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Thermal degradation of polymer blends containing the poly(hydryoxy ether of Bisphenol-A)

Joseph S. Formosa

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THERMAL DEGRADATION OF POLYMER BLENDS CONTAINING
THE POLY(HYDROXY ETHER OF BISPHENOL-A)

by

Joseph S. Formosa

May, 1987

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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AKNOWLEDGEMENT

I would like to thank Pamela Marie for all her patience and support. I would also like to thank my advisor, Dr. Moskala, and the members of my research committee, Dr. Takacs, Dr. Tubbs, and Dr. Hornak for the guidance they provided.
ABSTRACT

The thermal degradation of blends of phenoxy with polycaprolactone, poly(1,4-butylene adipate), poly(1,4-cyclohexane-dimethylene succinate), poly(2,2-dimethyl-1,3-propylene succinate), and poly(hexamethylene sebacate) has been studied using thermogravimetric analysis, direct-pyrolysis mass spectrometry, and infrared spectroscopy. For each blend, the polyester component was less thermally stable in the blend compared to the pure state. The thermal stability of the phenoxy was not affected by the presence of the polyesters in the blends.

Blends of phenoxy with polycaprolactone and with poly (1,4-butylene adipate) degrade in two-step mechanisms where the amount of weight loss of each step was proportional to the composition of the blends. Direct-pyrolysis mass spectrometric analysis showed larger amounts of monomeric caprolactone evolved from polycaprolactone in the blend compared to pure polycaprolactone. Activation energies were calculated for these phenoxy/polyester blends from the thermogravimetric analysis data using the Flynn-Wall method. Mechanisms are presented in explanation of the observed destabilization of the polyesters.
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ABBREVIATIONS

Tg- glass transition temperature
PS- polystryrene
PPO - poly(2,6-dimethyl-1,4-phenylene oxide)
TGA- thermogravimetric analysis
GC/MS- gas chromatography/mass spectrometry
Ea- activation energy
C- conversion
T- temperature
R- universal gas constant
HH-PS- head-to-head polystyrene
HT-PS- head-to-tail polystyrene
PMMA- poly(methyl methacrylate)
TVA- thermovolatilization analysis
PVA- poly(vinyl acetate)
PVC- poly(vinyl chloride)
PAR- polyarylate
PET- poly(ethylene terephthalate)
PP- polypropylene
PE- polyethylene
PVDC- poly(vinylidene chloride)
PAN- polyacrylonitrile
Phenoxy- poly(hydroxy ether of bisphenol-A)
PBT- poly(butylene terephthalate)
PEO- poly(ethylene oxide)
PVME- poly(vinyl methyl ether)
PHT- poly(hexamethylene terephthalate)
PCL- polycaprolactone
PBA- poly(butylene adipate)
PEA- poly(ethylene adipate)
PDPS- poly(2,2-dimethyl-1,3-propylene succinate)
PDPA- poly(2,2-dimethyl-1,3-propylene adipate)
PCDS- poly(1,4-cyclohexane-dimethanol succinate)
LCST- lower critical solution temperature
THF- tetrahydrofuran
DMF- dimethylformamide
DSC- differential scanning calorimetry
DP-MS- direct pyrolysis-mass spectrometry
A- Arrhenius pre-exponential constant
B- heating rate
Tmax- temperature of maximum rate of weight loss
P- pressure
mm HG- millimeters of Mercury
EI- electron impact
CI- chemical impact
m/z- mass to charge ratio
TIC- total ion chromatograph
PHS- poly(hexamethylene sebacate)
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1.0 INTRODUCTION

A polymer blend is a physical mixture of two or more polymers. Blends may be either miscible with the polymer chains mixed at a molecular level or immiscible where the polymers segregate into distinct phases. One criterion for miscibility of a polymer blend is whether a sample of that blend is clear. Samples of a miscible polymer blend will be clear films whereas samples of immiscible blends will be cloudy assuming, the refractive indices of the blend components are different. Another criterion for a miscible blend is that it will have a single glass transition temperature (Tg). The Tg of a miscible blend will depend upon the composition of the blend components according to the Fox equation (1). An immiscible blend will generally have two distinct Tg's corresponding to the Tg's of the components. In the event that the components have Tg's which are similar, it will be difficult to resolve the Tg of the blend, as a result, a different criterion must be used to determine miscibility of the blend. For a blend with a crystallizable polymer, melting point depression can be used to determine the compatibility of the blend.

Since the introduction in the 1960's of the first important commercial polymer blend, an impact modified version of nylon 6/6, the consumption of blends has grown
at a tremendous rate (2). "Of the approximately 2.5 billion-pound annual consumption of engineering polymers, at least 15 to 20 per cent is currently thought to be composed of alloys and blends" (2). Experts predict this number will double or even triple in the next ten years. Polymers and their blends are typically processed in the melt. As a result, the thermal stability of such materials is of primary importance.

Studies of the thermal degradation of polymer blends are relatively few and those concerning miscible blends are rare. This is understandable as most polymer blends are immiscible due to the thermodynamics required for a blend to be miscible. In order for a system to be miscible the free energy of mixing (ΔG) must be negative.

\[ ΔG = ΔH - T(ΔS) \]

Due to the size of polymers, the gain in entropy (ΔS) due to mixing is very small. Therefore, for a blend to be miscible, an exothermic change in enthalpy (ΔH) must occur. Usually, this is through some intermolecular forces of attraction such as hydrogen bonding or dipole-dipole interactions.

The thermal degradation of miscible and immiscible polymer blends containing phenoxy and various polyesters has been studied. Similar studies are discussed in an effort to draw conclusions based on earlier reported experiments.
1.1 Thermal Degradation of Polymer Blends

The thermal degradation of polymer blends has been studied by a variety of analytical techniques including thermogravimetric analysis, direct pyrolysis-mass spectrometry, and thermovolatilization analysis (3-17). The aim of these studies was to determine the effect blending has on the thermal stability of the blend components. In some blends, neither component showed any change in thermal stability as a result of blending. In others, some polymers showed signs of decreased thermal stability when in a blend. And other polymers were observed to be stabilized by the presence of a second polymer.

For reasons already mentioned, the bulk of the literature concerning the thermal degradation of polymer blends deals with immiscible blend systems. Any changes in the thermal degradation of a polymer in an immiscible system must be the result of either a reaction at the phase boundary involving polymer segments or long chain radicals or a result of a reaction involving small molecular or radical species formed in one phase which diffuse into the other. As the polymers in a miscible blend are in close contact with each other, there is no need for diffusion of reactive species to occur in order for the blend components to interact. Therefore, it is expected that any changes in the thermal stability of blend components would be greater in miscible blends.
One example of a miscible polymer blend whose thermal degradation has been studied is that of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with polystyrene (PS). Jachowicz and co-workers used thermogravimetric analysis (TGA) to study the degradation of this blend and mass spectrometry with gas chromatography (GC/MS) to study the volatiles of the decomposition (3). These workers determined that PPO was more stable than PS and small amounts of PPO resulted in an increase in thermal stability of the PS in the blend. Figure 1 shows the thermograms of PPO, PS and the blends in different compositions. The blends appear to be of intermediate stability of the two pure polymers. The thermogravimetric curves represent data taken at a programmed heating rate of 10°C/min. It was observed through the analysis of the volatiles with GC/MS that the PS does not affect the degradation mechanism of PPO, thereby not affecting the shape of the TGA curve. The reverse is not true. The TGA study and the GC/MS point out that PPO changes the degradation mechanism of PS. The PPO does not alter the depropagation step, production of styrene, but due to its labile protons, PPO reduces the amount of intramolecular transfer reactions which occurs (3).

