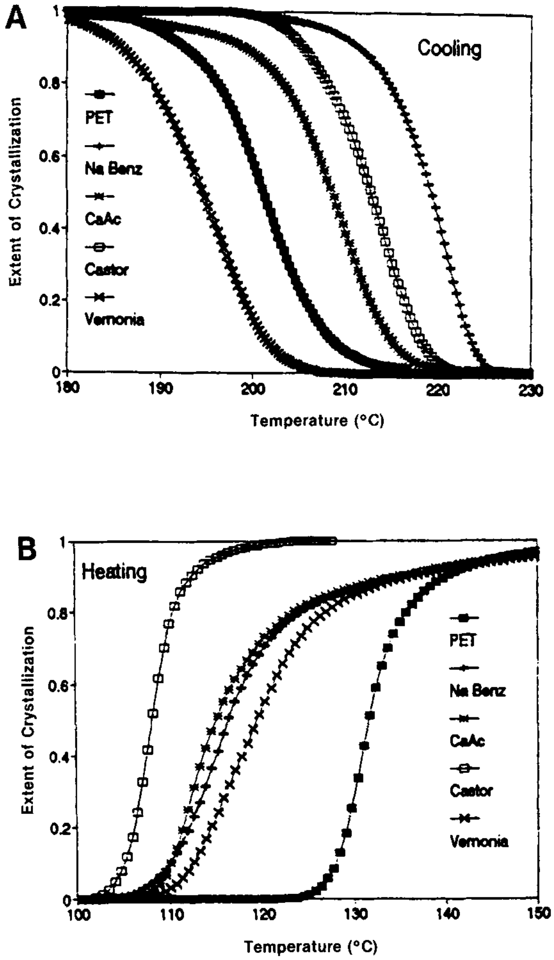

FIG. 9. Extent of crystallization of poly(ethylene terephthalate) (PET) in compositions containing 10 wt% castor or vernonia oil, compared to neat PET, and PET containing 1 wt% nucleating agent, calcium acetate or sodium benzoate, measured in cooling from the melt state (A) and heating from the quenched glassy state (B).

benzoate, in crystallization from the glassy state. Compositions containing castor oil also have greater overall PET crystallinity than neat PET in many cases (71). Thus, castor oil semi-IPNs, when properly engineered for use in reactive injection molding processes, could form the basis of tougher, faster-crystallizing PET materials.

CONCLUSIONS

Up until now, triglyceride oil IPN research has concentrated on morphology and physical properties of amorphous compositions. From the large amount of work that has been done in this field, much has been learned about how to control phase continuity and domain size and to correlate morphology and physical properties. To a large extent, however, the use of semicrystalline polymers in IPNs has been ignored. Because PET is a semicrystalline polymer, the effect of crystallinity on IPN morphology and physical properties becomes a significant new variable to be considered. Only a small number of the questions related to crystallizable IPNs has been addressed, and perhaps more questions have been raised by the work than answered. It is hoped that interest in the area of semicrystalline IPNs may be stimulated by this work.

Prior IPN systems were primarily based on miscible monomers that polymerize to form immiscible networks, which were produced by either the simultaneous or sequential method of IPN synthesis. Castor oil semi-IPNs have been produced with fully polymerized PET, taking advantage of ester interchange reactions to create an initially miscible mixture prior to crosslinking and subsequent phase separation. The resulting structure is shown to contain a significant fraction of copolymer, both in the network as well as the uncrosslinked portion. The extent of copolymerization becomes another synthetic variable, which may be controlled to tailor structure, morphology and physical properties. Creation of IPN materials from fully polymerized immiscible polymers through a bond interchange copolymerization process, followed by crosslinking, is a concept applicable to many other systems and opens the possibility of creating novel IPN compositions and microstructures.

ACKNOWLEDGMENTS

The authors express appreciation to EniChem America, Inc. for their financial support, and also thank the Plastics Institute of America for bestowing their 1991–1992 supplemental fellowship grant to L. W. Barrett.

