

# Semi-Interpenetrating Polymer Networks Composed of Poly(ethylene terephthalate) and Vernonia Oil

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## SYNOPSIS

Semi-interpenetrating networks have been synthesized from vernonia oil-sebacic acid polyester network and poly(ethylene terephthalate) (PET). Bond interchange reactions during mixing of the two materials led to the formation of a miscible copolymer mixture, in which the vernonia oil was then cross-linked with sebacic acid. The materials were phase-separated, exhibiting two glass transitions, when the network was synthesized at 160°C, below the crystallization temperature of PET; however, a single stable glass transition ( $T_g$ ) results after the material is heated to above the melting temperature of PET and cooled. When the vernonia polyester network was completely formed at 250°C, above the crystallization temperature of PET, noncrystalline, single- $T_g$  material was created. The two-phase semi-IPNs were much tougher than were their constituent materials, with the 50% semi-IPN over 15 times tougher than the PET from which it was made and over 50 times tougher than the neat vernonia oil elastomer, with tensile energy to break of 1780 kJ/m<sup>3</sup>. The single- $T_g$  material was nearly 2.5 times as tough as the two-phase material, with energy to break of 4400 kJ/m<sup>3</sup>. The microstructure of the two-phase 50% semi-IPN was investigated by transmission electron microscopy, which showed regularly shaped spherulites of 10–20  $\mu\text{m}$  in diameter, as compared to irregularly shaped spherulites observed in a similar 50/50 castor oil urethane/PET semi-IPN, in which the network formed simultaneously with PET crystallization. Scanning electron microscopy of the semi-IPN fracture surfaces showed microscopic fibrils several hundred nanometers in diameter in both the two-phase and single- $T_g$  materials, although only the two-phase semi-IPN had a macroscopically rough surface. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Interpenetrating polymer network (IPN) research at Lehigh University involving naturally functionalized triglyceride oils has been primarily concerned with three oils: lesquerella oil,<sup>1–6</sup> vernonia oil,<sup>1,4,5,7–10</sup> and castor oil.<sup>1,2,4,5,7,8,10–16</sup> These oils are prepared by nature with multiple chemical functionality and are thus a renewable resource, providing an alternative to petroleum as a chemical feedstock. The oils may be cross-linked to form an elastomeric material, usually by step-growth reactions, which has prompted their use in IPNs along with chain-growth

polymerized plastics. Vernonia oil is among a small group of naturally epoxidized triglyceride oils<sup>17,18</sup> and has received considerable attention lately<sup>10,19–25</sup> as its status nears that of a commercial material.<sup>19,26–27</sup>

## Vernonia Oil

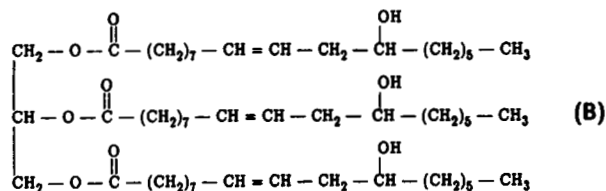
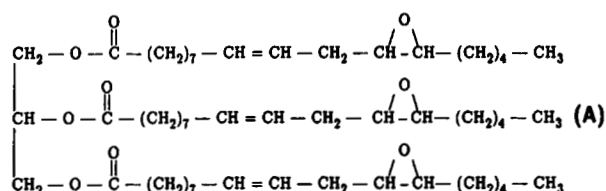
The presence of epoxy acids as a natural constituent of certain seed oils has been known since the 1950s, and over 60 species of plants that produce epoxy acids had been identified by 1970.<sup>17,18</sup> The oil from *Vernonia galamensis*, or simply vernonia oil, represents the most promising of these epoxidized oils, due to its ease of production,<sup>21</sup> seed oil content, and concentration of epoxidized triglyceride in the oil [75–80% vernolic acid triglycerides; the structure of trivernolin is depicted in Fig. 1(A)]<sup>8,21</sup> and high epoxide equivalent weight (typically about 400 g/equiv

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epoxide). Similar in structure to castor oil [Fig. 1(B)], which is already a high-volume commercial product due to its naturally occurring hydroxyl groups, vernonia is a rich natural source of epoxidized acids,<sup>20,28</sup> as well as dibasic acids.<sup>22,23</sup> Through pyrolytic decomposition, castor oil is now a major source of dibasic acids<sup>29</sup> such as decanedioic acid (sebacic acid); however, octanedioic and nonanedioic acids (subaric and azelaic acids, respectively) may be derived from vernonia oil in greater yields than from castor oil.<sup>22</sup>

The potential uses of vernonia oil by itself are many. The oil has a relatively low viscosity for its high epoxide equivalent weight, making it a prospective reactive diluent for coatings applications.<sup>24,27</sup> 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 bisphenol-A epoxy compounds.<sup>25</sup> Vernonia oil may compete with and someday replace synthetically epoxidized triglyceride oils now used in large quantities as poly(vinyl chloride) plasticizers and stabilizers.<sup>27,30-34</sup>

The vernonia oil polyester elastomer may be prepared by reaction with dibasic acids, themselves derived from the oil; thus, the elastomer is a product of renewable resources. Sperling et al.<sup>8,9</sup> produced vernonia/polystyrene interpenetrating polymer networks (IPNs) using sebacic acid as the vernonia oil cross-linker, which had properties ranging from reinforced elastomer to toughened plastic, depending



**Figure 1** Structure of (A) the major component of vernonia oil, triglyceride of vernolic acid or trivernolin and (B) the major component of castor oil, triglyceride of ricinoleic acid.

on the overall composition. Ayorinde et al., whose research group has previously reported preparing subaric acid from vernonia oil,<sup>22</sup> made polystyrene IPNs using subaric acid as the cross-linker.<sup>35</sup>

### PET/Triglyceride Oil Semi-IPNs

Barrett and Sperling<sup>7,14-16</sup> recently studied semi-IPNs made from castor oil and poly(ethylene terephthalate) (PET). The materials were semi-IPNs, as the PET remains uncross-linked. The use of naturally functionalized triglyceride oils with thermoplastic polymers has mostly been limited to that of a plasticizer or stabilizer.<sup>27,30-34</sup> Compared to much of the prior IPN literature, in which chain-polymerizable, amorphous plastics are used, PET is a semicrystalline, step-growth polymer. 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. 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.<sup>36</sup> 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.<sup>7,14-16</sup> In this paper, the work is extended to cover the synthesis and properties of vernonia-sebacic polyester network/PET semi-IPNs and to address key differences between corresponding vernonia and castor oil materials.

IPNs may, in general, be formed by two methods.<sup>37</sup> In the sequential method, a cross-linked network is formed, then swelled with the monomer and cross-linker 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 cross-linkers of both materials may be mixed and polymerized together simultaneously. Because of the noninterfering polymerizations of styrene (free-radical chain growth) and vernonia (step growth), simultaneous IPN formation is possible, in which all the reactants are mixed at once and polymerized. Prior triglyceride oil IPN synthesis 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 swollen

network (sequential method), phase separating as polymerization and cross-linking occurs. It is the relationship between cross-linking and phase-separation kinetics that controls the final IPN morphology<sup>38</sup> and, hence, the mechanical behavior.

In the present research, fully polymerized PET is the starting material, which puts some constraints on the IPN formation process. PET may be considered as the condensation product of terephthalic acid and ethylene glycol. Because the vernonia oil would polymerize with terephthalic acid in competition with ethylene glycol, simultaneous semi-IPN formation from monomers is not possible, since non-interfering polymerization routes are required for this method of IPN synthesis. Although PET and vernonia oil polyester network are both polyesters, PET is aromatic and vernonia oil is aliphatic and the two are immiscible. Thus, vernonia oil will not dissolve in PET, nor will polymerized PET swell a vernonia oil network, making sequential IPN formation impossible. To control the IPN morphology of PET and the vernonia oil network, the two components must first be very well mixed or miscible, then be allowed to phase separate as the vernonia oil cross-linking occurs.