The activation energies (Ea) of these blends were
Figure 1. Nonisothermal thermogravimetric curves (Heating rate 10°C/min) of PS, PPO and PPO-PS blends. (Reproduced from reference 3).
calculated using the Freeman-Carroll method (4). This method uses the equation

\[-\frac{\log(dC/dT)}{\Delta \log(1-C)} = \frac{Ea(\Delta l/T)}{2.3R(\Delta \log(1-C))} - n\]

where C, degree of conversion, is defined as active weight remaining divided by the final weight for a given weight loss event, T is the absolute temperature, R is the gas constant, dC/dT represents the rate of weight loss at T, and n is the apparent order of reaction. These calculated values were compared to that of a graft co-polymer of PPO and PS. Due to the similarity of these values, it was concluded that the physical structure of PPO/PS mixtures has no effect on the kinetics of their decomposition. In these blends and copolymers, the Ea's of the blends were lower than was expected based on an additivity of the Ea's of the pure polymers. This is further evidence of destabilization of the blend components.

Jachowicz and co-workers complemented this work with analysis of the miscible blend of PPO with head-to-head (HH) PS (5). It is reported that HH-PS undergoes statistical scission at the C-C bond which the adjacent phenyl groups have caused to be weakened (6). This differs from conventional head-to-tail (HT) PS which is reported to decompose in a stepwise fashion after
abstraction of a hydrogen as shown below.

\[ \text{CH}_2\text{C}-\text{CH}_2\text{CH}-\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{=CH} + \text{CH}_2\text{C}-\text{CH}_2\text{CH}_2 \]

\[ \text{CH}_2\text{C}-\text{CH}_2\text{=CH}_2 + \cdot \text{CH}-\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{=CH}_2 + \cdot \text{CH}-\text{CH}_2\text{CH}_2 \]

Reaction I represents a form of propagation. The depropagation center is reproduced with formation of mobile, low molecular weight inactive products. Reaction II is first order termination. It results in the formation of low molecular weight radicals and a deactivated polymer chain ends. Reaction medium controls which reaction is favored. In pure PS, reaction I dominates. In environments with labile protons, as in blends with PPO, reaction II predominates.

Due to the differences in degradation mechanism, the thermal stability of HH-PS was unaffected by the PPO in the blend, unlike HT-PS. In fact, there was evidence of destabilization of PPO in the presence of PS. To date, this is the only reported study concerning the thermal degradation reactions of a miscible polymer blend.
1.1.1 Thermal Degradation of Immiscible Polymer Blends

Of the reported literature concerning the thermal degradation of immiscible polymer blends, most of the work has been produced by a team led by I.C. McNeil. Table I lists several immiscible blends studied by McNeil and co-workers. For review, several of these immiscible blend systems will be discussed which are representative of the different types of behavior observed for the thermal degradation of polymer blends.

The blend of polystyrene (PS) with poly(methyl methacrylate) (PMMA) is an immiscible blend whose thermal degradation behavior showed no evidence for interaction leading to either increased or decreased thermal stability (7). The thermal stability of both polymers has been extensively studied (8,9). McNeil used a technique called thermovolatilization analysis (TVA) to study this and other blends. TVA is similar to TGA in that the polymer samples are heated in an oven to degrade the sample, but in a TVA study, the pressure of the volatiles of the thermal degradation are measured. A TVA curve is a plot of Pirani output (pressure gauge) versus temperature or time. All work was performed under nitrogen to avoid oxidative degradation. The TVA data and product analysis by gas-liquid chromatography led to the conclusion that the polymers in this blend decompose
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<td>AMS monomer evolved at lower temperatures. HCL production retarded.</td>
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<td>PS monomer evolution retarded slightly. Evolution of acetic acid also retarded.</td>
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in the same manner as in the pure state.

A second blend involving PS exhibited evidence of a stabilizing affect of blending two polymers. In the blend of PS with poly(vinyl acetate) (PVA) both polymers showed signs of increased thermal stability (11). Again, TVA was used and the degradation of the 50/50 weight % blend was compared to the behavior of a sample of PS and PVA in the unmixed state. Deacetylation of PVA was delayed slightly as was production of styrene monomer. The radicals formed during the PS decomposition reacted readily with the polyene chain formed during the PVA degradation which resulted in delayed evidence of weight loss. This was confirmed by decomposing PS in the presence of the residue of the degradation of PVA. The polyene residue of PVA has the same stabilizing affect on PS.

In the blend of PVA with PVC, both polymers showed signs of destabilization (12). Hydrogen chloride, a degradation product of PVC is believed to catalyze the deacetylation process in PVA. Acetic acid is also thought to catalyze the dehydrochlorination of PVC, but not as noticeably. Figure 2 shows the TGA curves recorded at 5°C/min in a nitrogen atmosphere for the two pure polymers and for the 50/50 weight % blend. The second set of curves shows the experimental TGA curve which was expected based on the curves of PVC and PVA. The lower thermal stability in the first step represents early
Figure 2. TGA curves for (a) PVC and PVA, and (b) comparison of expected and observed behavior of a 1/1 mixture of the polymers. Samples as 10 mg powders, degraded at 5°C/min under dynamic nitrogen atmosphere. (Reproduced from reference 11).
evolution of both acetic acid and hydrogen chloride. This behavior was confirmed by an experiment where PVA was degraded in an atmosphere of HCl. The results confirmed the hypothesis that volatiles of the PVC decomposition, namely HCl, diffused into the region of PVA and destabilized the polymer.

The papers mentioned are significant for the qualitative results observed, however, the thermal degradation of immiscible polymer blends have also been studied quantitatively. Calahorra and co-workers studied the immiscible blend of polyarylate (PAr) and poly(ethylene terephtalate) (PET) using TGA (13). Using the Freeman-Carroll method discussed previously, the activation energies of the pure polymers and the blends in different compositions were calculated. Measurements of the activation energies showed that at low PAr concentration, there was a slight stabilization of the blend. However, when the PAr content exceeded 30%, both polymers in the blend exhibited destabilization.

