10-1-1987

Thermal degradation of polymer blends containing poly(vinyl chloride)

David W. Lee

Follow this and additional works at: http://scholarworks.rit.edu/theses

Recommended Citation
THERMAL DEGRADATION OF POLYMER BLENDS
CONTAINING POLY(VINYL CHLORIDE)

DAVID W. LEE

OCTOBER 1987

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

APPROVED:
E. Moskala
Project Adviser

Department Head

Library

Rochester Institute of Technology
Rochester, New York 14623
Department of Chemistry
Title of Thesis: The Thermal Degradation of Polymer Blends Containing Poly(vinyl Chloride). I, David W. Lee hereby grant permission to the Wallace Memorial Library, of R.I.T., to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profi
DEDICATION

I would like to dedicate this thesis to my fiancée, Catherine Ann DiSalvo, and to my parents for all of their unending love and constant support.
TABLE OF CONTENTS

Abstract .............................................................................................. i
Acknowledgements........................................................................... ii
List of Figures.................................................................................... iii
List of Symbols................................................................................... vi
List of Tables....................................................................................... vii
1......INTRODUCTION....................................................................... 1
   1.1......Thermogravimetric Analysis................................. 1
       1.1.1.....Instrumentation........................................... 1
       1.1.2.....Applications of Thermogravimetric
                     Analysis.................................................. 7
   1.2......Thermal Degradation of Poly(vinyl Chloride) Blends......... 18
   1.3......Miscibility of EVA/PVC Blends............................... 24
2......PURPOSE............................................................................... 29
3......EXPERIMENTAL..................................................................... 31
   3.1......Polymers Used In This Study.............................. 32
   3.2......Sample Preparation............................................ 33
   3.3......Instrumentation.................................................. 34
4......THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)/
       POLY(VINYL ACETATE) BLENDS.................................... 35
   4.1......Thermogravimetric Analysis................................. 35
   4.2......Mass Spectrometric Analysis............................... 42
5......THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)/
       ETHYLENE–VINYL ACETATE COPOLYMER BLENDS............ 51
   5.1......EVA70/PVC Blends.............................................. 51
       5.1.1.....Thermogravimetric Analysis.......................... 51
       5.1.2.....Mass Spectrometric Analysis......................... 59
ABSTRACT

The thermal degradation of blends of poly(vinyl chloride) (PVC) with poly(vinyl acetate) (PVA), and two ethylene-vinyl acetate copolymers containing 70 weight percent vinyl-acetate (EVA70) and 45 weight percent vinyl acetate (EVA45) were studied by thermogravimetric analysis and direct-pyrolysis mass spectrometry. The PVC, PVA, EVA45 and EVA70 degrade in two-step processes for each polymer. The PVA/PVC, EVA45/PVC and the EVA70/PVC blends do show some interaction during the first step of the degradation process while the respective second steps are unaffected. The acid produced by the degradation of one polymer causes accelerated loss of the other acid in the blend. The extent of the interaction is a function of the miscibility of the blends.
ACKNOWLEDGEMENT

I would like to thank my advisor, Dr. Moskala, and the members of my graduate committee for all that they have done.
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Relative thermal stability of polymers by dynamic thermogravimetric analysis. (Reproduced from reference 3)</td>
</tr>
<tr>
<td>2</td>
<td>Thermograms for (a) PVC and PVA, and (b) Comparison of observed and predicted behavior of a 50/50 blend of the polymers. Samples as 10 mg powders, degraded at 5°C/minute under a dynamic atmosphere (75 ml/min). (Reproduced from reference 30)</td>
</tr>
<tr>
<td>3</td>
<td>TGA thermograms of PVC recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute</td>
</tr>
<tr>
<td>4</td>
<td>TGA thermograms of PVA recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute</td>
</tr>
<tr>
<td>5</td>
<td>TGA thermograms of a 50/50 PVA/PVC blend recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute</td>
</tr>
<tr>
<td>6</td>
<td>Observed and predicted thermograms for a 50/50 PVA/PVC blend at 1°C/minute</td>
</tr>
<tr>
<td>7</td>
<td>(a) The mass spectrum of PVA recorded at a heating rate of 1°C/minute with $T=304^\circ C$</td>
</tr>
<tr>
<td></td>
<td>(b) The total ion chromatograph of PVA recorded at a heating rate of 1°C/minute</td>
</tr>
<tr>
<td>8</td>
<td>Mass spectra of PVA recorded as a function of time, temperature and intensity</td>
</tr>
<tr>
<td>9</td>
<td>(a) The mass spectrum of PVC recorded at a heating rate of 1°C/minute with $T=283^\circ C$</td>
</tr>
<tr>
<td></td>
<td>(b) The total ion chromatograph of PVC recorded at a heating rate of 1°C/minute</td>
</tr>
<tr>
<td>10</td>
<td>(a) The mass spectrum of a 50/50 PVC/PVA blend recorded at a heating rate of 1°C/minute with $T=279^\circ C$</td>
</tr>
<tr>
<td></td>
<td>(b) The total ion chromatograph of a 50/50 PVC/PVA blend recorded at a heating rate of 1°C/minute</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Continued)

11 DPMS data for the estimation of evolved acids from the degradation of PVC, PVA, and a 50/50 (w/w) PVC/PVA blend
+ from pure PVC, Δ from pure PVA, □ from PVC in the blend

12 TGA thermograms of EVA 70 recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute...

13 TGA thermograms of a 50/50 EVA70/PVC blend recorded at (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute...

14 Observed and predicted thermograms for a 50/50 EVA70/PVC blend at a heating rate of 1°C/minute...

15 (a) The mass spectrum of EVA 70 recorded at a heating rate of 1°C/minute with T=311°C...

16 (a) The mass spectrum of a 50/50 EVA70/PVC blend recorded at a heating rate of 1°C/minute with T=275°C...

17 DPMS data for the estimation of evolved acids from the degradation of PVC, EVA70, and a 50/50 (w/w) PVC/EVA70 blend
+ from pure PVC, Δ from pure EVA70, □ from EVA70 in the blend...

18 TGA thermograms of EVA45 recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute...

19 TGA thermograms of a 50/50 EVA45/PVC blend recorded at (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute...
LIST OF FIGURES (Continued)

20  Observed and predicted thermograms for a 50/50 EVA45/PVC blend at a heating rate of 1°C/minute..................................................67

21  DPMS data for the estimation of evolved acids from the degradation of PVC, EVA45, and a 50/50 (w/w) PVC/EVA45 blend.
    + from pure PVC, □ from PVC in the blend
    Δ from pure EVA45, <> from EVA45 in the blend...72
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl Chloride)</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl Acetate)</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene Vinyl–Acetate Copolymer</td>
</tr>
<tr>
<td>PVB</td>
<td>Poly(vinyl Butyral)</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen Chloride</td>
</tr>
<tr>
<td>HAc</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl Methacrylate)</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower Critical Solution Temperature</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DPMS</td>
<td>Direct-Pyrolysis Mass Spectrometry</td>
</tr>
<tr>
<td>TIC</td>
<td>Total Ion Current</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Description of polymers used in this study</td>
</tr>
<tr>
<td>2</td>
<td>The observed and predicted temperatures at which a 25% weight-loss occurs for a 10/90 (w/w) EVA70/PVC blend recorded at various heating rates</td>
</tr>
<tr>
<td>3</td>
<td>The observed and predicted temperatures at which a 25% weight-loss occurs for a 50/50 (w/w) EVA45/PVC blend recorded at various heating rates</td>
</tr>
<tr>
<td>4</td>
<td>The observed and predicted temperatures at which a 25% weight-loss occurs for a 10/90 (w/w) EVA45/PVC recorded at various heating rates</td>
</tr>
</tbody>
</table>
INTRODUCTION

The research presented in this thesis involves a study of the effects of miscibility on the thermal degradation of poly(vinyl chloride) blends by thermogravimetric analysis and direct pyrolysis-mass spectrometry. PVC degrades by a two step process which involves in the first step the loss of hydrogen chloride (HCl) followed by the decomposition of the resulting polyene chain in the second step. The miscibility and thermal degradation of PVC/Ethylene Vinyl-Acetate (EVA) Copolymer blends were studied. These blends exhibit varying degrees of miscibility depending upon the vinyl-acetate concentration in the copolymer. PVC/EVA blends exhibit at least partially compatible when the vinyl-acetate concentration is between 45 and 70 weight percent. In this chapter the thermal degradation of PVC blends, the miscibility of EVA/PVC blends and applications of thermogravimetric analysis to the study of polymeric systems will be reviewed. Also, the instrumentation involved with thermogravimetric analysis will be discussed.