REFERENCES

1. Sperling, L.H., C.E. Carraher, S.P. Qureshi, J.A. Manson and L.W. Barrett, in *Polymers from Biotechnology,* edited by C.G. Gebelein, Plenum Press, New York, 1991.
2. Sperling, L.H., J.A. Manson and M.A. Linné, *J. Polym. Mater. 1*:54 (1984).
3. Linné, M.A., L.H. Sperling, A.M. Fernandez, S. Qureshi and J.A. Manson, in *Rubber Modified Thermoset Resins,* edited by C.K. Riew, and J.K. Gillham, Advances in Chemistry Series No. 208, American Chemical Society, Washington, D.C., 1984.
4. Sperling, L.H., and J.A. Manson, *J. Am. Oil Chem. Soc. 60*:1887 (1983).
5. Sperling, L.H., J.A. Manson, S.A. Qureshi and A.M. Fernandez, *Ind. Eng. Chem. Prod. Res. Dev. 20*;163 (1981).
6. Sperling, L.H., N.A. Devia, J.A. Manson and A. Conde, in *Modification of Polymers,* edited by C.E. Carraher, Jr., and M. Tsuda, ACS Symposium Series No. 121, American Chemical Society, Washington, D.C., 1980.
7. Devia, N., J.A. Manson, L.H. Sperling and A. Conde, *Macromolecules 12*:360 (1979).
8. Devia-Manjarres, N., A. Conde, G.M. Yenwo, J.E. Pulido, J.A. Manson and L.H. Sperling, *Polym Eng. & Sci. 17*:294 (1977).
9. Yenwo, G.M., J.A. Manson, J. Pulido, L.H. Sperling, A. Conde and N. Devia, *J. Appl. Polym. Sci. 21*:1531 (1977).
10. Ramos, L.C.D., J.S. Tango, A. Savi and N.R. Leal, *J. Am. Oil Chem. Soc. 61*:1841 (1984).
11. Vasishtha, A.K., R.K. Trivedi and G. Das, *Ibid. 67*:333 (1990).
12. Perdue, R.E., Jr., *Agric. Eng.,* May/June 1989.
13. Carlson, K.D., and S.P. Chang, *J. Am. Oil Chem. Soc. 62*:934 (1985).
14. Roetheli, J.C., L.K. Glaser and R.D. Brigham, *Castor: Assessing the Feasibility of U.S. Production,* Summary of USDA/Texas A&M University Workshop, Plainview, Texas, September 18–19, 1990.
15. Earle, F.E., *J. Am. Oil Chem. Soc. 47*:510 (1970).
16. Krewson, C.F., *Ibid. 45*:250 (1968).
17. Ayorinde, F.O., K.D. Carlson, R.P. Pavlik and J. McVety, *Ibid. 67*:512 (1990).
18. Fernandez, A.M., J.A. Manson and L.H. Sperling, in *Renewable Resource Materials: New Polymer Sources,* edited by C.E. Carraher, Jr., and L.H. Sperling, Plenum Press, New York, 1986.