Mucha and Kryszewski also used this same method to determine the activation energy of two immiscible blend systems (14). The blends of polypropylene (PP) with polyethylene (PE) showed signs of increased stability when the activation energies for the blends were compared to that of the pure polymers. PP appears more thermally stable when blended with PE because steric repulsion
between methyl groups in neighboring PP chains is reduced. Blends of poly(vinylidene chloride) (PVDC) with polyacrylonitrile (PAN) appeared less stable compared to the blend components. The presence of nitrile groups from PAN catalyze the dehydrochlorination of PVDC in a manner reminiscent of the PVA/PVC blends.
1.2 Miscibility of Phenoxy/Polyester Blends

The poly(hydroxy ether of bisphenol-A) (phenoxy) has been shown to be miscible with a broad range of polymers (15). Most of these polymers represent polymers which act as proton acceptors as phenoxy exhibits proton donor characteristics when interacting with a second polymer. Phenoxy is a tough, high modulus material with relatively high thermal stability. It is commonly used as a coating, adhesive, and packaging material (16). The repeat unit for phenoxy is shown where \( n \) commonly has a value of 100.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{CH}_{2}\text{O}
\end{array}
\]

Several workers have observed a single \( T_g \) for blends of phenoxy with polymers such as poly(butylene terephthalate) (PBT), poly(ethylene oxide) (PEO), poly(vinyl methyl ether) (PVME), and poly(hexamethylene terephthalate) (PHT), polycaprolactone (PCL), poly(1,4-butylene adipate) (PBA), poly(ethylene adipate) (PEA), poly(2,2-dimethyl-1,3-propylene succinate) (PDPS), poly(2,2-dimethyl-1-3-propylene adipate) (PDPA), and poly(1,4-cyclohexane-dimethanol succinate) (PCDS) (17). Specific intermolecular interactions have been identified between the components of blends phenoxy with PCL. Infrared spectroscopy has shown hydrogen bonding exists between the phenoxy
hydroxyl group and the PCL ester group (18). A second paper also discussed the formation of hydrogen bonding as being responsible for the exothermic interactions and hence miscibility in blends of phenoxy with PBA, PEA, PDPS, PDPA, and PCDS (19).

The potential for interactions leading to hydrogen bonding is not always sufficient to insure miscibility. An example of this is phenoxy with poly(ethylene terephthalate) (PET) (17). It was found that PET was incompatible with phenoxy over the entire composition range. This was the case in several other polyesters studied in blends with phenoxy (19,20). In some blends, it was determined that factors such as structural shielding effects or the stereo-configuration of the polymer prevented miscibility. Therefore, the potential for intermolecular interactions does not necessarily ensure miscibility. Figure 3 shows a plot of the Flory blend interaction parameter versus the number of aliphatic carbons per ester linkage in the polyester structure as determined by Paul and co-workers (19). The Flory interaction parameter was calculated from the melting point depression of the crystallizable component in the blend (i.e. polyesters). As Figure 3 illustrates, there is a range outside of which lie polyesters which are immiscible with phenoxy despite the hydrogen bonding contribution.
Figure 3. Blend interaction parameter as a function of the number of aliphatic carbons per ester linkage in the polyester structure.
(Reproduced from reference 19).
Many miscible blends exhibit a lower critical solution temperature (LCST). This is evident by the blend becoming cloudy at elevated temperatures due to the segregation of the components of the blend. The blends phenoxy with PDPS and PDPA exhibit an LCST. Some speculate that many blends which have been studied may in fact have an LCST beyond the temperature at which thermal stability becomes a factor (21). An example of this is the blend of polycarbonate (PC) with PCL (22). LCST's were observed for these blends but were very close to the temperature at which PCL begins to degrade. For phenoxy PCL blends, no LCST has been detected.

In blends of phenoxy with polyesters, because of the structure of the blend components, the potential exists for transesterification. Transesterification has been observed in two phenoxy/polyester blends, phenoxy/PBT and phenoxy/PCDS (23,19). At elevated temperatures, the following generalized reaction occurred in both blends.

\[
\text{R-C-OR'} + \text{H-OR}'' \rightarrow \text{R-C-OR}'' + \text{H-OR}'
\]

For phenoxy/PBT, a temperature of 250°C was required for transesterification to occur in addition to mixing in a Brabender mixer. For phenoxy/PCDS, static conditions at 160°C for 24 hours resulted in transesterification. This reaction was evident by an increase in relative viscosity.
2.0 OBJECTIVES

Polymers and their blends are often processed in the melt. Therefore, the thermal stability of these materials is very important. When these materials decompose, a loss of desired mechanical properties may result which could make the material inappropriate for the end use application. Blends of phenoxy with these polyesters may result in new material systems with the desirable properties of the components. Therefore, it is important to know how blending affects the thermal stability of the components.

The phase behavior of these blends has been extensively studied in papers previously reviewed (15-24). It was important to determine whether the factors of hydrogen bonding, miscibility, transesterification, and phase separation will affect the thermal stability of these blends. As has been discussed, immiscible blend components can interact with a resulting change in the thermal stability of the components, it was of interest to determine if these effects were more pronounced in miscible polymer blends. As opposed to immiscible blends, the effects due to diffusion of reactive species or reactions occurring at phase boundaries are less important in miscible blends. As the polymer segments are physically closer to each other, it seems possible that any changes in thermal stability would be more pronounced in these blends.
3.0 EXPERIMENTAL

3.1 Materials

The polymers and their repeat units that were studied are shown in Table II. This table also shows the abbreviation of each polymer studied, the inherent viscosity, and molecular weight where possible. The PCL used in this study was donated by Union Carbide Corporation and was a high molecular weight thermoplastic resin designated PCL-700. Phenoxy resin and the other polyesters were purchased from Aldrich Chemical company.
TABLE II
Structures of Polymers Included in This Study

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<thead>
<tr>
<th>POLYMERS (ABBREVIATION)</th>
<th>REPEAT UNITS</th>
<th>INHERENT VISCOSITY</th>
<th>MOLECULAR WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(hydroxy ether of bisphenol-A) (phenoxy)</td>
<td>- CH₃-C-C(CH₂OH)_₂-CH₂CH₂O-</td>
<td>0.36</td>
<td>30,000</td>
</tr>
<tr>
<td>Poly(caprolactone) (PCL)</td>
<td>-CH₂CH₂CH₂CH₂CH₂C-0-</td>
<td>0.56</td>
<td>40,000</td>
</tr>
<tr>
<td>Poly(1,4-butylene adipate) (PBA)</td>
<td>-(-CH₂)₄-O-C-(-CH₂)₄-C-0-</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Poly(1,4-cyclohexane dimethanol succinate) (PCDS)</td>
<td>-CH₂-S-C-CH₂O-C-(-CH₂)₂-C-0-</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>Poly(2,2-dimethyl-1,3-propylene succinate) (PDPS)</td>
<td>-CH₂-C-CH₂O-C-(-CH₂)₂-C-0-</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Poly(hexamethylene sebacate) (PHS)</td>
<td>-(-CH₂)₆-O-C-(-CH₂)₈-C-0-</td>
<td>0.16</td>
<td>-</td>
</tr>
</tbody>
</table>

1 concentration = 0.5 g/dL, inherent viscosity ± 0.05

a chloroform, 25°C
b benzene, 30°C
c benzene, 25°C
d unspecified molecular weight, as reported by manufacturer
3.2 Sample preparation

Films of the pure polymers and the blends were prepared by solution casting from a common solvent. Solutions of phenoxy and PCL, PBA, PDPS, and PHS were prepared (1% w/v) and combined, with stirring, in volume ratios to obtain the desired blend compositions. Films of these phenoxy/polyester blends were cast at room temperature from tetrahydrofuran (THF). The blend solutions were poured into petri dishes. After the majority of the THF had evaporated, the films were placed in a vacuum oven for 24 hours at 70°C to remove residual solvent.

