Miscibility studies of poly (methyl acrylate) poly (vinyl acetate) and poly (vinyl acetate)/ poly (vinylidene fluoride) blends using differential scanning calorimetry and fourier transform infra red spectroscopy

Godwin O. Oghide

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MISCIBILITY STUDIES OF POLY(METHYL ACRYLATE)/ POLY(VINYL ACETATE) AND POLY(VINYL ACETATE)/POLY(VINYLDENE FLUORIDE) BLENDS USING DIFFERENTIAL SCANNING CALORIMETRY AND FOURIER-TRANSFORM INFRA-RED SPECTROSCOPY

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

BY

GODWIN OSARENMWINDA OGHIDE

DEPARTMENT OF CHEMISTRY
ATLANTA, GEORGIA
DECEMBER 1985
ABSTRACT

CHEMISTRY

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B.S. KENTUCKY STATE UNIVERSITY, 1980  
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MISCIBILITY STUDIES OF POLY(METHYL ACRYLATE)/POLY(VINYL ACETATE) AND POLY (VINYL ACETATE)/POLY(VINYLDENE FLUORIDE) BLENDS USING DIFFERENTIAL SCANNING CALORIMETRY AND FOURIER-TRANSFORM INFRA-RED SPECTROSCOPY

Advisor: Professor Edward Korda  
Thesis dated December 1985

The miscibility of poly(methyl acrylate)/poly(vinyl acetate) (PMA/PVAc) and poly(vinyl acetate)/poly(vinylidene fluoride) (PVAc/PVF₂) blends has been studied. Films of compositions 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 (w/w) were cast for each system. Films of PMA/PVAc were found transparent and those of the PVAc/PVF₂ were slightly opaque. While all the compositions of the PMA/PVAc exhibit single sharp Tgs, as measured with the differential scanning calorimeter, almost all of those of the PVAc/PVF₂ exhibit single broad Tgs. By the single Tg criterion, the PVA/PVAc and PVAc/PVF₂ systems are miscible in all proportions. Fourier transform infra-red spectroscopy spectra indicate molecular interaction complex involvement in the two systems. Evidence for such interaction was found to be significant in the 80% PMA/20% PVAc and 20% PVAc/80% PVF₂ compositions.
DEDICATION

To my mother, Ilevba, to my sisters: Ester, Mabel, Margaret, Felicia and Mary and their families, to my brothers: Gabriel, David, Anthony and Henry and their families for their love and support. Finally, to the beloved memories of my late father and sister, Pa Oghide Uwaifo and Grace, for the special role they played in my life.
ACKNOWLEDGEMENTS

The author expresses his sincere gratitude to his advisor, Professor Edward Korda, for his consistent help, guidance, understanding, and encouragement throughout the course of these studies. A special thanks to Dr. Frank Cummings for his inspiration and understanding.

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INTRODUCTION

Recently, polymer blends have become a very important subject for scientific investigation owing to their potential technical importance.\textsuperscript{1-4} A polymer blend may be defined as a combination of two or more polymers resulting from common processing steps, such as mixing of two polymers in the molten state or casting from a common solvent.\textsuperscript{3,5} Blending has been found to be a useful method for the modification of polymer properties. Compared to copolymerization, which has been the main alternative route for the modification of polymer properties, blending is a less expensive method. Although blending does not always provide a satisfactory alternative to copolymerization, it has been successfully used in an increasing number of applications in recent years. Such successes have encouraged more attempts to apply blending techniques to a wide range of industrial polymer-related applications.