To solve the problem of initial immiscibility, it was discovered that continued heating of triglyceride oil and PET results in a miscible mixture, a consequence of bond interchange reactions that form a compatibilizing copolymer.<sup>10,15,16</sup> Since PET contains ester groups and vernonia oil contains both ester and epoxide groups, either ester-ester or hydroxyl-ester interchange (after the epoxide ring is opened through acid catalysis or hydrolysis), or both, take place.<sup>10,15,16</sup> In either case, the resulting semi-IPN will be a hybrid structure, in which the cross-linked and/or uncross-linked materials may be copolymers and not pure components. Thus, the extent to which the bond interchange reactions take place will affect 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, semi-IPNs, and related materials.

## EXPERIMENTAL

### Materials and Syntheses

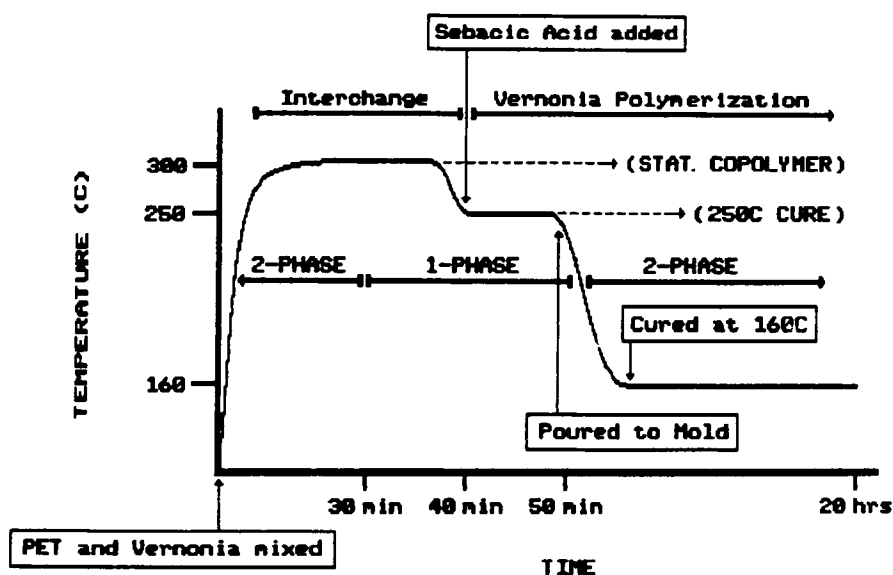
Poly(ethylene terephthalate) was supplied by EniChem America, Inc., with intrinsic viscosity of

0.60 dL/g, as measured at 25°C in 60/40 by weight 1,1,2,2-tetrachloroethane/phenol, corresponding to viscosity average molecular weight of 12,700 g/mol.<sup>39</sup> The PET was dried at 120°C in a vacuum oven for at least 48 h prior to use.

Refined vernonia oil was obtained through the Performance Resins & Coatings Division of Rhone-Poulenc, Inc.† The equivalent weight was 411 g per mol epoxide groups. Theoretically, pure triglyceride of vernolic acid would have an equivalent weight of 309 g/equiv, so that at 411 g/equiv the refined oil is approximately 75% pure triglyceride of vernolic acid, which compares reasonably with the 75–80% purity range previously reported.<sup>8,21</sup> The purity of vernonia oil refers to the purity of its acid residues, which are approximately randomly distributed among the glyceride backbones available. Thus, vernonia contains 59% trivernolin, 28% divernolin, 10% monovernolin, and 3% unepoxidized triglyceride.<sup>27</sup>

A range of PET/vernonia oil semi-IPN compositions were made in a flask with magnetic stirring. The general procedure is outlined schematically in a temperature vs. time diagram, shown in Figure 2. First, the required amount of PET was melted in vernonia oil in the flask at about 280°C, under nitrogen atmosphere and with stirring; then, the temperature was raised to 300°C. With continued stirring at 300°C, the initially immiscible mixture becomes miscible, as evidenced by its clarity, due to bond interchange reactions.<sup>10,15,16</sup> Holding the mixture at 300°C for longer periods of time allows the interchange reactions to continue, forming greater amounts of copolymer, and, eventually, the entire mixture becomes a single-phase statistical copolymer composition.<sup>10</sup> Various reaction times at 300°C were tried after the point of clarity was reached with the 50/50 composition, but 10 min was used for the range of compositions reported herein. After the desired reaction time at 300°C was reached, the mixture was cooled to 280°C, and the required amount of sebacic acid was added, which reduces the temperature to about 250°C, where the mixture is held for another period of time. During the time at 250°C, the sebacic acid reacts with the vernonia epoxide groups to form a polyester network. The gel point under these conditions occurs after approximately 15 min. Again, various lengths of time at 250°C were tried for the 50/50 composition, but 5 min was used

† Vernonia oil is now available in small quantities from Rhone-Poulenc Performance Resins & Coatings Division, 9808 Bluegrass Parkway, Louisville, KY 40299-1906.



**Figure 2** Schematic diagram of semi-IPN synthesis process (axes are not to scale). The solid line shows the time-temperature course taken to produce the compositional range of semi-IPNs described within the paper. Dashed lines indicate the formation of statistical copolymer by allowing interchange to continue at 300°C, and the process by which the vernonia polyester network was fully cross-linked at 250°C, above the crystallization temperature of PET.

for the range of compositions reported, after which 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. Alternatively, rather than allowing the 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.

### Measurement Techniques

Differential scanning calorimetry (DSC) was done with a Mettler TA-3000, with sample size kept close to 15 mg. The typical scan sequence started with cooling to -150°C, recording heat flow data during heating from -150 to 300°C at 20°C/min, rapidly cooling with liquid nitrogen back to -150°C, and repeating the -150 to 300°C heating scan. Glass transition data in this paper is presented as the derivative of exothermal heat flow, so that what is actually plotted is the rate of change in heat capacity vs. temperature, which goes through a minimum at the glass transition during heating. Glass transition values reported are the (negative) peak tempera-

tures of the derivative heat flow vs. temperature data.

Mechanical tensile testing was done at room temperature using an Instron material test system interfaced to an IBM PS/2 microcomputer. The general test procedure and sample preparation is described in the ASTM D-1708 microtensile test method. The strain rate was 112%/min, calculated from 25 mm/min displacement for specimens of gauge length 22.25 mm. Load vs. displacement data was converted directly to stress vs. strain without making any corrections, as it is assumed that strain outside the gauge section was minimal. Tensile strength, Young's modulus, and percent elongation were calculated in a straightforward manner after the ASTM standard, and energy to break, or toughness, was calculated from the area under the stress-strain curve.

Fourier transform infrared (FTIR) spectroscopy was carried out using a Mattson Polaris spectrometer interfaced to a Zenith-386 microcomputer. Sample preparation was generally done by taking the methylene chloride solution of the material to be analyzed, adding the solution dropwise onto silver chloride (AgCl) plates, and allowing the solvent to evaporate. In general, 64 scans from 800 to 4000  $\text{cm}^{-1}$  were taken at 2  $\text{cm}^{-1}$  resolution and averaged,

smoothed, and base-lined. For comparative purposes, spectra were normalized so that absorbance of the ester carbonyl stretching at  $1730\text{ cm}^{-1}$  was set equal to unity, so that what is plotted is the ratio of absorbance at that wavenumber to the absorbance of the ester groups.