The blends containing PCDS were prepared following a procedure discussed by Barlow and co-workers (19). This involved casting the films near the melting temperature to prevent phase segregation due to crystallization during the solvent evaporation stage. For these systems, the higher boiling dimethylformamide, DMF, was used as the solvent. Initial drying was carried out at 130°C and the final drying in a vacuum oven at 100°C for 24 hours.

Films cast on KBr windows for analysis via infrared spectroscopy were prepared in the same manner as the sample films prepared for the thermogravimetric analysis. Solutions of the polymers or the blends were used to coat KBr windows and the solvent evaporated.
3.3 Instrumentation

The thermogravimetric analysis, TGA, was performed on a Perkin-Elmer TGS-2 system under a dynamic nitrogen atmosphere (40 ml/min). The degradation studies were performed at heating rates of 0.5°C/min, 1°C/min, 5°C/min, 10°C/min, 20°C/min and 40°C/min. Sample weights were between 3 and 5 mg. Differential scanning calorimetry, DSC, was also used to study these degradation processes. A Perkin-Elmer DSC-4 system was used with a modified flow cap. The purge gas was nitrogen at a flow rate of 40 psi, which is the flow rate commonly used for DSC degradation analysis. A heating rate of 1°C/min was used and sample sizes ranged from 15 to 20 mg.

The degradation products were also studied using direct-pyrolysis mass spectrometry, DP-MS. Samples were inserted directly into the ionization chamber and heated from 100°C to 350°C at 0.5°C/min. The instrument, a Hewlett-Packard GC/MS #5996 was limited to a maximum oven temperature of 350°C. Electron impact ionization spectra were collected at a reduced electron voltage setting of 18 eV.

Polymer and polymer blend samples were heated in the TGA oven to various temperatures. The residues remaining after a sample was partially degraded were analyzed by infrared spectroscopy. The residues were
removed from the sample pans by dissolving them in THF. The resulting THF solutions were used to cast films on KBr salt windows. A Perkin-Elmer 680 spectrophotometer was used to record the infrared spectrum from 4000 to 600 cm$^{-1}$.

Inherent viscosities of the polymers were obtained using a Ubbelohde viscometer (No. 1, A558, 0.01 centistroke/second). The concentrations of the solutions were 0.5 g/dL. The solvents and temperatures used for each polymer are indicated in Table II.
4.0 RESULTS AND DISCUSSION

4.1 Phenoxy/Polycaprolactone Blends

4.1.1 Thermogravimetric Analysis

Figure 4 shows the TGA curves for phenoxy and for PCL recorded at a heating rate of 1°C/min, where (1-C) is plotted versus temperature with C, conversion, defined as the active weight remaining divided by the final weight for a given weight loss event. The derivatives of these curves, also shown, indicate that both polymers degrade in a single step. Phenoxy is known as a thermally stable polymer and PCL is only slightly less stable. After TGA curves were obtained at several heating rates, the activation energies of the thermal degradation of phenoxy and of PCL were calculated. According to the Flynn-Wall method for calculating activation energies from thermograms recorded at constant heating rates, the rate of conversion is

\[
d\frac{C}{dt} = \frac{A}{B} f(C) e(-E_a/RT)
\]

where B is the heating rate, A is the Arrhenius pre-exponential constant, E_a is the activation energy and f(C) is a function of degree of conversion (24). At a constant degree of conversion

\[
d \log(B)/d(1/T) = (0.457/R)E_a
\]

or

\[
\Delta \log(B)/\Delta(1/T) = (0.457/R)E_a
\]
Figure 4. TGA curves of pure phenoxy and PCL recorded at a heating rate of 1°C/min.
Therefore, the activation energy at a fixed C may be calculated by plotting log(B) vs. (1/T). These plots are shown in Figures 5 and 6 for phenoxy and PCL, respectively. For phenoxy, the apparent activation energy was 44 ± 2 kcal/mole and for PCL it was 31 ± 1.0 kcal/mole. The fact that these lines are parallel confirms the assumption that both polymers degrade by a mechanism which is independent of degree of conversion. Also, the lines are straight which means the process is not affected by changes in the heating rate.

Figure 7 shows the TGA curves recorded at a heating rate of 1°C/min for the pure polymers and the different blends. The blends appear to decrease in thermal stability with decreasing phenoxy content. All the blends degrade by a two step process. This is confirmed by the presence of two peaks in the derivatives of the TGA curves of the blends. Furthermore, the breaks in the TGA curves of the blends are proportional to the compositions of the blends. This lead to the supposition that the blend components decompose in a step-wise fashion with all the PCL degrading before the phenoxy begins to degrade. If this is true, the compositions of the blends can be calculated, from the TGA data, using the areas of the derivative curves. These values are presented in Table III.

Table III also contains the temperatures at which the thermal decomposition is a maximum (Tmax) for each
Figure 5. Flynn-Wall plots for pure phenoxy.
Figure 6. Flynn-Wall plots for pure PCL.
Figure 7. TGA curves of phenoxy/PCL blends recorded at a heating rate of 1°C/min
TABLE III
Tmax, Activation Energies and Calculated Compositions of Phenoxy/PCL Blends.

<table>
<thead>
<tr>
<th>Phenoxy/PCL Calculated PCL phenoxy blend composition</th>
<th>Tmax(^1) (°C)</th>
<th>Ea(^2) kcal/mol</th>
<th>Tmax(^1) (°C)</th>
<th>Ea(^2) kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>---</td>
<td>---</td>
<td>395</td>
<td>44</td>
</tr>
<tr>
<td>80/20</td>
<td>77/23</td>
<td>350</td>
<td>28</td>
<td>396</td>
</tr>
<tr>
<td>65/35</td>
<td>68/32</td>
<td>345</td>
<td>27</td>
<td>395</td>
</tr>
<tr>
<td>50/50</td>
<td>56/44</td>
<td>326</td>
<td>26</td>
<td>395</td>
</tr>
<tr>
<td>35/65</td>
<td>34/66</td>
<td>318</td>
<td>23</td>
<td>394</td>
</tr>
<tr>
<td>20/80</td>
<td>22/78</td>
<td>317</td>
<td>21</td>
<td>392</td>
</tr>
<tr>
<td>10/90</td>
<td>11/89</td>
<td>282</td>
<td>12</td>
<td>348</td>
</tr>
<tr>
<td>0/100</td>
<td>---</td>
<td>379</td>
<td>31</td>
<td>---</td>
</tr>
</tbody>
</table>

1 From thermograms recorded at 1°C/min, Tmax ± 0.5°C.
2 Calculated via the Flynn-Wall method, Ea ± 3%. 
sample. This temperature was obtained from the point on the TGA curve where the derivative was at a maximum. These temperature values were confirmed by differential scanning calorimetry (DSC). Figure 8 shows the DSC curves for phenoxy, PCL and the 50/50 blend recorded at 10°C/min under nitrogen. The DSC data did not show any evidence for any reactions occurring prior to the thermal degradation. The destabilization of PCL in the blend was of the same order of magnitude (40°C) as was seen in the previous TGA analysis of the 50/50 phenoxy/PCL blend.