There are two types of polymer blends: immiscible and miscible. Immiscible blends are characterized by phase separation and multiple glass transition temperatures (T_g). A miscible polymer has properties distinctly different from two-phase polymer mixtures in that the miscible blend exhibits a single T_g. The glass transition temperature of a polymer is the temperature at which the amorphous phase of the polymer is converted from a rubbery to a glassy state.\textsuperscript{6} Since the glass transition temperature is related to the physical properties, such as
modulus-temperature behavior, creep, viscosity, crystallization rate and impact strength, there will be a pronounced difference between miscible and immiscible polymer blends.\textsuperscript{7}

Examples of some commercially useful immiscible polymer blends are bisphenol A polycarbonate/ABC (Cycoloy, Bayblend), polypropylene/ethylene-propylene rubber (TPR, Somel, Telcar), chlorinated polyethylene/PVC and poly(methyl methacrylate)/PVC (Kydex, DKE).\textsuperscript{7} An example of a miscible polymer blend is the widely used Noryl which is a blend of high impact polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide). This blend was developed in 1965 by General Electric and is available in more than sixteen grades. Noryl is used in small and large appliances, communications, business machines, automobiles, television components, electrical construction and in some specialty areas such as aircraft and recreational equipment.\textsuperscript{3}

Due to thermodynamic reasons, most polymer pairs are not miscible on the molecular level. In a nutshell, the Gibbs free energy of mixing consists of three contributions: the combinatorial entropy of mixing, the exchange interaction, and an equation of state or free-volume term.\textsuperscript{8-15} The last factor is in general unfavorable for mixing and increasingly so at higher temperatures. This extra unfavorable factor requires that a specific interaction (molecular interaction complex) such as hydrogen bonding, donor-acceptor interaction, charge transfer, etc., resulting in a negative exchange interaction contribution to the free energy of mixing, be a prerequisite for polymer-polymer miscibility.
The frequently used term when discussing polymer miscibility is the solubility parameter, \( \delta \),

\[
\delta = (\Delta U_V/V^o)^{1/2}
\]

where \( \Delta U_V (= \Delta H_V - RT) \) is the molar energy of vaporization at the boiling point and \( V^o \) is the molar volume of the liquid. The solubility parameter has the unit of \((\text{energy/volume})^{1/2}\); it is the square root of the cohesive energy density. The solubility parameter for a polymer is not directly determined experimentally since a polymer is ordinarily not vaporizable. However, the solubility parameter of a polymer is defined as equal to the solubility parameter of the solvent in which it dissolves (a) in all proportions, (b) without heat change, (c) without volume change and (d) without reaction or any special association.\(^{16}\)

Solubility parameters of solvents have been found to be related to the structure, molecular weight, and density of the solvent molecule.\(^1\) This relation has been applied to polymers where

\[
\delta = \bar{\rho}_{fi}/M_0
\]

in which \( \bar{\rho} \) is the density of the amorphous polymer at the solution temperature, \( \bar{\psi}_{fi} \) is the sum of all the molar attraction constants, and \( M_0 \) is the formula weight of the repeating unit. Small and Hoy have
published a table of molar-attraction constants which makes the estimation of solubility parameters very easy to determine. The solubility parameters (Table 1) of the polymers used in these studies were obtained from the Polymer Handbook. Since the solubility parameter of a solvent is based only on liquids which are not hydrogen bonded, erroneous solubility parameter values could be obtained when these tables of $\sqrt{F_i}$ are used for alcohols, amines, carboxylic acids or other strongly hydrogen bonded compounds, unless such functional groups constitute only a small part of the molecule.

Generally, miscibility is predicted if the absolute value of the difference in solubility parameters of the polymer and the solvent is zero or small. In terms of a specific figure, solubility can be expected if the difference is less than about 2 (cal cm$^{-3}$) $^{1/2}$, and there are no strong polar or hydrogen bonding interactions in either the polymer or the solvent. Also, it has been observed that mutual solubility may not be achieved even if the solubility parameters of the polymer and solvent are approximately equal when the two ingredients of the mixture have different tendencies for hydrogen bond formation. These miscibility factors, therefore, imply that in selecting polymers for miscible blends, the solubility parameters and the tendencies for hydrogen bond formation of the polymers and the solvent should be taken into proper consideration. The hydrogen bonding tendency for most polymers and solvents have been characterized qualitatively in the literature as poor, moderate, or strong.
The purpose of this investigation was to acquire the technique of making and evaluating the properties of miscible polymer blends. The method of approach was to study the miscibility behavior of two systems, amorphous/amorphous (A) and amorphous/crystalline (B). System A is poly(methyl acrylate)/poly(vinyl acetate) (PMA/PVAc) and B is poly(vinyl acetate)/poly(vinylidene fluoride) (PVAc/PVF2).