1.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) may be defined as a thermoanalytical tool which follows the weight changes of a material as a function of either time or temperature. Dynamic TGA follows the weight-loss at a programmed
heating rate while isothermal TGA follows the weight-loss as a function of time at a constant temperature.

1.1.1 Thermogravimetric Instrumentation

The instrument employed, when performing TGA of a material, is the thermobalance. A thermobalance continuously weighs a sample as a function of temperature or time. The first thermobalance was introduced in 1915 by Honda (1). However, it was not until the early 1940’s that a thermobalance was constructed that was both rugged and sensitive enough for use in an industrial laboratory (2). Many of the earliest uses for thermogravimetric analysis involved determining the stability of various inorganic precipitates. Duval published a series of papers investigating the pyrolysis of several hundred precipitates (2,3) and recorded the first TGA scan of a polymeric material when he burned filter paper in a Chevenard balance in 1948 (3,4).

TGA of polymers was furthered by Jellinek who, in 1949, studied the vacuum degradation of several polymers including polystyrene and polyethylene (3,5). Since that time, there have been numerous papers and reviews detailing the analysis of homopolymers, copolymers and polymer blends (24-34). Several of these studies will be reviewed in latter sections.

According to W. W. Wendlandt (6) the development of
thermogravimetric analysis up to 1965 was brought about by
the need to solve chemical problems relating to the
degradation in controlled atmospheres and operation at
reduced pressures. The developments that have occurred
since that time have served to improve the state of the
art in thermal analysis research. The thermobalance has
undergone several modifications since it was introduced in
1915 to reach the point where it is today.

A modern thermobalance is composed primarily of four
components: (a) recording balance, (b) furnace, (c)
furnace temperature programmer, and (d) recorder. The
specific details of each component depend on the
particular instrument. Due to the wide variety of
thermobalances only a brief review of the four components
will be discussed. All thermal analyses performed in this
study were done on a Perkin-Elmer TGS-2 Thermogravimetric
System coupled to a Perkin-Elmer System 4 microprocessor.

The recording balance is the most important component
of the thermobalance. In addition to the requirements of
an analytical balance, such as accuracy, precision, and
insensitivity to temperatures changes, the thermobalance
also should be able to quickly respond to changes in mass
due to the degradation of the sample. There are three
classifications of recording balances based upon their
mode of operation. A deflection type balance converts
deflections about some point into mass-change curves.
Deflection-type include the cantilever, helix spring, torsion wire and beam balances. The most sensitive type of recording balance detects changes in the mass based on a change in resonance frequency. The quartz crystal microbalance is the most common balance of this type (7). The most widely used recording balance is the null-type balance. The null-type balance uses a sensing element that reacts to deviations from the null or equilibrium position of the balance beam. The sensing element usually consists of a pair of photocells, a shutter that is connected to the balance arm, and a lamp. Once an initial equilibrium has been set any changes from this equilibrium cause deviations which must be compensated for. If the balance arm rotates, the light falling on the detectors is no longer of equal intensity. A restoring force which is either mechanical or electrical in nature, returns the balance to its null position. When the restoring force is electrical in nature, it is applied as a change in electrical current passing in a coil that is interacting with a magnetic field. The change in current is proportional to the change in mass of the sample. The Perkin-Elmer TGS-2 Thermogravimetric System utilizes a null-type recording balance. This balance operates best when the sample weight is between 0.5 and 10 milligrams.

There are a wide variety of furnaces each designed for a specific temperature range. The most common operating temperature range is from 25°C to 1000°C (7).
Due to such problems as oxidation, evaporation and thermal shock, furnaces may need to be replaced on a regular basis. These problems are increasingly important for the higher temperature furnaces, however, they may be minimized by taking appropriate precautions such as careful estimation of the maximum temperature for a specific furnace element and limiting the time spent at the maximum temperature. The furnace in a Perkin-Elmer TGS-2 Thermogravimetric System consists of an alumina cylinder (12.7 mm x 19 mm) mounted on a ceramic tube. The furnace resistance element is made of platinum wire with an approximate maximum temperature of 1400°C.

The rate of heating and cooling of a furnace is controlled by a furnace temperature programmer. The ideal programmer for dynamic TGA should be capable of linear temperature programming in the desired range. Additionally, the output from the programmer must be both reproducible and stable in the desired range. Temperature controllers range from the simple on-off type controller to more sophisticated models. On-off type controllers should not be used for maximum accuracy because they give rise to thermal gradients in the furnace and sample. Gradients may be minimized by using slower heating rates (8) and smaller samples sizes in the form of thin films (9). In the Perkin-Elmer TGS-2 model the temperature is monitored by the System 4 microprocessor controller. This microprocessor has the ability to perform either dynamic
or isothermal TGA, as well as multiple ramp experiments and hold periods. Another advantage of the System 4 microprocessor is in its ability to automatically calibrate the temperature scale. This is accomplished by the furnace element also acting as a temperature sensor by measuring the resistance in the line (10).

A recorder is used to collect the data from the thermobalance. There are many different types of recorders that have been coupled to thermobalances. These recorders range from photographic light-beam galvanometers to the modern electronic models (7). Due to their wide range of flexibility, modern digital systems are particularly desirable if kinetic parameters are to be estimated. Also, with the aid of a computer, such functions as curve smoothing, differentiation, integration and other mathematical functions can be performed with relative ease. The Perkin-Elmer system has an optional thermal analysis data station which easily performs many of these tasks.
1.1.2 Applications of TGA

Thermogravimetric analysis has several applications to the study of polymeric materials. Generally, these applications can be grouped into two categories: qualitative and quantitative applications. The most widely recognized qualitative application for TGA has been for comparing the thermal stabilities of various polymers. However, there are limitations when determining thermal stability by TGA. There are two main factors that one must consider when comparing thermal stabilities of polymers. The first factor to keep in mind is that different thermograms often may not be strictly compared. The weight-loss curve obtained from TGA is extremely dependent upon experimental conditions. Differences in flow rate of the purge gas, atmosphere, sample weight, and sample geometry make it difficult to compile and compare thermograms from different sources unless the thermograms were obtained under identical conditions. Even if the weight-loss curves were obtained under the same conditions, there is debate about how to compare the thermal stabilities of the various polymers (11). The other factor to consider is the definition of stability. Doyle proposed the idea of procedural decomposition temperatures which stressed the area under the curve as an estimation of the thermal stability of the polymer (11). In order to put materials on an equal basis, Doyle
proposed that all experiments be performed from 25°C to 900°C. These "procedural decomposition temperatures" (pdt's) depend upon conditions employed such as the type of atmospheric gas used and rate of heating. The pdt is then determined from the area under the curve and the temperature range employed from equations proposed by Doyle (11). Figure 1 shows the degradation of five different polymers, poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), high pressure polyethylene (HPPE), polytetrafluoroethylene (PTFE), and an aromatic polypyromellitimide (PI). Initially PVC has a greater weight loss than PMMA, but at higher temperatures PMMA has lost more weight. This presents the question "Which polymer is more thermally stable?" When comparing the relative thermal stability of different polymers, one must be consistent in determining the thermal stability.

Another application for TGA is the thermal analysis of additives in a polymeric system. The analysis may be performed if there are no interactions between the additive and the polymer and if the additive is completely volatilized before degradation of the polymer. Then it is assumed that the first step in the degradation corresponds to the loss of the additive. Chiu determined the amount of plasticizer in a plasticized poly(vinyl butyral) (PVB) resin (4). The degradation of PVB resin occurs in a one-step process. However, when a plasticizer is added to the system, degradation occurs in two steps. The first step
Figure 1. Relative thermal stability of polymers by dynamic thermogravimetry. (Reproduced from reference 3).
corresponds to the volatilization of the plasticizer while
the second step involves the degradation of the polymer.

Thermogravimetric analysis has also been used to
study the amount of filler in a polymeric sample. The
amounts of carbon and silica filler may be individually
determined in a silica- and carbon-filled
polytetrafluoroethylene (PTFE) sample (4). The sample
would be degraded in a nitrogen atmosphere at a programmed
heating rate up to 620°C where the degradation of PTFE is
complete. Air would be allowed into the system and the
carbon filler combusted. The weight remaining corresponds
to the weight of silica-filler. In order for this
 technique to be accurate the polymer should completely
degrad and leave a minimum of residue.