The Tmax values for the presumably PCL phenoxy fractions in the blends are compared to the phenoxy content in Figure 9. Based on this plot, it is clear that the PCL fraction is less thermally stable in the presence of phenoxy and this destabilization is a maximum in the 10/90 blend. Tmax of phenoxy is not significantly affected by the composition of the blend except in the blend containing 10% phenoxy. Phenoxy may degrade at lower temperatures in this blend simply because after the PCL has degraded only a small amount of sample remains (approx. 0.4 mg). It is well known that sample size will affect the appearance of a thermogram (25). A sample of phenoxy weighing 0.4 mg was degraded via TGA and was determined to have a Tmax value of 360°C.

The destabilization of the PCL fraction is seen more clearly in Figure 10. This shows the experimental
Figure 8. DSC data curves for degradation of: A) phenol, B) PCL, and C) 50 weight % blend recorded at 1°C/min under a dynamic nitrogen atmosphere.
Figure 9. Dependence of $T_{max}$ of each component in the blend on weight % phenoxy in the blend. (Heating rate was 1°C/min)
Figure 10. TGA curves for 50/50 phenoxy/PCL blend, A-experimental, B-expected. Heating rate was 1°C/min.
TGA curve for the 50/50 phenoxy/PCL blend and the curve which was expected based on an average of the thermal degradation of the two polymers. The second half of the two curves, the phenoxy region, compare very well. The PCL, however, is less stable in the experimental curve in comparison to the curve which was expected.

The activation energy for the 50/50 blend was calculated by the Flynn-Wall method. Conversions were chosen which would enable Ea values to be determined for the two degradation steps as well as the crossover region. The Arrhenius plot of this data is shown in Figure 11. The first two lines represent data for the degradation of phenoxy, the second two lines the crossover region, and the final two lines, the data for the degradation of PCL. The slope of the two lines in the crossover region change between the two conversion values as a result of a change in thermal degradation mechanism. The two lines corresponding to phenoxy degradation and the two lines corresponding to PCL degradation are parallel. This implies that the mechanisms for these two steps do not change between the two conversion values for each process.

The activation energies calculated for this and the other blends are presented in Table III. In each case, an error of approximately ±3% was calculated based on the deviation from linearity for each plot of log B.
Figure 11. Flynn-Wall plots for 50/50 phenoxyl/PCL blend.
versus $1/T$. Comparing these $E_a$ values to those obtained for the pure polymers by the same method supports the evidence that PCL is destabilized in the presence of phenoxy. The activation energies for the blend components follow the trend observed in Figure 9 pertaining to $T_{\text{max}}$ values of each component in the blends.

Several factors must be considered in determining the mechanism through which phenoxy destabilizes PCL. The fact that PCL is most destabilized in the blend with the lowest phenoxy content might be explained by the fact that phenoxy is a more viscous polymer. As a result, in the phenoxy rich blends, volatiles from the decomposition of PCL must diffuse through a more viscous environment before becoming evident as weight loss. It is possible that the PCL is destabilized to the same degree in each blend but the evidence is delayed due to the viscosity factor.

It has been proposed that PCL decomposes to the cyclic monomer upon heating via an intramolecular chain transfer process (26). As stated previously, hydrogen bonding exists between the ester group of PCL and the hydroxyl group of phenoxy in these blends. This interaction may enhance the depolymerization of PCL. Furthermore, it has been shown that polyesters and phenoxy can transesterify at high temperature. The chain scission of PCL may induce further depolymerization of PCL leading to an earlier production of volatile material.
4.1.2 Infrared Spectrometric Analysis

As stated, phenoxy/PCL blends have previously been studied by infrared spectroscopy (18). Here, it will be used to determine if the blends degrade in a step-by-step fashion as assumed. Figure 12 shows the spectra of PCL, phenoxy and a 50/50 blend. These spectra shown are for polymeric samples which were not heated in any manner. For PCL, the region of interest is the carbonyl region between 1800 and 1650 cm\(^{-1}\). For phenoxy, it is the hydroxyl region between 3800 and 3000 cm\(^{-1}\). In the spectrum of each pure polymer, the region of interest for the second blend component is free of absorbances. Therefore, it is possible to study changes which occur in these regions as a result of blending the polymers and as a result of the thermal degradation of the blends.

The spectrum of the blend appears to be a simple addition of the spectra of the components. One noticeable difference is a shifting of certain peak positions due to the hydrogen bonding between the phenoxy hydroxyl group and PCL carbonyl group. In pure phenoxy, the hydroxyl absorbance is 3446 cm\(^{-1}\) compared to 3491 cm\(^{-1}\) in the 50 wt% blend. Similarly, the absorbance due to the carbonyl group of PCL is shifted from 1736 cm\(^{-1}\) to 1731 cm\(^{-1}\) in the blend. In addition, the carbonyl absorbance of the blend is broader with a tail observed. This has
Figure 12. Infrared spectra of (A) PCL, (B) phenoxy, and (C) a 50/50 blend. Samples were unheated.
been studied and shown to be due to the hydrogen bonding.

To determine how the phenoxy/PCL blends decompose, samples of the polymers and the 50 wt% blend were heated to 375°C at 1°C/min. This is the temperature at which the 50 wt% blend has lost 50% of its original weight. Figure 13 shows the spectra of samples of phenoxy and the 50 wt% blend which were heated to 375°C at a heating rate of 1°C/min. Comparing the spectra of samples heated to 375°C to those unheated makes it possible to determine what is in the blend sample at this temperature.

There are several indications that the 50 wt% blend sample heated to 375°C now contains mostly phenoxy. The large absorbance due to the carbonyl group of PCL is greatly reduced. This loss of carbonyl absorbance implies a loss of PCL. Furthermore, the observed shift of the hydroxyl absorption in the blend is now less significant. The position of the absorption of the hydroxyl group of the partially degraded blend sample is nearly identical with the absorption of the hydroxyl group of the heated phenoxy sample. As mentioned, this shifting effect was due to hydrogen bonding between phenoxy and PCL. If the 50% weight loss was PCL decomposing, it seems likely that the effects due to hydrogen bonding would be lessened.