The PMA/PVAc and PVAc/PVF2 have been reported to be miscible as determined by various methods. The first report on the work that was done on the PMA/PVAc was the solution method reported in 1955. According to the report, equal amounts of the polymers were dissolved in three different solvents: acetone, dioxane and benzene. For all concentrations tried, they found no evidences of phase separation; each solution was clear. The second report on this system was on the torsional or shear modulus studies in which torsional moduli of the various films were obtained with a torsion wire type of apparatus. Plots on a log scale of the shear modulus versus temperature showed a single $T_g$ for the 50/50 composition cast from acetone. On the bases of the single $T_g$ and the clarity of the film, the system was deemed miscible.

In 1985 there was a third report on the PMA/PVAc system. The thermodynamic interaction between the PMA and PVAc molecules was studied using the method of inverse gas chromatography. In their analysis they used several polar and nonpolar solvent probes to determine the polymer-solvent interaction parameters, and from the data and measurements using several polymer blends as stationary phases values of the polymer-polymer interaction parameters for various blend compositions were evaluated.
By considering the wide variety of the probes with respect to polarity, hydrogen bonding, or donor-acceptor interaction capability, the closeness of the interaction parameters values for any given probe indicated that the polymers were of very similar chemical nature and of similar P-V-T properties. Thus, they found that "complementary dissimilarity" character, which leads to specific interactions, was absent between PMA and PVAc polymers.

Part II of the series of reports\textsuperscript{21} on the transitional behavior of blends containing PVF\textsubscript{2} and various oxygen-containing polymers dealt with the miscibility of PVAc/PVF\textsubscript{2} using differential thermal analysis (DTA) and Rheovibron (dynamic mechanical test). According to the report, solutions containing these polymers were clear, and the dried films developed opacity in proportion to the PVF\textsubscript{2} crystallinity. Before testing, all samples were annealed at 120\degree C for approximately one hr to maximize PVF\textsubscript{2} crystallinity. Thermal analysis data were obtained using a heating and cooling rate of 10\degree C/min between the limits of -150\degree and 200\degree C. Also, dynamic mechanical properties were obtained at 110 Hz using the Rheovibron. DTA and Rheovibron measurements showed (1) the existence of a single, composition dependent, glass transition temperature and (2) \( \alpha \) relaxation peak, respectively. In dynamic mechanical properties test, the \( \alpha \) peak is considered to be the result of a glass transition. The \( T_g \) for the pure PVF\textsubscript{2} was not detected by the DTA, but from the extrapolation of the plot of \( T_g \) versus composition, a value of -10\degree C was obtained for the \( T_g \) of pure PVF\textsubscript{2}. 
In Part IV of the same series,\textsuperscript{22} the depression of the PVF\textsubscript{2} melting point was analyzed using standard thermodynamic arguments to determine the heats of mixing between the amorphous diluents, PVAc being one of them, and PVF\textsubscript{2}. The heats of mixing were found to be exothermic indicating the presence of strong interactions between the binary pairs. From their data on the interaction strengths and the dipole moments of the various diluents, they concluded that the exothermic heat of mixing resulted from strong dipole-dipole interactions.

To my knowledge, there have been no Fourier-transform infrared spectroscopy (FTIR) investigations done on these systems. Hence, the PMA/PVAc and PVAc/PVF\textsubscript{2} systems were chosen for this study. Various compositions of the blend for the two polymer systems were prepared and their glass transition temperature determined with the differential scanning calorimeter (DSC). For these same systems and compositions the presence or absence of molecular interaction complexes were studied extensively with the aid of FTIR.
EXPERIMENTAL

Materials and Solutions

Table 1 lists the polymers that were used in this study. These polymers were purchased from Scientific Polymer Products. The molecular weight of the PVAc(ii) was determined at a concentration of 0.122 g/48.8 mL of polymer in chloroform at a flow rate of 2.0 mL/min with a Waters model 150C gel permeation chromatograph (GPC), M730 data module, on 10^4-\mu-styragel columns. The apparatus was calibrated with polystyrene standards. The molecular weights of the other polymers were obtained from the manufacturer.