19. Ayorinde, F.O., J. Clifton, Jr., O.A. Afolabi and R.L. Shepard, *J. Am. Oil Chem. Soc. 65*:942 (1988).
20. Ayorinde, F.O., B.D. Butler and M.T. Clayton, *Ibid. 67*:844 (1990).
21. Siddiqi, S.F., F. Ahmad, M.S. Siddiqi, S.M. Osman and G.R. Fenwick, *Ibid. 61*:798 (1984).
22. Ayorinde, F.O., G. Osman, R.L. Shepard and F.T. Powers, *Ibid. 65*:1774 (1988).
23. Ayorinde, F.O., F.T. Powers, L.D. Streete, R.L. Shepard and D.N. Tabi, *Ibid. 66*:690 (1989).
24. Dirlikov, S.K., I. Frischinger, M.S. Islam, and J. Graham, *Polym. Mat. Sci. Eng. 62*:217 (1990).
25. Frischinger, I., and S.K. Dirlikov, *Ibid. 65*:178 (1991).
26. Sears, J.K., and J.R. Darby, *The Technology of Plasticizers,* John Wiley & Sons, New York, 1982.
27. Chung, J.Y.J., J.D. Jones and H.M. Li, U.S. Patent 4,539,352 (1985).
28. Wypych, J., in *Polyvinyl Chloride Stabilization,* Elsevier, Amsterdam, 1986.
29. Cuadrado, T.R., and R.J.J. Williams, *Polymer Comm. 30*:239 (1989).
30. Riser, G.R., J.J. Hunter, J.S. Ard and L.P. Witnauer, *J. Am. Oil Chem. Soc. 39*:266 (1962).
31. Röbbelen, G.R., R.K. Downey and A. Ashri, *Oil Seed Crops of the World,* McGraw-Hill, New York, 1989.
32. Silverstein, R.M., G.C. Bassler and T.C. Morrill, *Spectroscopic Identification of Organic Compounds,* 4th edn., Wiley, New York, 1981.
33. Wolff, I.A., and T.K. Miwa, *J. Am. Oil Chem. Soc. 42*:208 (1964).
34. Murphy, C.J., R.L. Texter and A.M. Blanchard, *Proc. Pa. Acad. Sci. 61*:92 (1987).
35. Afolabi, O.A., M.E. Aluko, G.C. Wang, W.A. Anderson and F.O. Ayorinde, *J. Am. Oil Chem. Soc. 66*:983 (1989).
36. Yenwo, G.M., L.H. Sperling, J.E. Pulido, J.A. Manson and A. Conde, *Polym. Eng. & Sci. 17*:251 (1977).
37. Devia-Manjarres, N., J.A. Manson, L.H. Sperling and A. Conde, *Ibid. 18*:200 (1978).
38. Binder, R.G., T.H. Applewhite, G.O. Kohler and L.A. Goldblatt, *J. Am. Oil Chem. Soc. 39*:513 (1962).
39. Swern, D., in *Bailey's Industrial Oil and Fat Products,* 3rd edn., edited by D. Swern, Wiley Interscience, New York, Chapter 1, 1964.
40. Moreau, R.A., K.D.F. Liu and A.H.C. Huang, *Plant Physiol. 65*:1176 (1980).
41. Fernandez, A.M., C.J. Murphy, M.T. DeCrosta, J.A. Manson and L.H. Sperling, in *Polymer Applications of Renewable Resource Materials,* edited by C.E. Carraher and L.H. Sperling, Plenum Press, New York, 1983.
42. Odian, G., *Principles of Polymerization,* 2nd edn., Wiley Interscience, New York, 1981, p. 119.
43. Sperling, L.H., *Introduction to Physical Polymer Science,* Wiley-Interscience, New York, 1986, p. 343.
44. Wolf, B.A., in *Polymer Handbook,* 2nd edn., edited by J. Brandup, and E.H. Immergut, Wiley Interscience, New York, Chapter IV, Section 40, 1974.
45. Sperling, L.H., in *Interpenetrating Polymer Networks and Related Materials,* Plenum Press, New York, 1981.
46. Utracki, L.A., in *Interpenetrating Polymer Networks,* edited by D. Klempner, L.H. Sperling and L.A. Utracki, ACS Advances in Chemistry Series 239, American Chemical Society, Washington, D.C., 1993, in press.
47. Erhan, S.M., and R. Kleiman, *J. Am. Oil Chem. Soc. 67*:670 (1990).
48. Suthar, B., N. Parikh and N. Patel, *Polym. Int. 25(3)*:173 (1991).
49. Rajalingam, P., and G. Radhakrishnan, *Ibid. 25(2)*:87 (1991).
50. Patel, N., and B. Suthar, *Polym. Plast. Technol. Eng. 29(5,6)*:535 (1990).
51. Tan, P., *PMSE Preprints 65*:182 (1991).
52. Tan, P., and H. Zie, *Hecheng Xiangjiao Gongye 7*:180 (1984).
53. Liang, J.L., H.T. Liu, W.H. Ku and G.M. Wang, *Abstracts IUPAC International Symposium on Polymers and Advanced Technologies,* Jerusalem, Israel, August, 1987.
54. Song, M., and Z. Donghua, *Plastics Industry (P.R.C.) 2*:42 (1987).
55. Rajalingham, P., and G. Radhakrishnan, *Abstract for poster session, International Symposium on Multiphase Macromolecular Systems,* American Chemical Society, Division of Polymer Chemistry, 14th Biennial Meeting, San Diego, California, November, 1988.
56. Afolabi, O.A., M.E. Aluko, G.C. Wang, W.A. Anderson and F.O. Ayorinde, *J. Am. Oil Chem. Soc. 66*:983 (1989).
57. Qureshi, S.A., J.A. Manson, L.H. Sperling and C.J. Murphy, in *Polymer Applications of Renewable Resource Materials,* edited by C.E. Carraher, Jr., and L.H. Sperling, Plenum Press, New York, 1983.
58. Klempner, D., L.H. Sperling and L.A. Utracki (eds.), *Interpenetrating Polymer Networks,* ACS Advances in Chemistry Series No. 239, American Chemical Society, Washington, D.C., 1193, in press.
59. Manson, J.A., and L.H. Sperling, *Polymer Blends and Composites,* Plenum Press, New York, 1976.
60. Jordhamo, G.M., J.A. Manson and L.H. Sperling, *Polym. Eng. & Sci. 26*:517 (1986).
61. Patel, P., T. Shah and B. Suthar, *J. Appl. Polym. Sci. 40*:1037 (1990).
62. Patel, P., and B. Suthar, *Polym. Plast. Technol. Eng. 28*:1 (1989).
63. Patel, P., M. Patel and B. Suthar, *Brit. Polym. J. 20*:525 (1988).
64. Patel, P., and B. Suthar, *Polym. Eng. & Sci. 28*:901 (1988).
65. *Plastics Technology,* 1991, p. 62.
66. Rigby, P.J., *Modern Plastics 676(11)*:50 (1990).
67. Barrett, L.W., L.H. Sperling, J. Gilmer and S.G. Mylonakis, in *Interpenetrating Polymer Networks,* edited by D. Klempner, L.H. Sperling, and L.A. Utracki, ACS Advances in Chemistry Series 239, American Chemical Society, Washington, D.C., 1993, in press.
68. Barrett, L.W., and L.H. Sperling, *Polym. Eng. Sci.,* 1993, in press.
69. Barrett, L.W., G.S. Ferguson and L.H. Sperling, *J. Polym. Sci., Polym. Chem. Ed. 31*:1287 (1993).
70. Barrett, L.W., O.L. Shaffer and L.H. Sperling, *J. Appl. Polym. Sci.,* 1993, in press.
71. Barrett, L.W., L.H. Sperling, J. Gilmer and S.G. Mylonakis, *Ibid.,* 1993, in press.

[Received October 1, 1992; accepted February 3, 1993]