Usually the thermal stability of a copolymer is
between that of the two homopolymers and changes according
to the composition of the copolymer. Typically, the
weight-loss curve for a random copolymer is smooth and
intermediate of the two pure polymers while a block
copolymer shows an initial weight-loss approximately equal
to its composition.

The characterization of copolymers and blends
may be performed using thermogravimetric analysis. The
composition of an ethylene-vinyl acetate (EVA) copolymer
can be quantitatively determined by TGA. The first step
in the degradation is known to involve the deacetylation
of the copolymer (14). The vinyl acetate concentration
can then be calculated by the following equation:

\[
\% \text{ vinyl acetate} = \% \text{ weight-loss} \times \left( \frac{86.1}{60.1} \right)
\]

where 86.1 and 60.1 are the molecular weights of a vinyl acetate unit and acetic acid (HAc), respectively.

Another technique for analyzing copolymers involves the coupling of a thermogravimetric analyzer to another unit such as an automatic titrator (15). The titration may involve a common acid-base titration or a more complex situation involving an ion-selective electrode (ISE). For example, vinyl chloride-vinyl acetate copolymers produce both hydrogen chloride (HCl) and HAc during the first weight-loss event. Therefore, an acid-base titration can not quantitatively determine the amount of HCl or HAc but can only determine the total amount of acid evolved. The amount of chloride ions can be quantitatively determined in the presence of HAc by titrating with standard silver nitrate solution. The composition of the copolymer can then be determined.

Polymer blends may also be characterized by thermogravimetric analysis. If the components degrade in well defined steps, then the composition of the blend may be determined. The thermal stability of polymer blends may be compared against that of the pure polymers.

The determination of kinetic parameters is the most widely used quantitative application of TGA. The kinetic parameters of the degradation may be calculated from
thermograms collected by both isothermal and dynamic TGA techniques. There are four main advantages to using dynamic TGA rather than isothermal TGA to determine kinetic parameters. These advantages are:

"1) Considerably fewer data are required.
2) The continuous recording of weight-loss versus temperature ensures that no feature of the pyrolysis are overlooked.
3) A single trace is used over the entire TGA trace thereby avoiding a possible source of variation in the estimation of the kinetic parameters.
4) In the isothermal method, a sample may undergo premature reaction and this may make the subsequent kinetic data difficult to analyze properly."

The methods for determining the kinetic parameters utilize the degree of conversion, \( C \), which is defined as

\[
C = \frac{(w_o - w)}{(w_o - w_f)}
\]

where the weight of the sample is defined as 'w' and the subscripts 'o' and 'f' refer to initial and final values for the weight-loss event of interest. The rate of conversion, \( \frac{dC}{dt} \), for a given weight-loss event at a constant heating rate, \( B \), where \( B = \frac{dT}{dt} \), may be expressed as:

\[
\frac{dC}{dt} = B \frac{dC}{dT} = f(C) k(T) g(C,T) h(X,Y \ldots)
\]

\( f(C) \) and \( k(T) \) are functions of conversion and temperature, respectively, while \( g(C,T) \) is a function of both conversion and temperature. The last term in equation (1), \( h(X,Y \ldots) \), contains all other rate affecting
variables such as pressure, flow rate and atmosphere (19). If \( h(X, Y \ldots) \) is assumed to be constant and if no temperature-conversion cross term exists then equation (1) simplified to

\[
B \left( \frac{dc}{dT} \right) = f(C) k(T) \tag{2}
\]

It has been shown that these assumptions are not always valid because polymer degradations are known to be complex heterogeneous processes (16,17).

The simplest and most frequently used model for \( f(C) \) is

\[
f(C) = (1-C)^n \tag{3}
\]

where 'n' is the order of the degradation reaction. The function, \( k(T) \), is often represented by

\[
k(T) = A \exp\left[-E/RT\right] \tag{4}
\]

where 'A' is the Arrhenius pre-exponential factor, 'E' is the activation energy for the degradation, and 'R' is the universal gas constant. Therefore, \( dC/dt \), may be written

\[
dC/dT = \frac{1}{B} (1-C)^n A \exp\left[-E/RT\right] \tag{5}
\]

Equation (5) is regarded as the rate expression for any degradation process.

TGA methods for determining kinetic parameters from dynamic data are generally classified into two main categories: differential and integral methods.

Differential methods involve determining the parameters from the rate of weight loss. Integral methods for determining kinetic parameters attempt to mathematically
model the weight-loss event of interest. The Freeman-Carroll and Flynn-Wall methods, differential and integral, respectively, will be discussed.

The Freeman-Carroll method is a differential method for determining the activation energy and order of reaction from therogravimetric curves. This is the most widely used technique for the analysis of nonisothermal data. The Freeman-Carroll method involves taking the logarithm of equation 5 at different temperatures to yield the following equation:

$$\Delta \ln \left(\frac{dC}{dT}\right) = n \Delta \ln (1-C) - \frac{(E/R)\Delta(1/T)}{\Delta(1/T)}$$  \hspace{1cm} (6)

Rearranging equation (6), the relationship becomes

$$\frac{-\Delta \ln \left(\frac{dC}{dT}\right)}{\Delta(1/T)} = \frac{(+E/R) - n\Delta \ln (1-C)}{\Delta(1/T)}$$  \hspace{1cm} (7)

A plot of $$[-\Delta \ln \left(\frac{dC}{dT}/\Delta(1/T)\right)]$$ versus $$[\Delta \ln (1-C)/\Delta(1/T)]$$ will yield a straight line when $$\Delta(1/T)$$ is constant. However, if variable $$\Delta(1/T)$$ values are used equation (6) may be rearranged to give the following equation:

$$[-\Delta \ln \left(\frac{dC}{dT}/\Delta \ln (1-C)\right)] = \frac{(E/R)[\Delta(1/T)/\Delta \ln (1-C)] - n}{\Delta(1/T)}$$  \hspace{1cm} (8)

which fits the equation for a straight line.

The Freeman-Carroll method has the advantage in that only one TGA scan is needed and that the kinetics can be studied over the entire temperature range. A disadvantage of this method is that there is often enough scatter in the plot to make evaluation difficult.

Flynn and Wall have presented an integral method for
determining the activation energies from thermograms recorded at different heating rates \((21)\). This method allows the activation energy to be determined for constant degrees of conversion along the degradation reaction. If equation 5 is rearranged one obtains

\[
\frac{dC}{(1-C)^n} = \frac{(A/B)}{\exp[-E/RT]} \ dT
\]

integrating this expression yields:

\[
F(C) = \int_0^C \frac{dC}{(1-C)^n} = \left(\frac{A}{B}\right) \int_{T_0}^T \exp[-E/RT] \ dT
\]

where \(F(C)\) is the equation of the thermogram. This technique assumes that \(A\), \((1-C)^n\), and \(E\) are independent of \(T\) while \(A\) and \(E\) are independent of \(C\). The logarithm of equation (10) yields

\[
\log F(C) = \log(AE/R) - \log(B) + \log[p(E/RT)]
\]

where

\[
p(x) = e^{-x} - \int_{x_o}^x e^{-u} \ du
\]

and \(x = E/RT\). Using Doyle's approximation \((53)\), the \(\log[p(E/RT)]\) may be expressed as

\[
\log[p(E/RT)] = -2.315 - 0.457(E/RT)
\]

Equation (11) therefore becomes

\[
\log F(C) = \log(AE/R) - \log(B) - 2.315 - 0.457(E/RT)
\]

Differentiating equation (13) with respect to \(1/T\) at constant degrees of conversion, one obtains
\[
\frac{d}{d} \log(B) = \frac{0.457}{E} \frac{1}{T} \quad \frac{R}{1}
\]

The activation energy is then calculated from the slope of a graph of \( \log(B) \) versus \((1/T)\). If the resulting isoconversional lines are parallel, then the degradation proceeds by a single mechanism that is independent of the degree of conversion.