At 375°C, the blend had lost about 55% of its
Figure 13. Infrared spectra of (A) a 50/50 phenoxy/PCL blend and (B) phenoxy. Samples were heated to 375°C.
original weight and the phenoxy sample had lost around 10% of its original weight. The spectrum of phenoxy heated to 375°C and the spectrum of an unheated phenoxy sample appear very similar. One significant change is the appearance of an absorption around 1740 cm⁻¹. This could be the result of reactions converting the hydroxyl group to a carbonyl group or reactions of the ether groups leading to the formation of a carbonyl group. PCL heated to 375°C loses approximately 35% of its original weight. The most noticeable change in the spectra of an unheated PCL sample and one heated to 375°C occurs in the carbonyl region. The carbonyl peak of an unheated sample of PCL is resolvable into two peaks. One represents amorphous carbonyl groups and the other, crystalline carbonyl groups. As the PCL is heated, the amount of crystallinity decreases. In the spectrum of PCL which was heated to 375°C, it is very hard to resolve the two peaks as the amount of crystallinity has been significantly reduced due to degradation of the polymer.

The infrared analysis helps confirm the belief that phenoxy/PCL blends decompose in a step-by-step manner. The intensity of the absorbance associated with the carbonyl group of PCL is so greatly reduced in the spectrum of the blend sample which had been heated to 375°C that it seems likely that most of the PCL has degraded before phenoxy degradation occurs. The fact
that there is an absorbance in the spectrum of the partially degraded blend sample near the absorbance associated with the carbonyl group does not negate this conclusion. The absorbance is greatly reduced compared to the absorbance in the unheated samples. Its position is similar but not identical to the carbonyl absorption. Furthermore, in the spectrum of phenoxy heated to 375°C, there is an absorbance in this region which was clean in the unheated samples. It seems likely that during the thermal degradation of phenoxy, a carbonyl group is formed which has an absorbance in this region. This could be by the formation of a carboxylic acid group or a ketone or aldehyde. It is also possible that transesterification occurred during the thermal degradation of the blend. This would form grafts of PCL on the phenoxy chain.
4.1.3 Mass Spectrometric Analysis

The thermal degradation of phenoxy, PCL and their blends was studied via direct-pyrolysis mass spectrometry (DP-MS). Infrared spectroscopy allowed the residue of these materials to be analyzed at various stages during the degradation processes. DP-MS allowed the volatiles of these degradations to be studied. These analyses were performed in a vacuum where the pressure was less than \(10^{-6}\) torr as opposed to the TGA and DSC studies which were done under dynamic nitrogen atmospheres. By comparing Tmax values from the TGA experiments with the temperatures at which the total ion chromatograph is a maximum, it appears that the difference in atmosphere did not have an appreciable effect on these thermal degradation mechanisms. The DP-MS was programmed to heat the polymeric samples at a constant rate of 0.5°C/min from 100°C to 350°C.

In this mass spectrometry study, electron impact (EI) was the setting of the ionization mode. This meant volatiles of the thermal degradation reactions were ionized by interaction with an electron beam. This often leads to additional fragmentation which complicates the resulting mass spectral data. Softer ionization techniques have recently been used by Garozzo and co-workers to study the thermal degradation of aliphatic
polyesters, including PCL (27). Chemical impact (CI) ionization was used which minimizes the degree of fragmentation which occurs after volatilization. It had earlier been reported that cyclic oligomers were the primary thermal degradation products of PCL (26). The data obtained using EI ionization by Garozzo and co-workers did not allow the degradation products of PCL to be identified due to complications of intense fragmentation. Using CI ionization, however, the peaks due to cyclic oligomers were very intense. They proposed that the thermal degradation of PCL leads to the formation of cyclic monomer and oligomers via intramolecular exchange reactions.

Figure 14 shows the total ion chromatograph (TIC) recorded at 0.5°C/min and a spectrum selected at a temperature of 288°C. This is the temperature at which a 50/50 phenoxy/PCL blend has lost approximately 50% of its original weight as observed in a TGA study recorded at a heating rate of 0.5°C/min. Mass spectra were recorded as a function of time. It is possible to convert time (t) to temperature (T) by

\[ T = \frac{t}{2} + 100\,^\circ\text{C}. \]

The abundance of volatiles increases throughout the time range of this study. Based on TGA data at the same heating rate, it was expected that the volatiles would be evolving in increasing amounts as the Tmax, from TGA, for
Figure 14. A. The mass spectrum of PCL recorded at a heating rate of 0.5°C/min with T=288°C.

B. The total ion chromatograph of PCL at a heating rate of 0.5°C/min.
PCL at 0.5°C/min is 400°C.

The spectrum recorded at 288°C is very similar to the spectra recorded in the study previously mentioned. The most intense peaks are at m/z=55, 97, and 115. The fragments at m/z=55, shown below, are the result of a McLafferty rearrangement. It is a common fragment of lactone ionization and occurs when a pi system abstracts a γ hydrogen (28). Only small amounts of monomeric caprolactone (m/z=114) are detected due in part to this reaction and in part to the degradation mechanism of PCL.

The fragments of m/z=97 and 115 are the result of EI fragmentation of the cyclic oligomers of PCL. The cyclic oligomers, formed via intramolecular transfer reactions during the thermal degradation of PCL, are unable to withstand the EI ionization. The fragment at m/z=115 is the most abundant fragment in a series of fragments where m/z=115 + n(114) and n=0 to 6 (29). The general form of these fragments is

\[ H-(O-(\text{CH}_2)^5\text{C}O)-O-(\text{CH}_2)^5\text{C}O^+ \]

The fragment at m/z=97 is the most abundant fragment in a series of fragments where m/z=97 + n(114) and n=0 to 6. The general form of these fragments is

\[ \text{CH}_2=\text{CH}-(\text{CH}_2)^3\text{CO}-O-(\text{CH}_2)^5\text{C}O^+ \]

Figure 15 shows the TIC of a sample of a 50/50
Figure 15. A. The mass spectrum of a 50/50 phenoxy/PCL blend recorded at a heating rate of 0.5°C/min with T=288°C.

B. The total ion chromatograph of a 50/50 phenoxy/PCL blend recorded at a heating rate of 0.5°C/min.
phenoxy/PCL blend heated from 100°C to 350°C at a heating rate of 0.5°C/min. The volatiles of the first degradation step are identified as PCL degradation products. Near the oven limit of the DP-MS, new fragments are evolved which presumably are the result of phenoxy decomposition. This information provides additional support to the belief that the polymers in the blend degrade in a step by step manner. The mass spectrum shown was taken at 288°C which, as mentioned, represents the temperature of maximum rate of volatile evolution for PCL fraction of the 50/50 blend heated at 0.5°C/min. This temperature compares very well with the T_max observed by a TGA study of this material at the same heating rate (288°C versus 294°C) even though the environment was different (vacuum vs. nitrogen atmosphere).

There are several important differences, however, between the spectrum of pure PCL and PCL degraded in a 50/50 mixture with phenoxy. The intensity of the monomeric caprolactone peak in the blend is equal to that of the major oligomer fragment (115) which was a very intense peak in the mass spectrum of pure PCL. Also, the peaks at 55,56 are much more intense in the spectrum of the blend than in the spectrum of pure PCL in comparison to the abundance of the other fragment peaks. As a result, it is believed that more caprolactone monomer is being formed in the blend at the expense of larger,
oligomeric products. As there are no significant new peaks in the mass spectrum of the blend, it seems possible that the PCL degrades by the same general mechanisms in both instances. In the blend, the degradation leads to monomer formation compared to pure PCL degradation which leads to the formation of oligomers.