Solvents used for dissolving the polymers were toluene, density 0.865 g/mL, and NN-dimethyl acetamide (DMAC), density 0.9366 g/mL.

The surfaces on which the polymer films were cast were glass slides and sodium chloride (NaCl) plates, 38mm x 19mm x 4mm. The sodium chloride plates were purchased from Wilmad Glass Company.
Table 1. List of Polymers Used in This Study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Acronym</th>
<th>Molecular Weight (Kg/mol)</th>
<th>Density (g/mL)</th>
<th>aSolubility Parameter (cal cm⁻³)₁/₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(methyl acrylate)</td>
<td>PMA</td>
<td>10.6</td>
<td>30.7</td>
<td>1.17</td>
</tr>
<tr>
<td>Poly(vinyl acetate)i</td>
<td>PVAc(i)</td>
<td>47.7</td>
<td>195</td>
<td>1.11</td>
</tr>
<tr>
<td>Poly(vinyl acetate)ii</td>
<td>PVAc(ii)</td>
<td>69.5</td>
<td>212.6</td>
<td>1.19</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>PVF₂</td>
<td>-</td>
<td>-</td>
<td>1.76</td>
</tr>
</tbody>
</table>

aThe solubility parameter values are obtained from ref. 16.

bValue of the solubility parameter for N-dimethyl acetamide in which PVF₂ dissolves.
Methods

Preparation of Poly(methyl acrylate)/Poly(vinyl acetate) Blends

Blends used for the DSC study were prepared by slowly casting films from solution. The PMA was received as a 40% solution in toluene; this solution was diluted to 20% PMA by mixing 10.13 mL of the 40% PMA solution with 11.47 mL toluene. A corresponding 20% solution of PVAc(i) in toluene was prepared by dissolving 4.0 g PVAc(i) in 18.5 mL toluene.

From the solutions of the two homopolymers, the desired compositions of the blend mixtures were obtained. Each mixture was stirred at low speed with a Vortex mixer for at least seven minutes. Sample calculations of how the homopolymer solution and those of the blend were obtained are shown in Scheme 1. Films of the homopolymers and those of the blends were cast on glass slides at room temperature and then dried in a vacuum oven at 120°C for 48 hr to remove all traces of solvent and any artifacts from casting.

The films used for the FTIR study were prepared in a similar way as those used for the DSC study. From each homopolymer, a 2% solution in toluene was prepared, and the desired compositions of the blend mixtures were obtained. To ensure that films were sufficiently thin to exhibit absorbances in the range in which Beer-Lambert's law is obeyed, films of each solution were cast on hot sodium chloride plates using a liquid dropper. The films were dried in a vacuum oven at 120°C for 12 hr.
(a) Preparation of 20% PVAc solution in toluene.

Given: Density of PVAc = 1.11g/mL  
      Density of toluene = 0.865g/mL

Basis: 20g of mixture

Weight of PVAc required

\[ 0.2 \times 20g \]
\[ = 4g \]

Weight of toluene required:

\[ 0.8 \times 20g \]
\[ = 16g \]

Toluene in terms of volume:

\[ \text{Density} = \frac{\text{Mass}}{\text{Volume}} \]

Therefore, volume = \( \frac{\text{Mass}}{\text{Density}} \)

Substituting the values,

Volume of toluene = \( \frac{16g}{0.865g/mL} \)
\[ = 18.5\text{mL} \]
(b) Preparation of 20% PMA solution in toluene

Given: 40% solution of PMA in toluene

Density of PMA = 1.17g/mL

Density of toluene = 0.865g/mL

Therefore, density of 40% solution PMA in toluene is:

\[0.4 \times 1.17g/mL + 0.6 \times 0.865g/mL\]