The Freeman–Carroll and Flynn–Wall methods are just two of the many different techniques for determining the kinetic parameters of polymer degradation from TGA. There have been several papers that compare the various techniques (22, 23, 54). Equiazabal et al. studied the kinetics associated with the degradation of a polyarylate (PAR) polymer by the Freeman–Carroll and Flynn–Wall methods. The activation energy as calculated by the Freeman–Carroll method was 83.1 kcal/mole while the Flynn–Wall method yielded an activation energy of only 42.0 kcal/mole. These results illustrate the differences between activation energies calculated from these different methods. Cooney et al. studied the degradation kinetics of poly(ethylene terephthalate) (PET) by several methods and found that the activation energies varied from 101.6 kJ/mole to 199.3 kJ/mole depending upon the mathematical approach used. Due to the large variations in calculated activation energies, it was suggested that methods utilizing multiple heating rates more accurately determine the activation energy of the degradation because
these methods more realistically represent the variety of heating rates obtainable during the pyrolysis and combustion of a polymeric sample.
1.2 Thermal Degradation of Poly(vinyl Chloride) Blends

Until approximately 1970 there had been little literature concerning the thermal degradation of polymer blends even though their commercial importance had been increasing. Polymer blends are receiving greater attention for several reasons including the fact that blending polymers is often a quicker solution to a particular application than synthesizing new polymers. Polymer blends may offer greater ease of processability, improved mechanical properties and improved cost effectiveness. Due to the wide variety of commercial applications for PVC, the thermal degradation of both pure PVC and blends containing PVC has been of interest (24-30).

Previous studies of polymer degradation have often concentrated only on the degradation of pure homopolymers or copolymers. It has been shown that the degradation of one polymer may be affected by the presence of a second polymer or by the degradation products of the second polymer (24-30). Many of these studies have concentrated on immiscible polymer blends. There have been no studies reported in the literature on the thermal degradation of miscible polymer blends containing PVC.

McNeill and coworkers have reported on the degradation of several immiscible PVC blends (24-30). A blend consisting of PVC and chlorinated rubber has been shown to be destabilized when compared to the thermal
degradation of the unmixed polymers (27). HCl is the main volatile product from degradation of both polymers up to 350°C. Dehydrochlorination of the rubber occurs approximately 30°C earlier than PVC. McNeill observed that HCl in the blend is evolved at significantly lower temperatures than would be predicted. In order to determine which polymer was evolving HCl, McNeill used radioactive PVC and was able to monitor the evolution of HCl. He was able to determine that the less stable chlorinated rubber catalyzes the dehydrochlorination of pure PVC. The Cl· radicals from the chlorinated rubber migrate into the PVC phase and facilitate the dehydrochlorination of pure poly(vinyl chloride).

McNeill also studied the thermal degradation behavior of blends containing PVC and polystyrene (PS) (28). Unlike the destabilization observed for the chlorinated rubber-PVC blends, blends of PVC-PS were found to have additional stabilization. The evolution of volatile products was found to be delayed in this system. Dehydrochlorination of PVC was retarded up to 350°C. McNeill proposed that this was the result of chlorine radicals abstracting the tertiary hydrogen of PS. Once the hydrogen was abstracted, the PS decomposed to give a PS molecule with terminal unsaturation. The PS acts as a "radical sink" and undergoes chain scission but not volatile degradation. After the tertiary hydrogen of PS is abstracted, a PS molecule of lower weight and a
polystyryl radical are formed. The polystyryl radical is stabilized by the polyene structure of the PVC after dehydrochlorination has occurred. This polyene structure interferes with the intermolecular transfer process that would give rise to monomer, dimer and trimer formation from the degrading polystyryl radical. Despite the fact that initially the molecular weight falls, PS is stabilized in the blend with PVC.

The degradation of a blend containing PVC and poly(methyl methacrylate) (PMMA) was also studied by McNeill and coworkers (25,26). In this blend it was observed that in the early stages of degradation there was an increased amount of MMA monomer and that HCl production is slightly delayed. MMA monomer is evolved at lower temperatures due to the Cl· radicals diffusing into the PMMA phase. PMMA is known to depolymerize by a radical chain reaction. Therefore, the introduction of Cl· radicals will induce depolymerization at lower temperatures (31). PMMA competes with the degrading PVC for the chlorine radicals. This competition effectively reduces the number of Cl· radicals that can cause the autocatalytic dehydrochlorination of PVC. McNeill proposed that HCl from the degradation of PVC reacts with the ester groups of PMMA to cause the formation of anhydride structures. These anhydride structures effectively block the depolymerization of PMMA at higher temperatures. Infra-red spectra obtained after partial
degradation of the blend showed bands developing at 1800 and 1020 cm⁻¹. These frequencies are characteristic of the identical anhydride formed during the degradation of poly(methacrylic acid). Initially the depolymerization of PMMA is accelerated to yield MMA monomer while the later reaction involves the formation of the anhydride to block further depolymerization and stabilize the remaining PMMA.

McNeill et al. (30) studied the degradation of a PVA/PVC blend by thermal volatilization analysis, thermogravimetric analysis and evolved gas analysis for production of HCl and HAc. The degradation of a PVA/PVC blend is of particular interest due to the similar processes in the degradation reactions, each evolving an acid to yield similar polyene chains, and the effects the evolved acids will have on the thermal degradation behavior of the second polymer in the blend.

Figure 2(a) illustrates the results obtained by McNeill for the degradation of PVC and PVA. The similar degradation patterns are clearly evident. In each case, the first weight loss step corresponds to the elimination of either HCl or acetic acid to yield a polyene. The second step of the degradation is the decomposition of the polyene chain. The predicted thermogram, based upon the additivity of the thermograms for pure PVA and PVC, and the experimental thermograms for a PVA/PVC blend are compared in Figure 2(b). As can be seen, the observed
Figure 2. Thermograms for (a) PVC and PVA, and (b) Comparison of observed and predicted behavior of a 50/50 blend of the polymers. Samples as 10 mg powders, degraded at 5°C/minute under a dynamic atmosphere (75 ml/min). (Reproduced from reference 30)
thermogram is less thermally stable when compared to the predicted thermogram. The weight loss that occurs in the temperature range up to 400°C corresponds to the deacetylation of PVA and the dehydrochlorination of PVC. In the higher temperature range, above 400°C, the experimental and predicted thermograms are in close agreement. In an immiscible PVC/PVA blend any interaction between the two polymers should occur at the phase boundary. This type of interaction could not solely account for the degree of destabilization in the blend. The destabilization must be due to volatiles diffusing from one region in the blend into the other. McNeill concluded that production of both acids, especially acetic acid, was accelerated in the blend because of migrating volatile products catalyzing the loss of the other acid.

The thermal stability of a polymer blend may vary from being destabilized as in the case of PVC-chlorinated rubber to additional stabilization as in the PVC-PS blend. The stability of a blend is generally dependent upon several factors which include the thermal stability of the pure polymers, the degradation mechanism of the pure polymers, the ability of the volatile degradation products from one polymer to interact with a second polymer and the degree of compatibility of the blend.
1.3 Miscibility of EVA/PVC Blends

PVC is a widely used commercial product with a glass transition temperature of +85°C. It is often blended with a rubbery polymeric modifier in order to achieve certain desired physical properties and improve its processability. The study of the effects of these modifiers and their compatibility with PVC have been of great commercial interest.

The appearance of a clear film has often served as a rough guide to determining compatibility in a polymer blend. However, a more reliable method for determining compatibility is the presence of a single glass transition temperature (Tg) in a blend. Polymer blends that exhibit a single Tg are compatible, unless the two pure polymers have the same Tg.

The study of the morphology of blends has been a useful guide for determining the compatibility of polymer blends. Shah and Deanin (37) reported on the effects of modifiers on the morphology of PVC blends. When a semi-compatible rubbery modifier is added to PVC it forms separate micro-domains which improve the impact strength without affecting the glassy matrix of PVC. If a compatible modifier is added to the PVC it acts as a polymeric plasticizer on the PVC. Depending on the degree of compatibility between the components in the blend and the amount of modifier added, different phase relations
have been observed. These phase relations range from a two-phase system in which the rubber particles are dispersed in the PVC matrix to the perfect one phase system. Systems which exhibit semi-compatibility have also been reported (36-44). EVA/PVC blends have been shown to form one-phase, two-phase and semi-compatible phases. These blends have been thoroughly studied by various techniques (36-52) and it has been shown that by varying the concentration of vinyl acetate (VA) in the copolymer and the composition of EVA in the blend, one may observe the different phase relations.

The VA concentration in the EVA copolymer appears to be the controlling factor concerning the compatibility of the EVA/PVC blends. When the VA concentration is less than 40 or greater than 75 weight %, it is commonly accepted that the corresponding copolymer is immiscible with PVC. The EVA/PVC blend goes through what may be termed a "window of miscibility" when the VA concentration of the copolymer is between 40 and 75 weight % (39). In this VA concentration region there exists at least partial compatibility between the EVA copolymer and poly(vinyl chloride). Blends of EVA/PVC containing 60–75 weight % VA in the EVA copolymer have been found to be completely miscible; whereas, only partial compatibility has been suggested for blends when the VA concentration is between 40 and 60% (36-52).