There are several factors to be considered in determining the cause of the different relative intensities of the peaks of PCL in the blend and in the pure state. One factor which has been ruled out is the delaying effect due to the viscosity of phenoxy. It seemed possible that the oligomers may have been formed in the blend as in the pure PCL but that the more viscous blend environment prevented them from readily escaping and being detected. As a result of being held in the heated environment longer, further reactions may occur resulting in additional caprolactone being formed. If this were true, the mass spectrum of a less viscous blend such as the 10/90 phenoxy/PCL blend should appear more like pure PCL than the 50% blend. DP-MS of the 10% blend proved this to not be the case. Figure 16 shows the TIC of the 10% blend and a spectrum selected at 280°C. The peaks are similar to that of the 50% blend in composition and intensities. The reason for 2 peaks in the TIC of the 10% blend is unclear. The region up to approximately
Figure 16. A. Mass spectrum of 10/90 phenoxy/PCL blend recorded at 0.5°C/min with T=315.5°C.

B. The total ion chromatograph of a 10/90 phenoxy/PCL blend recorded at a heating rate of 0.5°C/min.
325°C (450 minutes) represents fragments identified as being products of the thermal degradation of PCL. Above this temperature, new volatiles are evolved, presumably the result of the degradation of phenoxy. It seems likely that the two peaks, both of which represent PCL degradation products, are a result of the capillary sample vessel which possibly was packed unevenly with the blend sample.

It was previously mentioned that hydrogen bonding exists between the carbonyl group of PCL and the hydroxyl group of phenoxy. The proximity of these two groups increases the potential for transesterification. Garozzo and co-workers proposed that PCL thermally degrades to cyclic monomer and oligomer via intramolecular transfer reactions (27). If transesterification were to have occurred in the blend, it would result in increasing the number of PCL chain ends. These chain ends are responsible for the intramolecular reaction leading to monomer and oligomers being formed. Figure 17a shows the transesterification reaction between phenoxy and PCL. Figure 17b shows the intramolecular transfer mechanism leading to monomeric PCL being formed. This is the same general reaction which will result in oligomers of caprolactone of various ring sizes being formed.
Figure 17. A. Transesterification reaction between phenoxy and PCL.
Figure 17. B. Intramolecular transfer reaction of PCL.
4.2 Poly(1,4-butylene adipate)

Poly(1,4-butylene adipate) (PBA) is the condensation product of adipic acid and 1,4-dibutanol. Structurally, it is very similar to PCL. PCL has five methylene groups per ester linkage whereas PBA has four. However, the ester groups of the PBA backbone alternate in orientation due to the way in which the polymer was produced. PBA has been shown to be miscible with phenoxy throughout the composition range with no detectable LCST (19). Figure 3 showed that PBA has a strong interaction parameter with phenoxy and it is presumed that hydrogen bonding exists between the hydroxyl group of phenoxy and the ester group of PBA. As in any phenoxy/polyester blend, the potential exists for transesterification to occur between the two polymers in the blends. It was of interest to determine if the condensation polymer, PBA, would show a similar degree of destabilization as the polylactone, PCL, when blended with phenoxy.

Figure 18 shows the TGA curves for all the polymers used in this study. They all decompose in a single step at roughly the same temperature with the exception of PBA. It has a Tmax value nearly 40°C lower than the other polyesters degraded at a heating rate of 1°C/min. Figure 19 shows the TGA curve for the 50/50 phenoxy/PBA sample and the curve expected based on the average of phenoxy and PBA data obtained at a heating
Figure 18. TGA curves of A) phenoxy, B) PDDS, C) PCDS, D) PHS, E) PCL and F) PBA recorded at 1°C/min.
Figure 19. TGA curves of 50/50 phenoxy/PBA blend, experimental and expected at 1°C/min.
rate of 1°C/min. The experimental curve shows that the thermal degradation of this blend is a two-step process where the areas of the derivative peaks are proportional to the composition of the blend. Up to 50% weight loss, the fraction assumed to be PBA of the blend is less stable than was expected. The portion of the curve associated with the phenoxy fraction of the 50/50 blend is only slightly less stable than was expected. Blends of PBA with phenoxy were also prepared in compositions of 80 wt% and 20 wt% phenoxy. Both blends decomposed in two-step processes with the weight loss of each step proportional to the composition of the blends.

The destabilization observed in the phenoxy/PBA blend was similar in magnitude to that observed in the phenoxy/PCL blend (approx. 50°C for a 50/50 blend heated at 1°C/min). It was presumed that PBA was destabilized by the same mechanism in blends with phenoxy as was PCL. Mass spectrometry studies have shown that poly(ethylene adipate) (PEA), whose structure is

\[
\left\{ \begin{array}{c}
0 \\
0 \\
O-C-(-CH_2)\frac{O}{2}C-O(-CH_2)\frac{2}{2}
\end{array} \right\}
\]

thermally degrades via intramolecular exchange reactions resulting in cyclic oligomers (38). As this is the same mechanism observed for the many aliphatic polyesters, it seems likely that PBA would degrade by the same mechanism. As a result, PBA would be susceptible to the
same destabilizing mechanisms as PCL, namely, the effects of transesterification and hydrogen bonding. Hydrogen bonding of the phenoxy hydroxyl group and polyester ester group will lead to a weakening of the C-O bond. This will make these bond more susceptible to attack of PBA chain segments via intramolecular transfer reactions. Transesterification will result in increasing the number of PBA end groups which are the site responsible for intramolecular transfer reactions. In addition, the end groups formed via transesterification, the oxides, will be more reactive than the hydroxyl groups which usually are the end groups of polyester chains.
4.3 Poly(1,4-cyclohexane-dimethylene succinate)

Poly(1,4-cyclohexane-dimethylene succinate) (PCDS) was observed to undergo transesterification with phenoxy in blend samples heated at 160°C for 24 hours. As crystallization occurs very slowly for PCDS, the interaction parameter between phenoxy and PCDS has not been calculated. However, Figure 3 shows what the interaction parameter between PCDS and phenoxy was expected to be based on the average number of methylene groups per ester linkage.

Figure 20 shows the TGA data of the 50/50 phenoxy/PCDS and the curve expected based on the average of phenoxy and PCDS. The experimental curve is only slightly less stable than was expected throughout the entire degradation process. The process is not a two-step process as was observed in the earlier phenoxy/polyester blends. The degree of destabilization is very slight. It is important to remember that several variables such as sample size, sample shape and purge gas flow rate will affect the position of a thermogram. The difference between the experimental curve and the expected curve is of the same magnitude as had been observed between successive thermal analysis of the same material. Therefore, the PCDS is not significantly
Figure 20. TGA curves of 50/50 phenoxy/PCDS blend, experimental and expected at 1°C/min.
affected by the presence of phenoxy. This is confirmed in Figure 21 which shows the relationship of Ea and phenoxy content in phenoxy/PCDS blends. The Ea values of the blend samples agree fairly well with an additivity relationship of the Ea's of phenoxy and PCDS.