Swelling of the semi-IPNs was done using the solvents methylene chloride (MeCl) and a 60/40 by weight mixture of 1,1,2-tetrachloroethane/phenol (TCE/Ph). Methylene chloride is a good solvent for the triglyceride oils, as well as a good swelling agent for triglyceride oil network,<sup>16</sup> but is ineffective at dissolving PET. TCE/Ph is not only able to dissolve PET, but can also dissolve triglyceride oil and swell its cross-linked network. The swelling ratio was measured by immersing a weighed sample of the material, allowing it to swell to equilibrium, and reweighing the swollen sample. From the densities of the solvent and material, the polymer volume fraction ( $V_2$ ) of the swollen sample may then be calculated, and the swelling ratio is defined as the inverse of the polymer volume fraction ( $1/V_2$ ).<sup>40</sup> After the swelling was complete, the swelling solution was evaporated, and the material that dissolved into solution was analyzed by FTIR.

Transmission electron microscopy (TEM) was performed using a Phillips EM-300 operated at 80 kV. Sections of the materials approximately 100 nm in thickness were prepared using a liquid nitrogen cooled ultramicrotome. The sections were then stained by placing them in the presence of osmium tetroxide ( $\text{OsO}_4$ ) and/or ruthenium tetroxide ( $\text{RuO}_4$ ) vapor for 30 min to 1 h.  $\text{OsO}_4$  is known to stain materials containing double bonds (such as the triglyceride oil network),<sup>41</sup> whereas  $\text{RuO}_4$  is able to stain materials containing aromatic rings (such as PET).<sup>42</sup> These staining agents are extremely hazardous and should always be used with great

caution. Scanning electron microscopy (SEM) was done on a JEOL 6300F instrument operated at 1.0 kV accelerating voltage on uncoated material or at 10 kV on material sputter-coated with a gold-palladium alloy. Secondary electron images were recorded directly from the cathode ray tube on Polaroid 55 film.

## RESULTS

First, the synthetic variables of time held at  $300^\circ\text{C}$  after clarity is reached and time held at  $250^\circ\text{C}$  after sebacic acid is added were investigated. During the time held at  $300^\circ\text{C}$ , bond interchange between vernonia and PET continues to occur,<sup>10</sup> forming copolymer that has the effect of increasing the miscibility of the vernonia and PET.<sup>15,16</sup> Thus, one would expect a more miscible system for longer times held at  $300^\circ\text{C}$ . During the time at  $250^\circ\text{C}$  after sebacic acid is added, the sebacic acid reacts with vernonia to form the polyester network, above the crystallization temperature of PET. Thus, longer times held at  $250^\circ\text{C}$  could affect the phase morphology by reaching greater extents of reaction for the vernonia network prior to PET crystallization and phase separation.

The properties resulting from varying the times held at 300 and  $250^\circ\text{C}$  for 50/50 vernonia-sebacic polyester/PET semi-IPNs are summarized in Table I. Tensile strength, modulus, elongation, tensile energy to break, swelling ratio ( $1/V_2$ ) in TCE/Ph, and glass transitions observed for the vernonia-sebacic polyester and PET transitions in the first heat ( $T_{g1V}$  and  $T_{g1P}$ , respectively) and the single glass transition observed in the second heat ( $T_{g2}$ ) are reported. Of the two factors, the time held at  $300^\circ\text{C}$  had a much more significant effect on the resulting

**Table I** Effect of Time and Temperature during Semi-IPN Synthesis

$t$ at $300^\circ\text{C}$ (min)	$t$ at $250^\circ\text{C}$ (min)	Tensile (KPa)	Modulus (MPa)	Elongation (%)	Energy ( $\text{kJ/m}^3$ )	$1/V_2$ (unitless)	$T_{g1V}$ ( $^\circ\text{C}$ )	$T_{g1P}$ ( $^\circ\text{C}$ )	$T_{g2}$ ( $^\circ\text{C}$ )
0	0	4750	41.0	32.2	1000	22.0	-37	36	-25
0	5	5320	36.4	34.5	1200	11.8	-34	41	-16
0	10	5050	29.1	38.5	1270	12.2	-32	45	-15
10	0	6540	30.9	42.1	1710	10.7	-27	44	-16
10	5	6030	25.8	46.7	1780	10.7	-22	44	-13
10	10	6320	32.3	40.9	1650	10.3	-20	43	-15
30	0	6880	42.8	35.9	1540	13.0	-26	33	-12
30	5	6960	37.2	45.4	2070	15.9	-22	38	-13
30	10	6240	39.0	39.7	1620	> 30	-26	39	-11

**Table II** Data for a Range of Vernonia–Sebacic Polyester/PET Semi-IPN Compositions

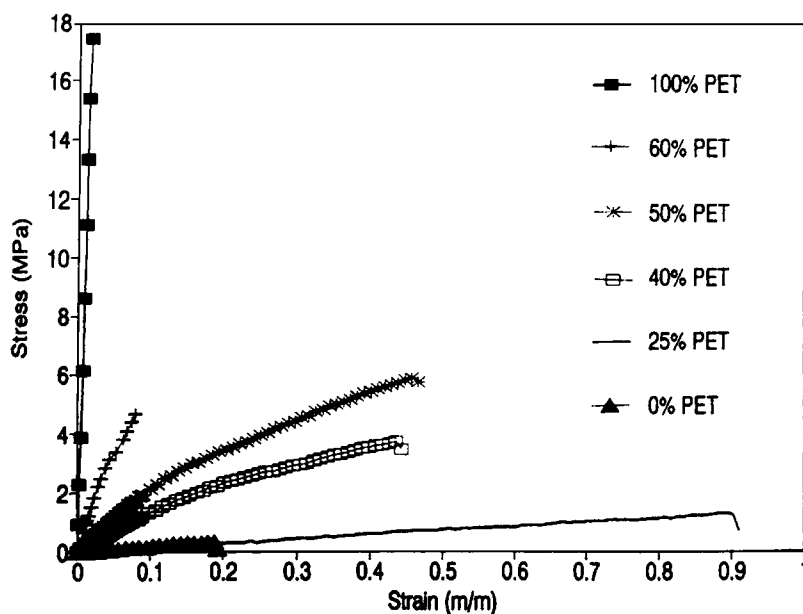
PET Content (%)	Tensile (KPa)	Modulus (MPa)	Elongation (%)	Energy (kJ/m <sup>3</sup> )	1/V <sub>2</sub> (unitless)	T <sub>g1V</sub> (°C)	T <sub>g1P</sub> (°C)	T <sub>g2</sub> (°C)
0	260	1.7	17.0	35	6.5	-40	—	-40
25	1,180	4.2	77.0	490	10.8	-30	46	-25
40	3,200	13.3	56.0	1440	11.3	-35	46	-23
50	6,030	25.8	46.7	1780	10.7	-22	44	-13
60	4,530	91.3	6.5	163	19.6	-26	47	8
75	—	—	—	—	—	-29	48	28
100	16,400	1270.0	1.1	114	—	—	79	77
50 <sup>a</sup>	5,050	16.3	125.0	4400	9.0	-6	-6	1

<sup>a</sup> This material was prepared by forming the vernonia oil network at 250°C (see text).

properties measured. In general, tensile strength increased with longer time at 300°C; however, best elongation and the least variation in mechanical properties were found at the intermediate time of 10 min at 300°C. Swelling is clearly at a minimum for materials held at 300°C for 10 min, indicating a more tightly cross-linked network. The single glass transition observed in the second heating of the materials shows a definite increase with the time held at 300°C and more generally increases with the total time held at both 300 and 250°C, from -25°C for zero time at high temperature up to -11°C for the total of 40 min held at high temperatures. Overall, the combination of 10 min at 300°C and 5 min at 250°C was chosen to be used for producing a wider

range of compositions, due to the good properties and minimal variations observed.