Runt et al. (39-41) have shown that blends of an
ethylene-vinyl acetate copolymer containing 45% by weight VA (EVA45) and PVC are completely miscible only at the composition extremes of the blend. When the EVA45 concentration is between 10 and 75%, the blends have been described as semi-compatible. There has been some debate regarding the nature of this compatibility and several articles have reviewed this aspect of the EVA45/PVC blend (36-52).

Another interesting feature of some of the EVA/PVC blends is the presence of a lower critical solution temperature (LSCT) prior to degradation of the blend. A blend of EVA/PVC containing 70% VA by weight in the EVA copolymer (EVA70) has been found to exhibit a LCST at the PVC rich composition extreme (39-41). Blends of EVA45/PVC are known to be particularly temperature sensitive. It has been shown that phase separation takes place at temperatures as low as 60°C (39-41). The resulting phase separation is almost complete by 130°C. The change in composition of a phase is dependent on the migration of PVC out of the phase with the lower glass transition temperature (Tg) at temperatures often lower than the Tg temperature of pure PVC (39).

Fourier-transform infrared (FTIR) studies on blends containing EVA45/PVC have established that a weak form of hydrogen bonding exists between the carbonyl oxygen of the copolymer and the methine hydrogen of PVC (42). The frequency of the carbonyl stretching band was monitored
and an estimation was made to the strength of the interaction as a function of temperature. It was observed that as the temperature was increased the frequency shifted to a higher wavenumber indicating a decrease in the strength of the hydrogen bond. At elevated temperatures above the LCST the shift in the wavenumber was not observed.

Differential scanning calorimetry (DSC) has also been used to study the compatibility in blends of EVA copolymers with PVC (43). Blends of EVA45/PVC were found to have two glass transitions shifting toward each other with increasing EVA content in the blend. The lower temperature transition was observed to spread over an extended temperature range thereby making an estimation of the Tg difficult. This broadening was explained by partial mixing of the two components to form a semi-compatible blend. Elmqvist and Svanson (43) also tested the temperature sensitivity of this blend by heating the sample to 170°C for 40 minutes. After quenching the sample down to room temperature, DSC results indicated that the polymers in the blend had separated into two distinct phases by the presence of two glass transition temperatures in the blend.

Compatibility and phase behavior of EVA/PVC blends have also been studied by dielectric relaxation studies. When studying the miscibility of polymer blends by dielectric relaxation techniques, one determines the
presence and location of the temperature maximum of the loss peaks at a given frequency. Homogeneous or miscible blends will generally give a single loss peak while immiscible or heterogeneous blends will yield multiple loss peaks. Runt and coworkers (39-41) have extensively studied two EVA/PVC blends by this method: EVA45/PVC and EVA70/PVC. EVA70/PVC blends at the different compositions exhibited a single loss peak with the exception of the 15/85 EVA70/PVC blend. This indicates that these blends are completely miscible over the composition range when the EVA70 content is greater than 15%. It was found for the 15/85 EVA70/PVC blend that upon heating a second loss peak becomes evident. The magnitude of the major loss peak increased with heating. This increase is consistent with a lower critical solution temperature which indicates a decrease of EVA70 in the higher relaxation phase.

The EVA45/PVC blend was also studied over the composition range by dielectric methods. The EVA45/PVC blends were found to be miscible at the composition extremes as evidenced by a single loss peak. However, at the intermediate compositions (approximately 10-75% EVA45) these blends exhibited two loss maxima corresponding to a two-phase blend. It was determined that one phase consisted of nearly pure PVC while the other comprised a mixed EVA45-PVC phase. The miscible and partially compatible blends underwent phase separation at temperatures as low as 55°C except for the 90/10 which was stable up to 120°C.
2.1 Purpose

The thermal stability of polymers and polymer blends must be considered when selecting polymeric materials for a specific application. Poly(vinyl chloride) is one of the most widely used commercial polymers. Its applications range from plastic wrapping to a fire retarder. However, PVC is not a very thermally stable polymer with an initial degradation temperature in a nitrogen atmosphere at approximately 250°C. There are also health factors to consider when choosing PVC since hydrogen chloride is given off when it degrades.

In addition to low thermal stability, PVC has a glass transition temperature of approximately +85°C. Therefore, at room temperatures PVC is a brittle polymer and may only be used for applications in which there is little stress involved.

Despite these potential problems, PVC is still widely used because it may be blended with another polymer or an additive in order to improve upon a specific property. Ethylene-vinyl acetate copolymers are often blended with PVC to plasticize the PVC. Blends containing EVA copolymers and PVC have the distinction of having varying degrees of miscibility. The study of the thermal stability of these blends should be of interest.

The purpose of this research is to study the effects of miscibility on the thermal degradation of polymer
blends containing PVC. McNeill (35) studied the immiscible poly(vinyl acetate)/PVC blend and observed that the blend was destabilized when compared to predicted behavior. The EVA copolymers degrade by a similar mechanism to that of PVA and have varying degrees of compatibility with PVC. Therefore, a study was performed in order to determine if the miscibility of the blend contributed to the degradation of the blend.
3 EXPERIMENTAL

3.1 Polymers Used In This Study

The PVC and PVA used were obtained from Polysciences Inc. and have reported number average molecular weights of 93,000 and 500,000 grams/mole respectively. The EVA70 and EVA45 samples were provided by Mobay Chemical Corporation. The molecular weight of the EVA samples are reported to be in the range from 100,000 to 120,000 grams/mole. Table 1 gives the structure, molecular weight, inherent viscosity and source for each of the samples used in this study.
<table>
<thead>
<tr>
<th>POLYMER</th>
<th>ABBREVIATION</th>
<th>STRUCTURE</th>
<th>MOLECULAR WEIGHT</th>
<th>INHERENT VISCOSITY&lt;sup&gt;c&lt;/sup&gt;</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLY(VINYL CHLORIDE)</td>
<td>PVC</td>
<td>(-\text{CH}_2-\text{CH}-)</td>
<td>93,000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.94</td>
<td>POLYSCIENCES INC.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{Cl}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POLY(VINYL ACETATE)</td>
<td>PVA</td>
<td>(-\text{CH}_2-\text{CH}-)</td>
<td>500,000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.46</td>
<td>POLYSCIENCES INC.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{0}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{C=0}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{CH}_3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETHYLENE-VINYL ACETATE EVA45</td>
<td>(-\text{CH}_2-\text{CH}_2) -- (\text{CH}_2-\text{CH})&lt;sub&gt;x&lt;/sub&gt;</td>
<td>100,000-120,000&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.51</td>
<td>MOBAY CHEMICAL CO.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{0}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{C=0}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{CH}_3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{45 wt % vinyl acetate}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETHYLENE-VINYL ACETATE EVA70</td>
<td></td>
<td></td>
<td></td>
<td>0.70</td>
<td>MOBAY CHEMICAL CO.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>\text{70 wt % vinyl acetate}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Number average molecular weight  
<sup>b</sup> Unspecified molecular weight reported by manufacturer  
<sup>c</sup> All solutions 0.5 g/dL in THF at 30°C
3.2 Sample Preparation

The polymers used in this study were purified by precipitation from a nonsolvent such as methanol for PVA and the EVA copolymers or hexane for PVC. The purified polymers were each dissolved in tetrahydrofuran (THF) to produce a 2% (w/v) solution. The solutions were prepared by mixing the appropriate volumes of the respective polymer solution into 20 ml sample vials. The sample vials were shaken for at least 1 hour to ensure proper mixing. The solutions containing the blends were cast into petri dishes. The petri dishes were placed in a hood and covered with a watchglass to prevent any contamination from the outside environment. The solvent was allowed to evaporate in a hood. In order to remove any residual solvent, the resulting film was placed in a vacuum oven at 70°C for 48 hours.

Despite the drying efforts, PVC and PVC rich films still retained approximately 4% residual THF solvent. In an effort to avoid this circumstance, the films in question were additionally treated by heating under a dynamic nitrogen atmosphere (40 ml/min) at 150°C for 10 minutes.
3.2 Instrumentation

The TGA experiments were performed on a Perkin-Elmer TGS-2 connected to a Perkin-Elmer thermal analysis data station. All analyses were run under a dynamic nitrogen atmosphere with a flow rate of 40 ml/min and programmed heating rates of 1, 5, 10, 20 and 40°C/minute. The sample weights ranged from 3 to 5 mg.