It seems logical to assume that the large, saturated cyclohexane ring of PCDS prevents phenoxy from destabilizing the polyester by sterically interfering with the interactions which occurred between phenoxy and the aliphatic polyesters. Also, it is possible that PCDS thermally degrades by a mechanism different than linear aliphatic polyesters. Due to the size and stiffness of the cyclohexane ring, it would be more difficult for PCDS to form cyclic oligomers during its degradation. Also, these cyclohexane rings may block the intermolecular interactions observed between phenoxy and the linear, aliphatic polyesters, PBA and PCL for example.

Special precautions were taken to prevent phase separation due to PCDS crystallinity during solvent evaporation. DSC studies on these samples indicated success in casting films of a miscible blends since only one composition dependent Tg was observed (approx. 50°C for a 50/50 phenoxy/PCDS blend at 20°C/min). This Tg was in agreement with the expected value calculated by the Fox equation using the Tg's of phenoxy and PCDS as 103°C and 0°C, respectively (1).
Figure 21. Activation energy versus phenoxy content for phenoxy/PCDS blends.
4.4 Poly(2,2-dimethyl-propylene succinate)

Poly(2,2-dimethyl-propylene succinate) (PDPS) is a branched, aliphatic polyester formed via a polycondensation reaction. Blends of phenoxy with PDPS have been shown to be miscible throughout the composition range at room temperature. At elevated temperatures, LCST's have been observed at several different compositions of phenoxy/PDPS blends. Figure 22 shows a plot of observed LCST versus phenoxy content (19). These temperatures are below the temperature at which PDPS begins to degrade. Therefore, in phenoxy/PDPS blends, phase separation occurs before the samples are heated enough to initiate degradation. As a result, the potential for transesterification to occur in these blends is less than in the previously discussed phenoxy/polyester blends. In addition, since the polymers phase separate at elevated temperatures, it seems unlikely that a significant degree of hydrogen bonding exists between phenoxy and PDPS above the LCST.

Figure 23 shows the TGA data for a 50/50 phenoxy/PDPS blend and the expected curve based on an average of phenoxy and PDPS data. As was expected, due to the phase behavior of the blend, these two curves are very similar. The experimental curve appears to be less stable over the entire range compared to the expected curve. These observations are very similar to the
Figure 22. Cloud point temperatures versus composition of phenoxy/PDPS blends.
(Reproduced from reference 19).
Figure 23. TGA curves of 50/50 phenoxy/PDPS blend, experimental and expected at 1°C/min.
phenoxy/PCDS blend. Both polyesters have branching or bulky backbone groups which may lead to a different degradation mechanism than linear polyesters. Also, since it is known that the phenoxy/PDPS blends have phase separated before degradation occurs, any destabilizing mechanism of phenoxy is lessened due to the polymer chains segregating.

Figure 24 shows the activation energies of phenoxy, PDPS and their blends as calculated by the Flynn-Wall method. The actual blend values compare fairly well with the calculated values based on an additivity contribution of each polymer.
Figure 24. Activation energy versus phenoxy content for phenoxy/PDPS blends.
4.5 Poly(hexamethylene sebacate)

Poly(hexamethylene sebacate) (PHS) is a linear, aliphatic polyester similar to PBA in structure. The interaction parameter calculated for blends of phenoxy with PHS shows a value which lies outside the miscibility range (Figure 2). Visual observations of these blends also show that phenoxy/PHS blends are immiscible. Films of these blends were milky white above the melting point of PHS and gave every appearance of being composed of multiple phases (19).

Figure 25 shows the TGA data for the 50/50 blend of phenoxy/PHS and the curve expected based on the average of these two polymers. The experimental curve does not appear to be a two step process, however, the derivative curve is very broad and may possibly represent two processes which occur at similar temperatures. As a result, it is not possible to resolve into two distinct degradation steps. Comparing the two curves suggests there are two degradation mechanisms. Up to a weight loss of approximately 50%, the experimental curve is at lower temperatures than the expected curve. After that point, the two curves agree very well. If it can be presumed that the first step represents PHS, its behavior is similar to that seen in other phenoxy blends with linear polyester, PBA and PCL.
Figure 25. TGA curves of 50/50 phenoxy/PHS blend, experimental and expected at 1°C/min.
As the structure of PHS is very similar to PBA and PEA in that each is a linear, aliphatic polyester formed via a polycondensation, it is expected that the thermal degradation of PHS occurs via intramolecular exchange reactions leading to cyclic oligomers. This mechanism appears to be catalyzed by the presence of phenoxy. As a result, if transesterification occurs between PHS and phenoxy, PHS would be destabilized in the blend. Also, hydrogen bonding may occur between phenoxy and PHS at the phase boundaries. These interactions would not be expected to exert a large influence on the degradation of PHS since it has been discussed that PHS and phenoxy blends are immiscible. As a result, a lesser amount of destabilization would occur in phenoxy/PHS blends than in the blends of phenoxy with PBA and with PCL.
CONCLUSIONS

The thermal degradation of several phenoxy/polyester blends has been studied to examine the affect of blending on the thermal stability of the polymers. In each blend, the polyester component of the blend was less thermally stable than was expected. The phenoxy portion of the blends was unaffected by the presence of the polyesters. It seems likely that this would be due to (a) hydrogen bonding making the polyesters more susceptible to intramolecular transfer reactions and (b) transesterification forming reactive polyester end groups which lead to intramolecular transfer reactions.

The degree of destabilization of the polyesters in the presence of phenoxy varied for each polyester. PCL and PBA, which were the most structurally similar, are destabilized to a larger degree by phenoxy. Blends of these polyesters with phenoxy degrade in two-step mechanisms where the amount of weight loss corresponding to each of the steps was proportional to the blend composition.

PHS is immiscible with phenoxy, however, it appeared slightly destabilized in blends with phenoxy. Although the degradation of phenoxy/PHS blends did not occur by a clear two-step process, as was observed in blends of phenoxy with PCL and PBA, there was some
evidence suggesting the degradation may be a two-step process. The blends of phenoxy with PCDS and PDPS were only destabilized. The bulky and branched backbones of PCDS and PDPS appears to have interfered with the interactions which destabilized the earlier polyesters. Activation energy values for phenoxy/PDPS and phenoxy/PCDS blends compare fairly well with values calculated based on an assumed additivity contribution of the blend components.

Additional work is needed to further support the claims of this research project. Gel-permeation chromatography (GPC) could be used to follow the molecular weight of phenoxy in the blends during the degradation of the polyesters. If transesterification occurs, the GPC would be able to detect an increase in the molecular weight. In addition, other phenoxy polyester blends could be analyzed in a similar manner to further examine the manner in which phenoxy lowers the thermal stability of polyesters. Since transesterification is known to occur in phenoxy/PBT blend (23), it seems like it should be the next system to be considered. As blends become more commercially important, it becomes necessary to understand the effects of blending on the thermal stability of polymers.
REFERENCES


REFERENCES (continued)