The same mix of properties tabulated in Table I are given in Table II for the range of compositions made wherein the miscible mixtures were held 10 min at 300°C, 5 min at 250°C, and the network synthesized at 160°C. Stress-strain curves are shown in Figure 3. The PET used to produce the semi-IPNs is seen to be quite brittle, due to its low molecular weight, which is just below the critical entanglement molecular weight.<sup>43</sup> The neat vernonia polyester elastomer is also seen to be a weak, rubbery material. When the two weak and brittle materials are combined as semi-IPNs, however, the toughness, as evidenced by the energy to break the sample (the

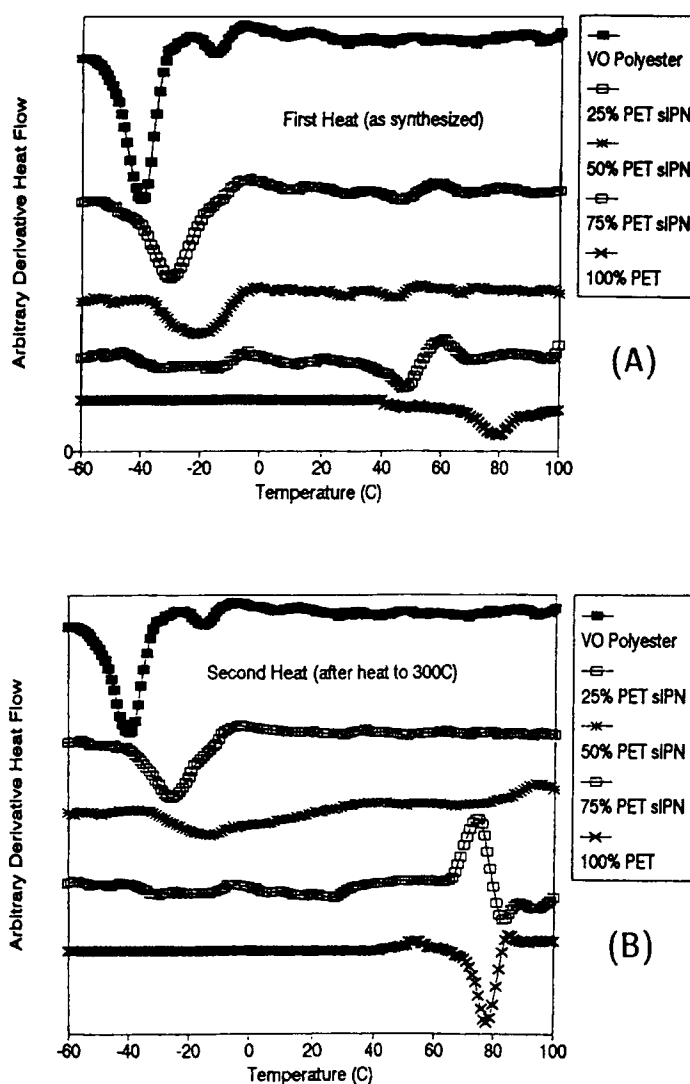


**Figure 3** Stress-strain behavior for a range of vernonia-sebacic polyester network/PET semi-IPN compositions.

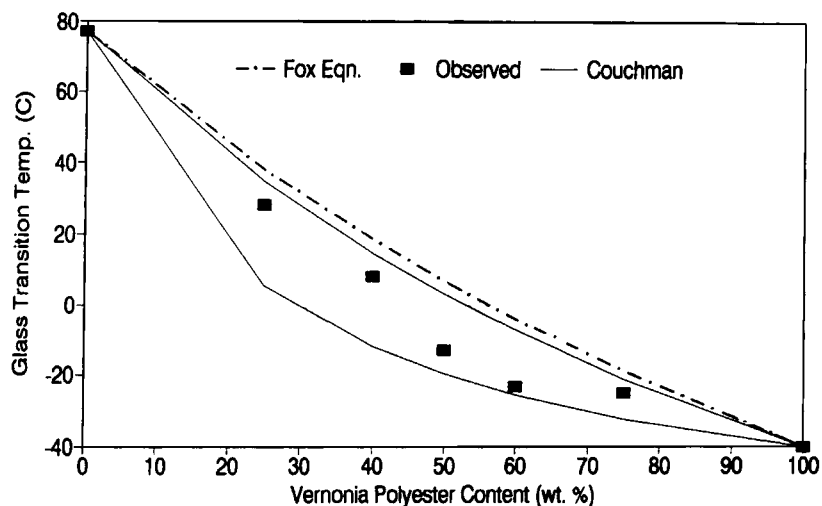
area under the stress-strain curve, divided by specimen volume), increases remarkably. The 25% PET semi-IPN almost seems anomalous, as its ultimate elongation is over four times that of the vernonia-sebacic polyester elastomer; however, all the semi-IPNs, with up to 50% PET, have much greater elongation than does the vernonia elastomer. The 75% PET semi-IPN was too brittle to be tested.

Plots of the derivative of DSC heat flow in the glass transition region are shown in Figure 4 for the first and second heating scans for some of the semi-IPN materials. In all of the semi-IPNs, two glass transitions were observed in the first heat, which

transformed into a single, broad transition in the second heat recorded after rapid cooling from 300°C. Thus, the materials are multiphase as prepared, but after heating to above the melting point of PET and cooling, they become nearly single phase or micro-heterogeneous. Although the second heat glass transitions are very broad and are not completely characterized by a single temperature, if the peak glass transition temperatures are plotted vs. composition, as in Figure 5, they are found to almost follow the Fox equation,<sup>40</sup> with slight negative deviation. The Fox equation predicts the glass transition temperature for miscible blends and statistical



**Figure 4** Glass transition behavior for several vernonia-sebacic polyester network/PET semi-IPN compositions. First-heat data, the materials as synthesized is shown in (A), while (B) shows second-heat data, recorded after cooling rapidly from 300°C. The 75% PET material is seen to crystallize in the second heating scan.

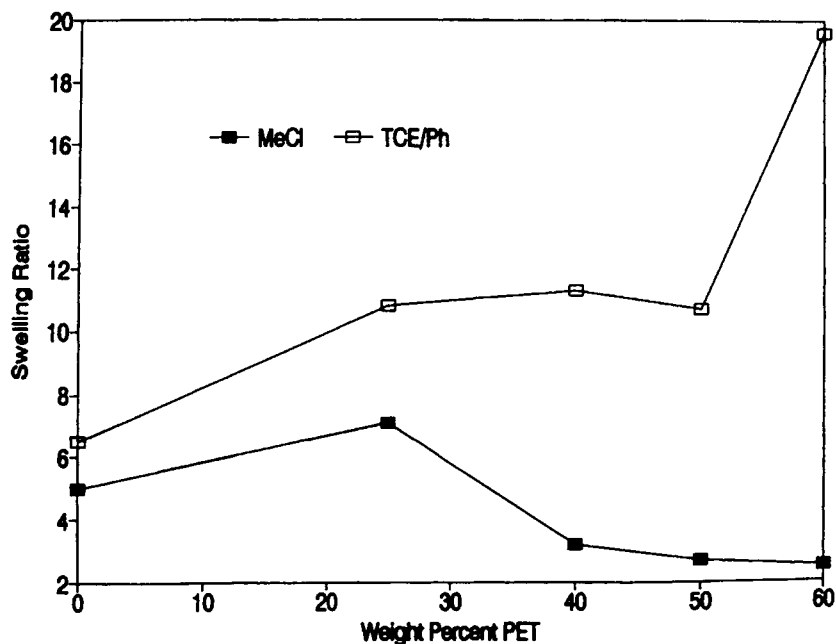


**Figure 5** Peak glass transition temperature vs. composition for the semi-IPN series, including theoretical calculations of the glass transition temperature based on the Fox and Couchman equations.

copolymers. The Couchman equation<sup>44</sup> is a more general expression,<sup>40</sup> taking into account the differences in heat capacity change of the components undergoing their glass transition. The change in heat capacity,  $\Delta C_p$ , of PET depends upon crystallinity and has been found to vary from 0.12 to 0.33 J/g °C in our DSC, depending upon thermal history. Using these two extremes, the semi-IPN data falls

within the bounds predicted by the Couchman equation (Fig. 5).