Direct pyrolysis-mass spectroscopic (DPMS) experiments were performed on a Hewlett-Packard Gas Chromatograph/Mass Spectrometer Model 5996. The pure polymers and blends were degraded directly into the ion source using a direct insertion probe heated from 100 to 350°C at a heating rate of 1°C/minute. Electron impact (EI) mass spectra were obtained at 18 eV. The mass analyzer and ion source were held constant at 200°C. The instrument scanned from m/z=3 to m/z=300 at a rate of 0.18 scans per second.
POLY(VINYL ACETATE)/POLY(VINYL CHLORIDE) BLENDS

PVC is a very commercially important polymer with several everyday applications. At room temperatures PVC does not have very good mechanical properties therefore, a plasticizer must be added to improve upon these properties. When PVC is blended with another polymer or plasticizer, the plasticizer is added in small quantities relative to the amount of PVC. The addition of a plasticizer may often sufficiently change the mechanical properties to make it feasible for use in a wider range of applications. Due to the commercial importance of PVC blends, a study of their thermal stability is interesting.

4.1 Thermogravimetric Analysis of PVA/PVC Blends

TGA thermograms for PVC and PVA recorded at heating rates of 1, 5, 10, 20, and 40°C/minute were shown in Figures 3 and 4, respectively. In these plots, C, which is the degree of conversion is defined as

\[ C = \frac{(w_o - w)}{(w_o - w_f)} \]

where \( w_o \) and \( w_f \) are the initial and final weights and \( w \) is the weight at any time. At each heating rate the polymers degrade in well defined two-step processes. The first step in the thermal degradation of both PVA and PVC involves the loss of either HAc or HCl to yield similar polyenes while the second step is the decomposition of the
Figure 3. TGA thermograms of PVC recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
Figure 4. TGA thermograms of PVA recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
resulting polyene chain (19,36). The activation energy for the first step of the degradation has been calculated by the Flynn-Wall method to be 38.8 kcal/mole for PVA and 35.5 kcal/mole for PVC. The calculated activation energies are in good agreement with previously reported values (55,56).

The degradation of a 50/50 PVA/PVC blend also proceeds by a two-step process. Figure 5 shows the weight-loss curves recorded at different heating rates for a 50/50 PVA/PVC blend.

The observed and predicted TGA thermograms for a 50/50 PVA/PVC blend at 1°C/minute are compared in Figure 6. The predicted thermogram was constructed from the additivity of the thermograms recorded at 1°C/minute for both pure PVA and PVC. As can be seen the blend is less thermally stable than would be predicted. These results are similar to those observed by McNeill for the same blend (see Figure 2) even though McNeill used a slightly different sample weight and flow rate. This accelerated weight loss is due to the effects of one acid produced by the degradation of a polymer reacting with the other polymer chain in the blend by the mechanisms proposed by McNeill (30). From the weight-loss curve of a 50/50 PVA/PVC blend recorded at a heating rate of 1°C/minute, the blend has only 64% of the original weight remaining at 290°C compared to a predicted weight percent of 75%. The amount of destabilization remained constant regardless of
Figure 5. TGA thermograms of a 50/50 PVA/PVC blend recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute (D) 20°C/minute, and (E) 40°C/minute.
Figure 6. Observed and predicted weight-loss curves at 10°C/minute for a 50/50 PVA/PVC blend.
the heating rate employed.

In order to determine what effect mixing has upon the thermal degradation of PVA/PVC blends, experiments were performed in which the samples consisted of layers of the pure polymers instead of blended films. The films of the pure polymers were added in approximately equal weights. The behavior of the samples remained relatively constant without regard to the order of the layering. At 290°C the weight-losses for the layered samples differed by only 2% which is within experimental error.

In addition to studying the thermal degradation behavior of the 50/50 PVA/PVC blend, the composition extremes were also studied. The 10/90 PVA/PVC blend at 290°C was shown to have 52% of the original weight remaining which is significantly less than the 66% expected. This blend has approximately an equal degree of destabilization to that of the 50/50 PVA/PVC blend because of the excess volatile HCl given off at this composition extreme. One might expect that by effectively increasing the HCl concentration, by addition of greater amounts of PVC to the blend, the deacetylation of PVA would occur to a greater degree. TGA analyses of the 90/10 PVA/PVC blend were not performed because the film had gross phase separation. Therefore, it was not possible to obtain a sample representative of the 90/10 PVA/PVC composition.
4.2 Direct Pyrolysis Mass Spectrometry of PVA/PVC Blends

The thermal degradation of polymers and polymer blends have been studied by direct pyrolysis-mass spectrometry. When this technique is used the sample bypasses the gas chromatograph on a GC/MS and is inserted directly into the ion source. The samples were degraded in vacuum from 100°C up to 350°C at a heating rate of 1°C/minute.

Figure 7(a) show the mass spectral analysis of PVA taken at the maximum of the total ion current (TIC) while Figure 7(b) shows the TIC for pure PVA. The TIC is related to the rate of ionization for the sample in question. When a sample is fragmented in a mass spectrometer a current is produced by the resulting positively charged ions. This current reaches a maximum when the rate of ionization is also at a maximum. As previously mentioned, the degradation of pure PVA occurs by a two-step process. The first step involves nearly complete deacetylation and the second step is the decomposition of the resulting polyene chain. Acetic acid should fragment to give peaks in the mass spectrum corresponding to mass to charge (m/z) ratios of 15, 43, 45 and the parent peak at 60 (40). At elevated temperatures HAc has been known to thermally degrade in small quantities to give carbon dioxide (m/z=44) and methane.
Figure 7. (a) The mass spectrum of PVA recorded at a heating rate of 1°C/minute with T=304°C, and (b) The total ion chromatograph of PVA recorded at a heating rate of 1°C/minute.
(m/z=16) (41). From Figure 7(a) the electron impact (EI) fragmentation of acetic acid yields peaks corresponding to m/z=15, 43, 45 and 60. There are peaks of smaller intensity that correspond to the thermal breakdown of HAc before reaching the ionization source.

The TIC for pure PVA is shown in Figure 7(b). The output from the mass spectrometer is in minutes. In order to convert minutes to temperature (°C), add one hundred to the time since the initial temperature is 100°C at zero minutes. The maximum observed by monitoring the TIC were in good agreement with maximum obtained from the derivative of the weight-loss curve from TGA experiments. The maximum of the TIC occurred at 304°C and the maximum of the derivative at 300°C.

Figure 8 shows a three-dimensional representation of the DPMS analysis of a poly(vinyl acetate) sample. The three axes represented are mass, time and intensity. In figure 8 one can observe the behavior of the peaks for the formation of ions due to the fragmentation of HAc. The initial detection of the peaks appears to not occur at the same time, however, this is a function of the lower detection limit which eliminates noise in the spectrum. The maximum for all the peaks occurs at the same time.

Figure 9(a) shows that the mass spectrum corresponding to the dehydrochlorination of PVC. This spectrum contains primarily a series of peaks at m/z=35, 36, 37 and 38 corresponding to positively charged ions of
Figure 9. (a) The mass spectrum of PVC recorded at a heating rate of 1°C/minute with $T=283°C$, and (b) The total ion chromatograph of PVC recorded at a heating rate of 1°C/minute.
$^{35}\text{Cl}$, $^{35}\text{Cl}$, $^{37}\text{Cl}$ and $^{37}\text{Cl}$. These results confirm that the degradation of PVC does involve the dehydrochlorination of the chain to yield a polyene. Trace amounts of benzene have also been observed at m/z=78 in the degradation of PVC. This is a result of a ring cyclization reaction that occurs during the dehydrochlorination of PVC.

The TIC for a PVC sample is shown in Figure 9(b). The temperature at the maximum of the TIC is 283°C while the temperature at the maximum of the derivative from TGA analyses is 280°C. A close relationship is seen again between these two values.

Figure 10(a) shows the DPMS results for a 50/50 PVA/PVC blend. During the degradation of the blend, all peaks due to the EI fragmentation of the blend corresponds exactly to the peaks from the EI fragmentation of PVA or PVC. McNeill observed that a trace amount of acetyl chloride is the only product from the blend that is not obtained from the degradation of the pure polymers. It is not possible to determine whether the peak in the mass spectrum at m/z=78 corresponds to acetyl chloride, benzene or a combination of both because acetyl chloride and benzene both have a molecular weight of 78 grams/mole.

The TIC for a 50/50 PVA/PVC sample is shown in Figure 10(b). As in the case of the pure polymers, the maximum of the TIC and the maximum obtained from the derivative of the weight-loss curve are in good agreement. The maximum
Figure 10. (a) The mass spectrum of a 50/50 PVC/PVA blend recorded at a heating rate of 1°C/minute with T=279°C, and (b) The total ion chromatograph of a 50/50 PVC/PVA blend recorded at a heating rate of 1°C/minute.
of the derivative of the weight-loss curve occurred at 282°C while the maximum obtained from the maximum of the TIC occurred at 279°C.