= 0.468g/mL + 0.519g/mL

= 0.987g/mL

Basis: 20g mixture

Weight of PMA required:

\[0.2 \times 20g\]

= 4g

In terms of volume,

\[\frac{4g}{0.987g/mL} \times \frac{1}{0.4}\]

= 10.13mL

That is, 10.13mL of 40% PMA in toluene is to be added to X mL of pure toluene. Since the basis is a 20g mixture and the density of 20% PMA in toluene is 0.926g/mL the volume of the final mixture will be:

\[\frac{20g}{0.926g/mL}\]

= 21.6mL
Finally, the amount of pure toluene required:

\[ 21.6\text{ml} - 10.13\text{mL} \]
\[ = 11.47\text{mL pure toluene} \]

CHECK on calculation (b)

Mass of 40% PMA solution = Mass of 20% PMA solution i.e.

\[ 10.13\text{mL} \times 0.98\text{g/mL} \times 0.4 = 21.6\text{mL} \times 0.926\text{g/mL} \times 0.2 \]

\[ 3.995\text{g} \quad = 4.000\text{g} \]

(c) Preparation of 20% PMA/80% PVAc blend.

Given: Density of 20% PMA solution = 0.926g/mL
Density of 20% PVAc solution = 0.14g/mL

Basis: 5g mixture

\[
\begin{array}{ccc}
\text{PMA} & & \text{PVAc} \\
0.2 \times 5g & + & 0.8 \times 5g \\
0.926\text{g/mL} & & 0.914\text{g/mL} \\
\end{array}
\]

In terms of volume:

\[ 0.2 \times 5g \quad + \quad 0.8 \times 5g \]
\[ = 1.08\text{mL} \quad + \quad 4.38\text{mL} \]
\[ = 5.46\text{mL} \]
Preparation of Poly(vinyl acetate)/Poly(vinylidene fluoride) Blends

Films used for the DSC and FTIR were cast from 2% solutions of the homopolymers [PVAc(ii) and PVF$_2$] in NN-dimethyl acetamide. Preparation of these films was similar to that described for the PMA/PVAc(i) system. Films for the DSC study were cast on glass slides, and those for the FTIR were cast on hot sodium chloride plates as described previously. The films for the DSC and FTIR studies were dried in a vacuum oven furnace at 160°C for 48 and 12 hr, respectively.

Instrumentation

Differential Scanning Calorimeter (DSC)

DSC measurements were conducted with a DU PONT 910 DSC module connected to the 990 Thermal Analyzer. The DSC system measures both the temperature and the heat change associated with transitions in materials. The measurements provide both qualitative and quantitative data about any physical or chemical change of the material involving either an endothermic or exothermic process.

The DSC module uses a constantan disc as the primary heat transfer element, which is enclosed in a silver heating block with a silver lid. The sample and an inert reference are placed in pans which are located on raised platforms on the disc (Figure 1a). Heat is transferred through the disc into the sample and reference via the sample pans.
Figure 1. Diagramatic view of 910 DSC module.
(a) DSC cell cross-section
(b) DSC longitudinal view
The differential heat flow to the sample and reference is monitored by chromel-constantan area thermocouples formed by the junction of a constantan disc and a chromel wafer covering the underside of each platform. Chromel and alumel wires connect to the chromel wafers. This thermocouple junction under the sample platform is used to measure the sample temperature.

Purge gas (nitrogen) is admitted to the sample chamber through an orifice in the block wall on the left between the two raised platforms (Figure 1b). The nitrogen enters the cell and is preheated by circulating through the block before entering the sample chamber at block temperature.

Data obtained from a DSC are a measure of the power input required to maintain equal temperatures between sample and reference as both are raised in temperature according to a predetermined program. The current required for the individual heaters is measured, and the differential is plotted by the analyzer.