The swelling behavior of the semi-IPNs in 1,1,2,2-tetrachloroethane/phenol (TCE/Ph) solvent is given in Table II and plotted in Figure 6. It may be seen that the semi-IPNs swell greater than does the neat vernonia-sebacic polyester network, but to a relatively constant level up to 50% PET. Above 60%



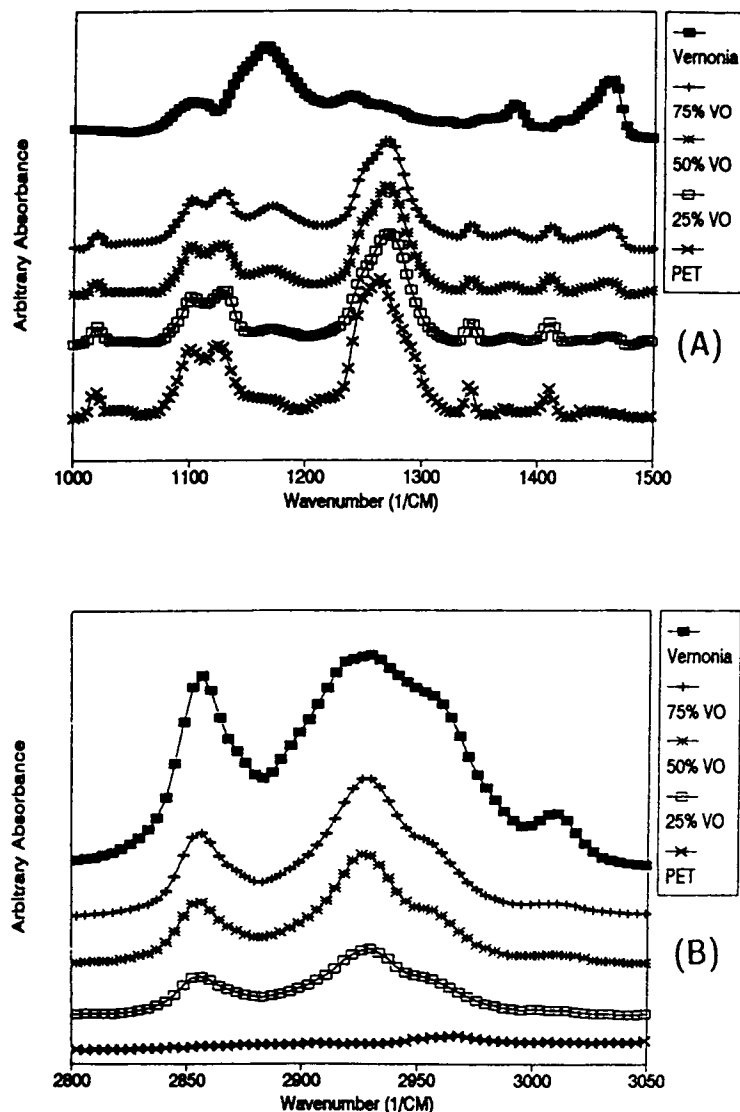
**Figure 6** Swelling ratio ( $1/V_2$ ) vs. composition, in methylene chloride (MeCl) and 60/40 by weight 1,1,2,2-tetrachloroethane/phenol mixture (TCE/Ph) for the semi-IPNs.



PET, the materials dissolved completely in the TCE/Ph, which is a solvent for PET. Swelling in methylene chloride (MeCl) showed opposite results, with swelling decreasing above 25% PET, since MeCl is not a PET solvent. The 75% PET semi-IPN disintegrated in the methylene chloride, without very much dissolving or any apparent swelling.

For all the semi-IPNs, the material that dissolved into the swelling solution was analyzed by FTIR. In Figure 7, absorption spectra of the dissolved material are shown in the two regions of greatest interest. Between 1000 and 1500  $\text{cm}^{-1}$ , where PET has distinctive absorbances due to various aromatic ring

vibrations,<sup>45</sup> the dissolved materials are seen to follow PET absorbances very closely. In the range 2800 to 3050  $\text{cm}^{-1}$ , where the vernonia oil methylene absorption is strong, the spectra appear very similar to those of vernonia oil. This indicates the presence of both PET and vernonia character in the dissolved material. Although homopolymer PET is believed to be a component in the semi-IPNs, only low molecular weight PET would dissolve in the methylene chloride. The vernonia epoxide absorbance at 845  $\text{cm}^{-1}$  (Refs. 8 and 9) was not observed in the dissolved materials, indicating that unreacted vernonia oil was not dissolved. Thus, the material dissolved



**Figure 7** Fourier transform infrared spectra of the portion of semi-IPN material that was soluble in methylene chloride. In (A), the region containing mostly PET aromatic absorptions is shown, while (B) shows the vernonia methylene absorption region.

from the semi-IPNs by methylene chloride is most likely a PET/vernonia copolymer, the result of bond interchange.<sup>10,15,16</sup>

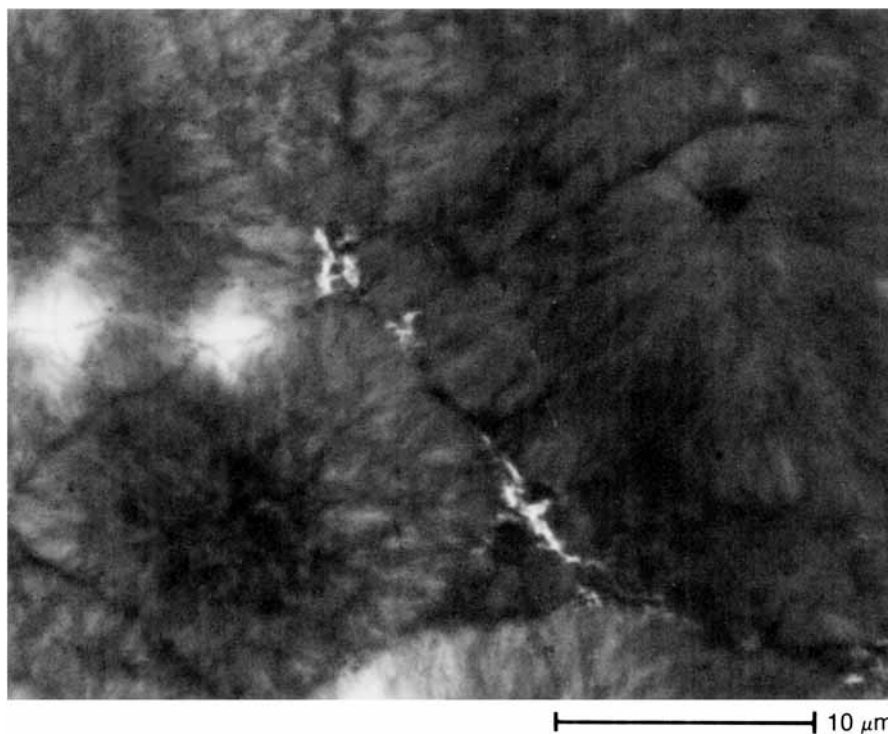
Transmission electron micrographs were taken on the 50/50 PET/vernonia-sebacic polyester semi-IPN, one of which is shown in Figure 8. The dominant morphological feature of the micrograph is the spherulitic structure, a result of the PET crystallization. The specimen was stained with both RuO<sub>4</sub> and OsO<sub>4</sub> in hopes of achieving contrast between the PET-rich and vernonia polyester-rich phases indicated by the DSC results; however, no such simple amorphous phase domains were observed. There is some contrast within the spherulites, and the interfaces are stained darker, where greater amounts of the vernonia polyester may be expected. That better phase resolution was not possible may be due to the composition of both phases being a mixture of both PET and vernonia.