The amounts of HCl and HAc evolved from these samples can be determined as a function of temperature from the mass spectra. The percentage of acid evolved is found by monitoring one of the peaks of interest and integrating the area under the curve at several temperatures. The peaks monitored were m/z=36 and 43 for the evolution of hydrogen chloride and acetic acid. Figure 11 shows the amounts of HCl and HAc evolved from PVC, PVA and a 50/50 PVA/PVC blend. In a 50/50 PVA/PVC blend, production of both acids is slightly accelerated when compared to the pure polymers. For example, at 290°C, the blend has evolved approximately 63% of the HCl possible while pure PVC has lost only 50%. The amount of HAc evolved at this temperature in the blend is accelerated from approximately 31% of the total evolved compared to only 21% evolved in pure PVA. These results indicate that the destabilization of an immiscible blend containing PVC and PVA arises from accelerated production of both acids.
Figure 11. DPMS data for the estimation of evolved from the degradation of PVC, PVA, and a 50/50 (w/w) PVC/PVA blend
+ from pure PVC,
□ from PVC in the blend
△ from pure PVA,
◇ from PVA in the blend.
Ethylene-vinyl acetate copolymer/poly(vinyl chloride) blends exhibit varying degrees of miscibility. The factor controlling the miscibility in these blends is the vinyl acetate concentration in the copolymer. When the VA concentration is less than 40 or greater than 75 weight % it is commonly accepted the corresponding copolymer is immiscible with PVC. The EVA/PVC blend goes through what may be termed a "window of miscibility" when the VA concentration of the copolymer is between 40 and 75 weight % (39). Runt et al. (39-41) have shown the EVA45/PVC blends are completely miscible only at the composition extremes. When the EVA 45 concentration is between 10 and 75%, the blends are semi-compatible. Blends of EVA/PVC containing 60-75 weight % VA in the EVA copolymer have been found to be completely miscible (39-41). Ethylene-vinyl acetate copolymers have been used as commercial modifiers for PVC. Because EVA/PVC blends have differing degrees of miscibility and are commercially important, a study of their thermal behavior might provide valuable information regarding their thermal stability and the effects of processing temperatures upon these blends.

5.1.1 Thermogravimetric Analyses of EVA-70/PVC Blends

The weight loss curves for pure EVA70 recorded at
heating rate of 1, 5 10, 20 and 40°C/minute are shown in Figure 12. The degradation of EVA copolymers is known to occur by a two process (19). The first step involves the deacetylation of the polymer while the second step in the degradation is a result of decomposition of the polyene chain. The activation energy for an EVA70 copolymer has not been reported upon in the literature. The activation energy for the deacetylation of an EVA70 copolymer has been calculated in this study to be 39.8 Kcal/mole by the Flynn-Wall method.

The degradation of a 50/50 EVA70/PVC blend proceeds by a two-step process. Figure 13 shows the weight-loss curves recorded at different heating rates for a 50/50 EVA70/PVC blend. The first step in the degradation of both pure PVA and EVA70 involve the deacetylation of the polymer; therefore, it might be assumed that an EVA70/PVC blend would degrade by processes similar to that proposed by McNeill for a PVA/PVC blend.

The observed and predicted thermograms for a 50/50 EVA70/PVC blend at a rate of 1°C/minute are compared in Figure 14. In this case, the blend is much less thermally stable than predicted. From the weight-loss curve of a 50/50 EVA70/PVC blend recorded at a heating rate of 1°C/minute, at 290°C the blend has 58% of the original weight remaining compared to a predicted weight percent of 77%. At 290°C a 50/50 EVA70/PVC blend is destabilized 20 percent more than would be predicted.
Figure 12. TGA thermograms of EVA70 recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
Figure 13. TGA thermograms of a 50/50 EVA70/PVC blend recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
Figure 14. Observed and predicted weight-loss curves for a 50/50 EVA70/PVC blend recorded at a heating rate of 1°C/minute.
compared to the 11% destabilization observed in a 50/50 PVA/PVC blend. It is very important to realize that the 50/50 EVA70/PVC blend contains a lower concentration of acetate groups than does a 50/50 PVA/PVC blend yet shows twice the amount of destabilization. This degree of destabilization remained constant with the different heating rates. These results indicate that the destabilization arises because of the close mixing in this miscible blend. Once volatile products are expelled from a polymer in the blend, they are already in a position to catalyze the loss of the other acid.

Layering experiments were performed to determine what effects mixing has upon the thermal degradation of a EVA70/PVC blend. There is slightly more weight loss when PVC is the bottom layer because PVC is less thermally stable than EVA70. When PVC is the bottom layer the evolved HCl must migrate through the EVA70 layer thereby causing destabilization. When the bottom layer consists PVC, there is 72% weight remaining compared to 77% when EVA70 is the bottom layer at 290°C and a heating rate of 1°C/minute.

Runt et al. (39-41) determined that a LCST exists in EVA70/PVC blends at the PVC composition extremes. Because it was already known that a blend containing PVC with less than 25% EVA70 will phase separate upon heating, the extent of the destabilization in a 10/90 EVA70/PVC blend was determined. As the heating rate was increased from
1°C/minute to 20°C/minute, the difference between the observed and predicted temperatures for a 25% weight-loss increased. Table 2 shows the observed and predicted temperatures for a 25% weight-loss.

**TABLE 2**

The observed and predicted temperatures at which a 25% weight-loss occurs for a 10/90 (w/w) EVA70/PVC blend recorded at various heating rates.

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>Observed Temp. (°C)</th>
<th>Predicted Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>270</td>
<td>283</td>
</tr>
<tr>
<td>5</td>
<td>282</td>
<td>303</td>
</tr>
<tr>
<td>10</td>
<td>289</td>
<td>316</td>
</tr>
<tr>
<td>20</td>
<td>303</td>
<td>334</td>
</tr>
</tbody>
</table>

These results can be easily explained if one recalls that the components of the blend are phase separating. When a slower heating rate is used, phase separation will occur to a greater extent before the onset of degradation of the blend. However, at the faster heating rates, the polymers in the blend are still significantly mixed on the molecular level when degradation occurs. Therefore, the extent of this destabilization is related to both the
miscibility of the blend and the heating rate employed.
5.1.2 Direct Pyrolysis Mass Spectrometry of EVA70/PVC Blends

Figure 15(a) shows the mass spectral analysis for EVA70 at the maximum of TIC. In Figure 15(a) the peaks qualitatively correspond to the same peaks observed for pure PVA. This result was expected since both evolve HAc during the first step of their degradations. Acetic acid has already been shown to fragment to yield a series of peaks at m/z=15, 43, 45 and 60.

The TIC for pure EVA70 is shown in Figure 15(b). The maximum observed by monitoring the TIC was in good agreement with the maximum of the derivative of the weight-loss curve from TGA experiments. The maximum of the TIC for EVA70 occurred at 311°C and the maximum of the derivative of the weight-loss curve was at 310°C.

Figure 16(a) shows the DPMS results for a 50/50 EVA70/PVA blend. During the degradation of this blend, there were no new observed fragmentation patterns in comparison to the pure polymers or in comparison to a 50/50 PVA/PVC blend. The TIC for a 50/50 EVA70/PVC blend are shown in Figure 16(b). The maximum of the TIC occurred at 275°C for a 50/50 EVA70/PVC blend. This maximum temperature is close to the maximum temperature of the derivative obtained from the weight-loss curves. The maximum of the derivative was at 280°C.

Figure 17 illustrates the amounts of HCl and HAc that
Figure 15. (a) The mass spectrum of EVA70 recorded at a heating rate of $1^\circ\text{C}/\text{minute}$ with $T=311^\circ\text{C}$, and (b) The Total ion chromatograph of EVA70 recorded at a heating rate of $1^\circ\text{C}/\text{minute}$.
Figure 16. (a) The mass spectrum of a 50/50 EVA70/PVC blend recorded at a heating rate of 1°C/minute with T=275°C, and (b) The total ion chromatograph of a 50/50 EVA70/PVC blend recorded at a heating rate of 1°C/minute.
are evolved as a function of temperature for PVC, EVA70 and a 50/50 EVA70/PVC blend. In the blend, production of both acids is greatly accelerated when compared to the pure polymers. This point is illustrated by the fact at 290°C the blend has evolved approximately 85% of the HCl possible while PVC has lost only 50%. The amount of HAc evolved at this temperature in the blend is accelerated from 58% evolved to only 24% evolved in EVA70. Compared to a PVA/PVC blend these results show a drastic increase in production of the acids even though there is fewer acetate units in the blend. Therefore, the miscibility of the blend must have a greater influence on the destabilization of the blend than that of the concentration of acetate units in the blend.
Figure 17. DPMS data for the estimation of evolved acids from the degradation of PVC, EVA70, and a 50/50 (w/w) PVC/EVA70 blend.