**Fourier-Transform Infrared**

Fourier-transform spectra were obtained on a Nicolet 5DXB FTIR spectrometer with a resolution of 4 cm\(^{-1}\). All data manipulation was done by the Nicolet computer controlling the spectrometer. FTIR uses a Michelson interferometer (Figure 2), which has two mutually perpendicular arms.\(^24,25\) One arm of the interferometer contains a stationary, plane mirror; the other arm contains a movable mirror.
Figure 2. Optical diagram of the Michelson interferometer.
Bisecting the two arms is a beamsplitter which splits the source beam into two equal beams. These two light beams travel down their respective arms of the interferometer and are reflected back to the beamsplitter and on to the detector. The two reunited beams will interfere constructively or destructively, depending on the relationship between their path difference (χ) and the wavelength (λ) of light.

When the movable mirror and the stationary mirror are positioned the same distance from the beamsplitter in their respective arms of the interferometer (χ=0), the paths of light beams are identical. Under these conditions all wavelengths of the radiation striking the beamsplitter after reflection add coherently to produce a maximum flux at the detector and generate what is known as the "center burst". As the movable mirror is displaced from this point, the path length in that arm of the interferometer is changed. This difference in path length causes each wavelength of source radiation to destructively interfere with itself at the beamsplitter. The resulting flux at the detector, which is the sum of the fluxes for each of the individual wavelengths, rapidly decreases with mirror displacement. By sampling the flux at the detector, one obtains an interferogram. For a monochromatic source of frequency v, the intensity on the interferogram is given by the expression

\[ I(\chi) = 2 RT I(v)(1 + \cos 2\pi\chi) \]
where $R$ is the reflectance of the beamsplitter, $T$ is the transmittance of the beamsplitter, $I(\nu)$ is the input energy at frequency $\nu$ and $\chi$ is the path difference.

The interferometer can be thought of as a means of encoding the initial frequencies into a special form that the detector can observe. The Fourier transformation is simply a mathematical means of sorting out the individual frequencies for the final presentation of the IR spectrum.
Measurements

Differential Scanning Calorimetry

The DSC was calibrated with ultrapure indium. The baseline slope was determined by placing two empty sample and reference pans in the DSC heating block and scanning from -60 to 80°C at a heating rate of 20°C per minute.

Sample film was carefully folded in the aluminum pan and encapsulated with a sample encapsulating press. The sample and the reference were inserted in the DSC heating cell. The silver lid was laid over the sample and the reference pans, and the cell was covered with the cooling can containing dry-ice and acetone. After the sample and reference had cooled to -60°C, the cooling can was replaced with the cell cover and the bell jar.

A scan of the sample was made at a heating rate of 20°C per min from -60°C to 80°C under nitrogen atmosphere. The sample was cooled at the same rate (20°C/min) back to -60°C and a second scan was made. This procedure was repeated a third time.

The Tg reported for this study was recorded from the third scan of the intersection of the extrapolated linear portions of the curve just preceding and following the endothermic Tg break (Fig. 3). For each system, PMA/PVAc and PVAc/PvF2, when a single Tg was found intermediate between those of the pure components at all compositions, the system
Figure 3. An ideal representation of $T_g$ and $T_m$ determination by DSC.
was deemed miscible. On the other hand when two values of $T_g$ were found, the system was deemed immiscible.

**Fourier-Transform Infrared**

The sodium chloride plate containing the film was attached to the sample holder, and the holder was inserted into the FTIR compartment. Ten scans at a resolution of 4 cm$^{-1}$ were signal-averaged and stored on a magnetic diskette. With the computer controlling the spectrometer, experimental, coadded addition and digital subtraction spectra for each component of the PMA/PVAc and PVAc/PVF$_2$ systems were obtained.
RESULTS AND DISCUSSION

Blends of PMA/PVAc and PVAc/PVF₂ systems were prepared for the following ratios: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100%. The T_g of each composition was determined with the DSC. For the same systems and compositions, the FTIR was used to obtain the experimental, coadded and digital subtraction spectra.

DSC

Polymer Blends of PMA/PVAc System

Given in Table 2a are the raw T_g values measured for the various compositions of poly(methyl acrylate)/poly(vinyl acetate) system. Each composition of this system exhibits a sharp single glass transition temperature (Figs. 4 to 10); therefore, this system is deemed miscible. As the ratio of one of the components is increased (Table 2), it is seen that the T_g value shifts gradually towards the T_g value of that pure component. Given in Table 2b are the least squares projected T_g values based on an assumed linear variation of T_g with blend composition. A plot of T_g versus blend composition is given in Figure 11.