By reacting the miscible vernonia/sebacic acid/PET mixture to completion above the crystallization temperature of PET, a 50/50 semi-IPN was synthesized so that the vernonia-sebacic polyester network would be completely formed before PET could crystallize. This was accomplished by pouring the mixture just after the addition of sebacic acid into a preheated mold and maintaining at 250°C under

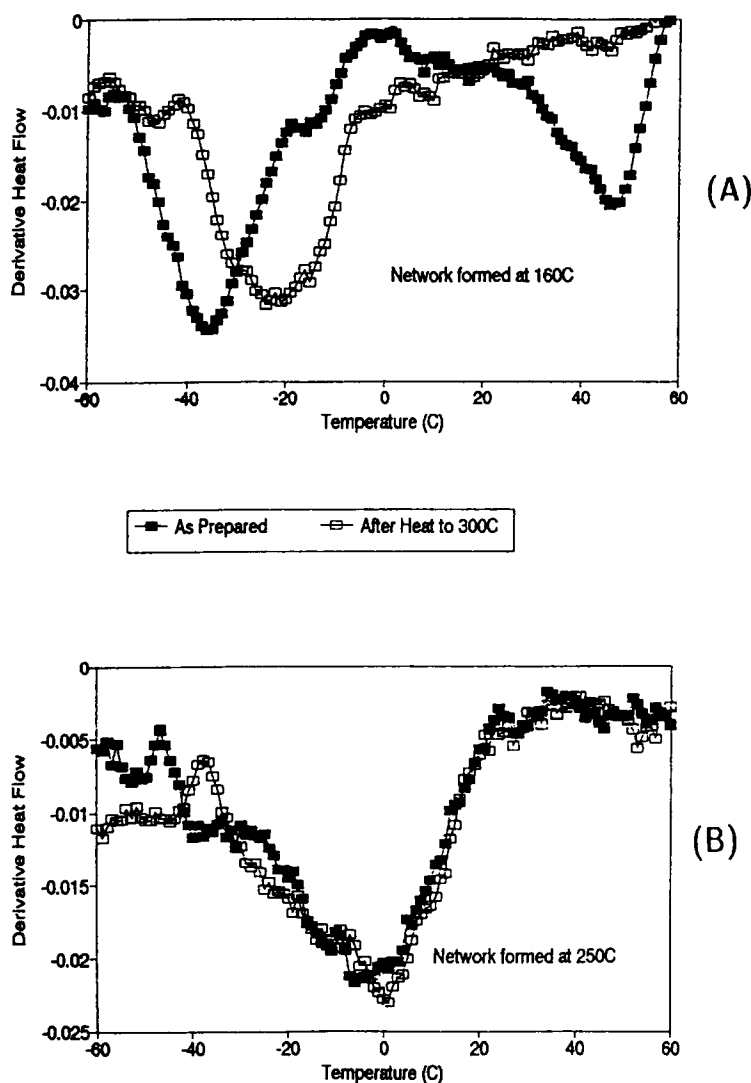
low nitrogen pressure for 3 h. The resulting material was much more rubbery than was the semi-IPN prepared by cooling to 160°C and much more optically clear. Glass transition DSC scans comparing the 160°C synthesis to the 250°C synthesis material are shown in Figure 9. When the network is able to form before PET can crystallize or phase separate, a single, broad glass transition results that does not change significantly upon further heating and cooling. This material also had no PET melting or crystallization peaks observable in the DSC scans.

Stress-strain data for the 50/50 vernonia-sebacic polyester network/PET semi-IPNs prepared at 250°C are included in Table II, where they may be compared with the two-phase 50% semi-IPN prepared at 160°C. The microheterogeneous, noncrystalline material made at 250°C is much more rubbery, with lower modulus and much greater elongation. Although the tensile strength and modulus are lower, toughness of the semi-IPN prepared at 250°C, above the PET crystallization temperature, is about 2.5 times greater than that when the network is formed at 160°C, after PET crystallization has taken place.

In Figures 10 and 11, the surfaces of the room-temperature fractured tensile specimens are compared through a series of scanning electron micro-



**Figure 8** Transmission electron micrograph of 50/50 PET/vernonia-sebacic polyester network semi-IPN, stained with both RuO<sub>4</sub> and OsO<sub>4</sub>.



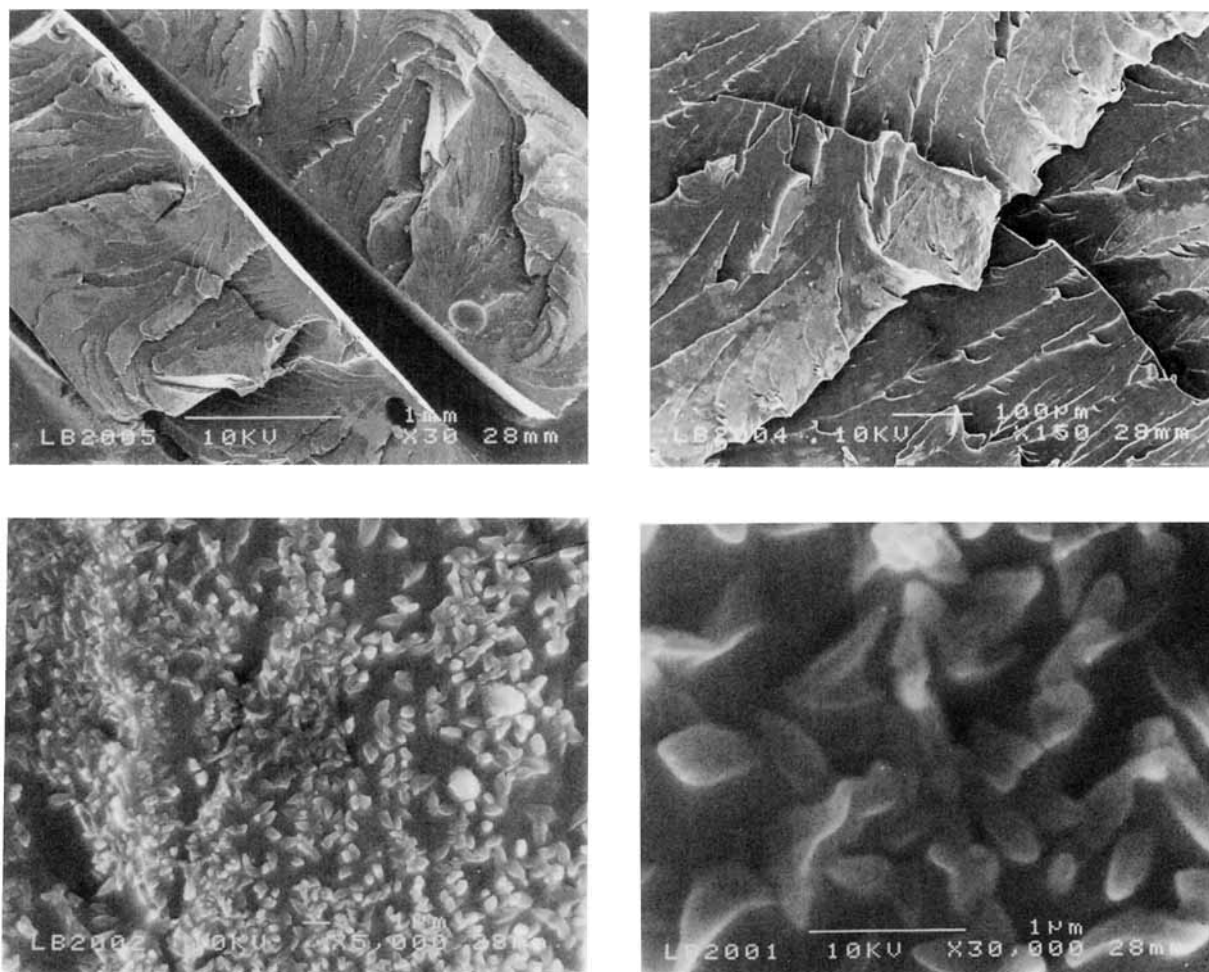
**Figure 9** First- and second-heat DSC glass transition behavior for 50/50 vernonia-sebacic polyester network/PET semi-IPNs made at different temperatures. When the vernonia network is formed at 160°C, the data of (A) is produced, while with network formation at 250°C, above the crystallization point of PET, (B) results.

graphs. The two-phase material synthesized at 160°C, depicted in Figure 10, had a macroscopically rough surface, and the intermediate magnification micrographs have features resembling those of craze bands.<sup>46</sup> At the lower magnification, the material synthesized at 250°C, depicted in Figure 11, appears very smooth by comparison. However, when looking at much higher magnification, the same features are observed in both materials, in which fibrillar structures on the order of several micrometers jut out from the surface. Similar fibrillar structures were found on both fracture surfaces, suggesting that their pullout and fracture is an important part of the fracture mechanism. Returning to the lower mag-

nification micrographs, light and dark gray areas are observed; the light gray areas are filled with the microfibrils, while the dark gray areas are very smooth even at high magnifications. The light and dark gray areas are nearly equally distributed and roughly in the same proportions for both materials.