+ from pure PVC,

Δ from pure EVA70,

□ from PVC in the blend,

◊ from EVA70 in the blend.
5.2.1 Thermogravimetric Analyses of EVA45/PVC Blends

TGA thermograms for the degradation of an EVA45 copolymer recorded at heating rates of 1, 5, 10, 20 and 40°C/minute are shown in Figure 18. The degradation of EVA copolymers have already been shown in a previous section to proceed by a two-step process. The activation energy for the loss of acetic acid for this EVA copolymer has been calculated by the Flynn-Wall method to be 41.8 kcal/mole.

The degradation of a 50/50 EVA45/PVC blend recorded at heating rates of 1, 5, 10, 20 and 40°C/minute is shown in Figure 19. The degradation of this blend also proceeds by a two-step process.

In Figure 20 the observed and predicted weight-loss curves for a 50/50 EVA45/PVC blend at 1°C/minute are compared. As might be expected from previous examples, the observed weight-loss curve is less thermally stable. The 50/50 EVA45/PVC blend composition is known to phase separate upon heating. As the heating rate was increased from 1°C/minute to 20°C/minute, the difference between the observed and predicted temperatures for a 25% weight-loss also increased. Table 3 shows the observed and predicted temperatures for a 25% weight-loss.
Figure 18. TGA thermograms of EVA45 recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
Figure 19. TGA thermograms of a 50/50 EVA45/PVC blend recorded at heating rates of (A) 1°C/minute, (B) 5°C/minute, (C) 10°C/minute, (D) 20°C/minute, and (E) 40°C/minute.
Figure 20. Observed and predicted thermograms for a 50/50 EVA45/PVC blend at a heating rate of 1°C/minute.
TABLE 3

The observed and predicted temperatures at which a 25\% weight-loss occurs for a 50/50 (w/w) EVA45/PVC blend recorded at various heating rates.

<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>Observed Wt. % (°C)</th>
<th>Predicted Wt. % (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>290</td>
<td>295</td>
</tr>
<tr>
<td>5</td>
<td>297</td>
<td>305</td>
</tr>
<tr>
<td>10</td>
<td>320</td>
<td>330</td>
</tr>
<tr>
<td>20</td>
<td>330</td>
<td>350</td>
</tr>
</tbody>
</table>

As expected the difference between the observed and predicted temperatures increases as the heating rate increases. As previously mentioned, blend exhibiting a LCST separate to a greater extent upon heating before the onset of degradation at the slower heating rates. There are two important factors to account for when considering the degree of destabilization in an EVA45/PVC blend. First, a 50/50 EVA45/PVC blend contains even fewer acetate units than the 50/50 EVA70/PVC blend. Secondly, a 50/50 EVA45/PVC blend has been observed to be partially compatible whereas a PVA/PVC blend is immiscible (40). This blend exhibits two phases, one pure PVC the other a mixed phase consisting of EVA45 and PVC.

Layering experiments were also performed on 50/50 EVA45/PVC blends. The results did not vary much when
equal amounts of the polymers were layered. There was 81% weight remaining when PVC was on the bottom layer compared to 83% when the bottom layer consisted of EVA45. The difference is within experimental error.

The composition extremes for an EVA45/PVC blend were also studied with respect to their thermal stability. It has already been shown that EVA45 forms miscible blends with PVC at the composition extremes and that phase separation will occur at these compositions (39-41). Table 4 compares the observed and predicted temperatures at a 25% weight-loss at different heating rates for the 10/90 blend composition. No destabilization was detected in the 90/10 EVA45/PVC blend.

**TABLE 4**

The observed and predicted temperatures at which a 25% weight-loss occurs for a 10/90 (w/w) EVA45/PVC recorded at various heating rates.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>Observed</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. %</td>
<td>Wt. %</td>
</tr>
<tr>
<td></td>
<td>(°C)</td>
<td>(°C)</td>
</tr>
<tr>
<td>1</td>
<td>272</td>
<td>284</td>
</tr>
<tr>
<td>5</td>
<td>288</td>
<td>305</td>
</tr>
<tr>
<td>10</td>
<td>308</td>
<td>326</td>
</tr>
<tr>
<td>20</td>
<td>314</td>
<td>334</td>
</tr>
</tbody>
</table>

Since the temperature difference increases with
increasing heating rate, the 10/90 blend must be passing through a lower critical solution temperature. Despite the fact that the 90/10 EVA45/PVC blend is phase separating there is very little destabilization. Even at the miscible composition extremes a blend of EVA45/PVC will phase separate. In a 90/10 EVA45/PVC blend there is very little HCl to cause any destabilization of the EVA45.
5.2.2 Direct Pyrolysis Mass Spectrometry of EVA45/PVC Blends

The results for an EVA45 copolymer and a 50/50 EVA45/PVC blend by DPMS were qualitatively similar to that obtained for an EVA70 copolymer and blend containing EVA70 and PVC. The m/z ratios observed were identical when comparing the pure polymers to the blends containing the polymers only the relative amounts of each varied. An EVA45/PVC blend must degrade by the same processes as the EVA70/PVC blend because of the similar m/z ratios detected in each case.

The EVA45 and 50/50 EVA45/PVC blend were the only case where the maximum of the derivative obtained from TGA did not match very well with the maximum from the total ion current. The maximum of the TIC for EVA45 and a 50/50 EVA45/PVC blend were 330°C and 311°C, respectively. The maximum of the derivative obtained from the weight-loss curves were 315°C and 289°C for the EVA45 and 50/50 EVA45/PVC blend.

Figure 21 illustrates the amount of both acids produced as a function of temperature for pure PVC, EVA45 and a 50/50 EVA45/PVC blend all at heating rates of 1°C/minute. Again, production of both acids is accelerated when compared to the pure polymers. However, when compared to the other blends studied, a 50/50 EVA45/PVC blend showed an intermediate degree of
Figure 21. DPMS data for the estimation of evolved acids from the degradation of PVC, EVA45, and a 50/50 (w/w) PVC/EVA45 blend.
+ from pure PVC,
\(\Delta\) from EVA45,
\(\Box\) from PVC in the blend,
\(\Diamond\) from EVA45 in the blend.
destabilization even though there are much fewer acetate groups in blend containing EVA45.
CONCLUSIONS

The thermal degradation of blends of PVC and vinyl-acetate containing polymers has been studied to examine the affects of miscibility on the thermal stability. The amount of destabilization differed between the blends depending upon the degree of miscibility of the blend. In each blend, the loss of HCl from the less thermally stable PVC catalyzes the loss of acetic acid from the polymer containing vinyl-acetate. The destabilization is continued by (a) the HAc catalyzing the loss of HCl and (b) the autocatalytic dehydrochlorination and deacetylation of the respective polymers (30).

The degree of destabilization of the EVA and PVA polymers in the presence of PVC varied for each blend. The EVA70/PVC blends showed the largest amount of destabilization even though there was a lower concentration of acetate units when compared to PVA/PVC blends of the same compositions. The thermal stability of EVA70/PVC blends should be of industrial interest because EVA70 is used commercially as a modifier for PVC. Therefore, the processing temperature and the amount of time spent at elevated temperatures should be a prime concern when blending EVA70 with PVC.

The EVA45/PVC blends were extremely temperature sensitive and phase separated upon heating. The degree of destabilization exhibited by these blends was found to be
a function of the heating rate. At the faster heating rates the blend phase separates to a lesser degree and therefore a greater amount of destabilization was observed.

Additional work is needed to further support the claims of this research project. Ion-selective and acid-base titrations could be used to follow the HCl and total acids evolved, respectively. If the HCl catalyzes the loss of HAc from the vinyl-acetate containing polymer, then titrations would be able to detect any premature evolution of either acid when compared to their respective pure polymers. As polymer blends are finding greater commercial importance, it becomes increasingly important to understand what affects miscibility has upon thermal stability.
REFERENCES

43. Elmqvist, C., Svanson, S. E., Europ. Polym. J., 1976, 12, 559-61