## DISCUSSION

For the vernonia/PET semi-IPNs where the reaction time at 300°C was varied, the data presented in Table I may be interpreted in terms of the amount of copolymer that has formed as a result of the high-

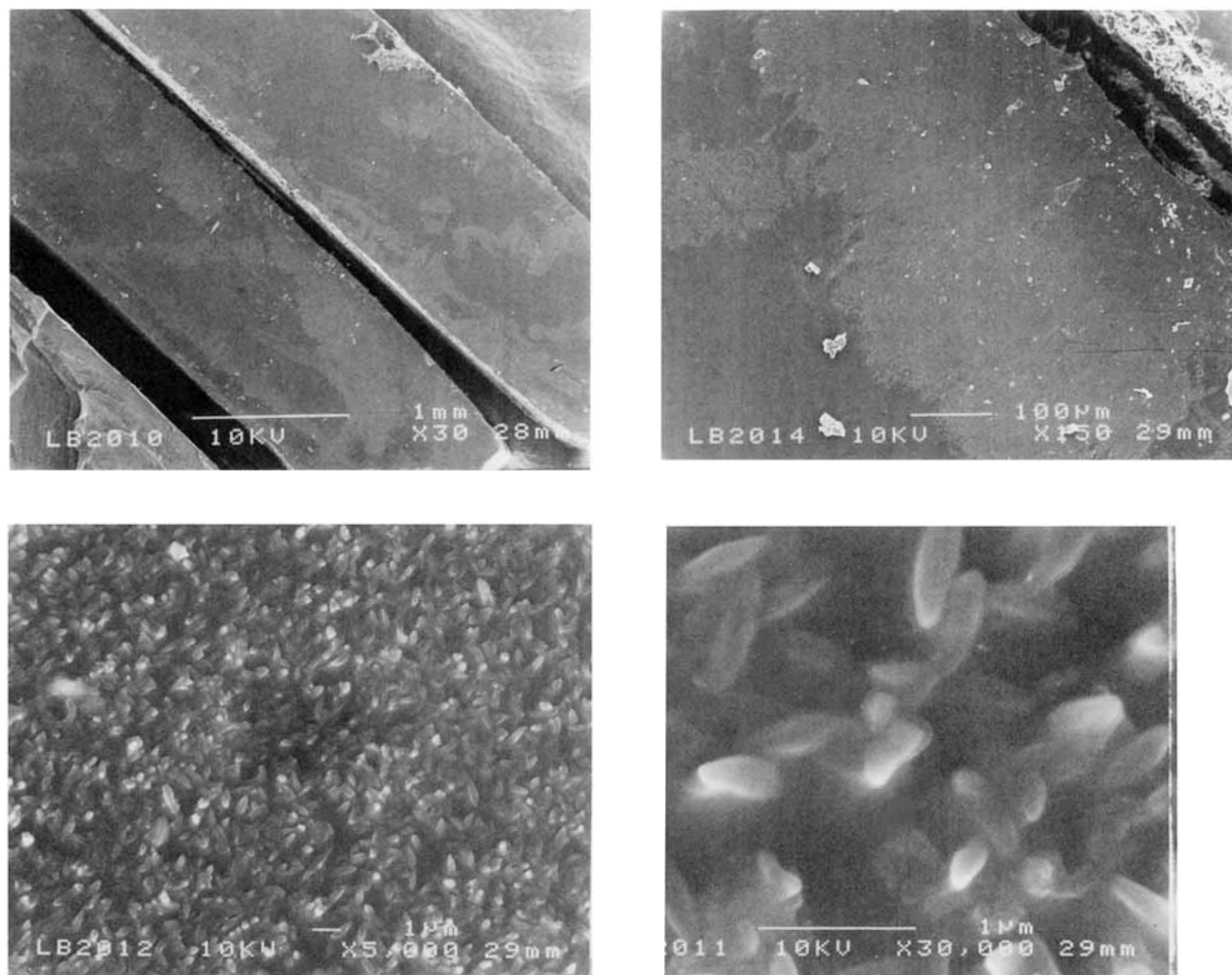


**Figure 10** Scanning electron micrographs of room-temperature tensile fracture surfaces for 50/50 PET/vernonia-sebacic polyester semi-IPN synthesized at 160°C. From top left moving clockwise, magnifications for original 4 × 5 in. prints are 30, 150, 5000, and 30,000 times.

temperature exposure. The glass transitions are of particular interest, as they are a measure of the composition of the two phases present upon phase separation after synthesis. With no further reaction time at 300°C beyond that required to bring about miscibility, only enough copolymer forms to ensure miscibility at 300°C, and upon cooling, two phases separate that are composed of fairly pure vernonia-sebacic polyester (lower-temperature phase  $T_{g1V}$ ) = -37°C, while pure vernonia-sebacic polyester has  $T_g$  = -40°C) and a PET/vernonia copolymer phase with  $T_{g1P}$  = 36°C (pure PET has  $T_g$  = 77°C). Using the Fox equation, the PET/vernonia phase is calculated to be about 85% PET and 15% vernonia oil, which is substantially the same composition of the PET-rich phase encountered in similar work with

castor oil.<sup>15,16</sup> With longer mixing times at 300°C, the PET-rich phase glass transition temperature, and thus composition, remains essentially constant, while that of the vernonia polyester phase increases in temperature. Thus, as greater amounts of copolymer are formed, upon cooling, more copolymer mixes with the vernonia polyester phase, so that both phases end up being composed of copolymer.

On the second DSC heating scans, where the material had been heated to 300°C and then cooled, the peak of the single, broad  $T_g$  is seen to rise slightly in temperature with time held at 300°C (Table I) or with total PET content (Table II and Fig. 5). Both of these trends are due to the amount and composition of the copolymer formed and the morphological effect of the finely dispersed phase do-

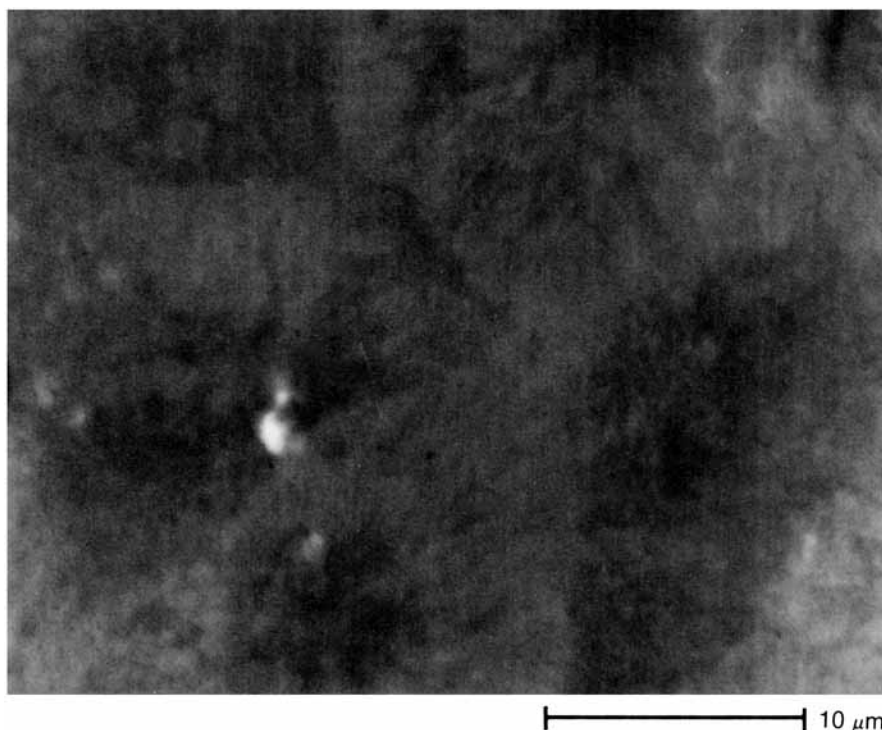


**Figure 11** Scanning electron micrographs of room-temperature tensile fracture surfaces for 50/50 PET/vernonia-sebacic polyester semi-IPN synthesized at 250°C. From top left moving clockwise, magnifications for original 4 × 5 in. prints are 30, 150, 5000, and 30,000 times.

mains. For longer reaction times at 300°C, greater amounts of copolymer are formed, which shifts the dominant vernonia polyester glass transition upward toward that of PET. As more PET is added, the copolymer formed has higher PET content, shifting the glass transition upward in temperature. The effect of microheterogeneous morphology is to create a wide spectrum of composition due to the mixed interphase, thus broadening the glass transition to cover the range between that of the components, leaving the peak of the broad transition to follow roughly the Fox and Couchman miscible blend/copolymer equations.

The semi-IPNs display two glass transitions when synthesized at 160°C, then only a single transition

after heating above the PET melting point and cooling, which raises some interesting questions: Is the single glass transition morphology thermally stable, and if so, why do two phases form upon synthesis? In attempting to answer these questions, the materials already heated and cooled to create a single  $T_g$  were again heated above the PET melting temperature to 250°C, held for 1 h, then cooled and maintained at 160°C for 18 h, just the same as when the original materials were synthesized. After this heat treatment, the glass transition curves were essentially unchanged from the second heat scans previously shown in Figure 4(B). Thus, the morphology changes rapidly on the first heating above the PET melting point to form microheterogeneous,



**Figure 12** Transmission electron micrograph of 50/50 PET/castor oil polyurethane network semi-IPN, stained with both  $\text{RuO}_4$  and  $\text{OsO}_4$ .

single- $T_g$  material, which is very stable upon further heat treatment. During network synthesis at  $160^\circ\text{C}$ , the PET is able to crystallize and phase separate long before the vernonia network reaches gelation. After the network is completely formed, if the PET is melted, it has a much harder time crystallizing upon cooling. Because of the PET crystallizing before network formation, the more stable microheterogeneous morphology of the semi-IPN cannot form until the network is formed and PET crystals are subsequently melted.

In the case of castor oil urethane network/PET semi-IPNs, the urethane network formation reaction is very rapid.<sup>15,16</sup> In this case, although the chemical structures involved are not very different, an important difference is that the castor oil urethane network gels nearly simultaneously with PET crystallization. A transmission electron micrograph of a 50/50 castor urethane network/PET semi-IPN is shown in Figure 12. The spherulite structure should be compared with that of the vernonia/PET semi-IPN shown in Figure 8. The vernonia/PET spherulites observed were much more regularly shaped, not much different than that observed in crystallization of a homopolymer,<sup>42</sup> while the castor/PET material has oblong spherulites and bent crys-

talline fronts. Also, unlike the vernonia semi-IPNs made at  $160^\circ\text{C}$ , these castor semi-IPNs were microheterogeneous as synthesized. Whether the crystals form before or during network formation apparently has a dramatic effect upon morphology.

When the vernonia network is completely formed in the miscible mixture at  $250^\circ\text{C}$ , above the crystallization temperature of PET, a material with single glass transition temperature, as depicted in Figure 9(B), is produced. In addition to the single  $T_g$ , no PET crystallinity was observed in this material by DSC. It is not completely clear whether the lack of PET crystallinity is due to excessive formation of interchange copolymer while held at  $250^\circ\text{C}$  or the fact that the vernonia network was completely formed while the materials were miscible. The fairly slow rate of bond interchange and the presence of PET crystallinity in uncross-linked material interchanged for longer periods strongly suggests the latter.<sup>10</sup>

Thus, when PET crystallization precedes cross-linking, nearly normal crystallinity develops along with macrophase separation, and when crystallization and cross-linking occur simultaneously, the PET crystalline spherulite structure is disrupted and microheterogeneous morphology develops. However,

when cross-linking is completed in a miscible mixture above the crystallization temperature, both phase separation and crystallization are almost completely inhibited.

The fracture surfaces observed under the SEM that compare the single- $T_g$  50/50 semi-IPN to the similar two-phase material are rather unusual, making them quite interesting (Figs. 10 and 11). The microfibrils may be the remainder of craze fibrils fractured during discontinuous crack growth, as they appear very similar to the fibril structures observed in the fatigue fracture of poly(vinyl chloride),<sup>47</sup> only three or four times larger in diameter. Discontinuous crack growth occurs when the craze damage is created prior to the crack propagating through the crazed region and is more common to cyclical loading fatigue fracture, where the crazes are formed over several load cycles before the crack rapidly runs through the damaged region.<sup>46</sup> In the present case, where the specimen was fractured under slowly increasing tensile stress, the craze fibrils would have had to form within the bulk of the material before the rupturing crack propagated through. Alternatively, the fibrils may be the remains of glassy phase domains that were pulled out from the rubbery matrix material and did not relax. Both materials form these microscopic fibrils, but the two-phase semi-IPN had a glassy phase, resulting in a macroscopically rough fracture surface, while the material with the single glass transition below room temperature remains rubbery during fracture, leaving a macroscopically smooth surface. Normally, a rubbery material should not form crazes; however, the breadth of the single glass transition [Fig. 9(B)] does not exclude the possibility of microphase separation, with glassy material leading to the microscopic fibrils.

The importance in sequence of gelation, crystallization, and phase separation cannot be overemphasized. In the 50/50 PET/vernonia semi-IPN synthesized after PET had crystallized, two phases were present, spherulites were very regular, and toughness was not very high. The similar 50/50 PET/castor urethane semi-IPN has more finely distributed, microheterogeneous phase domains<sup>15,16</sup> and irregularly shaped PET spherulites and greater toughness. When the vernonia network is completely formed while the PET and oil are miscible, above the crystallization temperature of PET, the two phases are so finely divided that the resulting material is microheterogeneous, bordering on single-phase, noncrystalline, and much tougher than any of the other PET/triglyceride oil network semi-IPNs.

## CONCLUSIONS

Semi-interpenetrating polymer networks were prepared with linear poly(ethylene terephthalate) and vernonia-sebacic polyester network. The toughness, as measured by the area under the tensile stress-strain curve of the semi-IPNs, was much greater than that of their constituent materials. The materials are two-phase when the network is synthesized at 160°C, below the crystallization temperature of PET, but form a microheterogeneous phase structure when heated above the PET melting temperature before the vernonia-sebacic polyester network is completely gelled. By contrast, when the vernonia network is formed above the crystallization temperature of PET in a miscible state, the resulting material had a single glass transition, was noncrystalline, and was much more rubbery and tough. In these semicrystalline semi-IPNs, whether the network is formed before or after crystallization and/or phase separation affects the crystalline and phase morphology considerably, which, in turn, is reflected in the physical properties of the resulting material. The amount of bond interchange that occurs and the sequence and kinetics of crystallization, cross-linking, and phase separation are factors that may be utilized to control the morphology and properties of materials in this and similar polymer systems.

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