Shown in Figure 12 is the thermogram obtained from the films of the homopolymers that were mixed physically in equal proportions. This thermogram shows the two phase nature of immiscible blend; each polymer characteristically exhibits its T_g.
### Table 2a. Glass Transition Temperature as a Function of Composition For PMA/PVAc System

<table>
<thead>
<tr>
<th>Composition w/w</th>
<th>Raw Data Tg/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA</td>
<td>PVAc</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>60</td>
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<td>60</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
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</tbody>
</table>

### Table 2b. Least Squares Projection of PMA/PVAc Raw Data

<table>
<thead>
<tr>
<th>%PVAc</th>
<th>Tg/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>32.1</td>
</tr>
<tr>
<td>90</td>
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<td>80</td>
<td>27.5</td>
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<td>70</td>
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<td>22.8</td>
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<td>20.4</td>
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<td>18.1</td>
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<td>30</td>
<td>15.7</td>
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<td>20</td>
<td>13.4</td>
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<tr>
<td>10</td>
<td>11.1</td>
</tr>
<tr>
<td>0</td>
<td>8.7</td>
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</tbody>
</table>
Figure 4. DSC thermogram of a pure poly(methyl acrylate).
Figure 5. DSC thermogram of 80% PMA/20% PVAc blend.
Figure 6. DSC thermogram of 60% PMA/40% PVAc blend.
Figure 7. DSC thermogram of 50% PMA/50% PVAc blend.
Figure 8. DSC thermogram of 40% PMA/60% PVAc blend.
Figure 9. DSC thermogram of 20% PMA/80% PVAc blend.
Figure 10. DSC thermogram of pure poly(vinyl acetate).
Figure 11. Change in $T_g$ as the weight percent ratio of the PVAc is changed for the PMA/PVAc system.
Figure 12. DSC thermogram of PMA/PVAc films mixed physically in equal proportions.
Polymer Blends of PVAc/PVF₂ System

Tables 3a and 3b show the raw \( T_g \) and the calculated least squares values for the various compositions of poly(vinyl acetate)/poly(vinylidene fluoride) blends. As a result of the high degree of crystallinity of the poly(vinylidene fluoride) the DSC is not able to detect the \( T_g \) of the homopolymer (Figure 13). However, a value of 13.5°C was obtained for PVF₂ by extrapolation from the least squares plot (Figure 14); this value is approximately equal to the 13.0°C given by the manufacturer. Shown in Figures 15 to 17 are the thermograms for the PVAc/PVF₂ blends. Although the three scans obtained for each blend are shown, the scan of useful information is the third scan. Each of these blends exhibits a single \( T_g \) value intermediate to those of the homopolymers; this system is therefore miscible. Except for the 50% PVAc/50% PVF₂, there is a gradual decrease of the \( T_g \) values as the amount of the PVAc (Table 3a) is decreased.
### Table 3a. Glass Transition Temperature as a Function of Composition For PVAc/PVF₂ System

<table>
<thead>
<tr>
<th>Composition w/w</th>
<th>Raw Data Tg/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>PVF₂</td>
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<tr>
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<td>0</td>
</tr>
<tr>
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<td>80</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

*The value of PVF₂ obtained from least squares
**The value of PVF₂ obtained from the manufacturer
Table 3b. Least Squares Projection of PVAc/PVF₂ Raw Data

<table>
<thead>
<tr>
<th>%PVAc</th>
<th>Tg/°C</th>
</tr>
</thead>
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<td>17.1</td>
</tr>
<tr>
<td>10</td>
<td>15.3</td>
</tr>
<tr>
<td>0</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Figure 13. DSC thermograms of pure poly(vinylidene fluoride) and pure poly(vinyl acetate).
Figure 14. Change in \( T_g \) as the weight percent ratio of the PVAc is changed for the PVAc/PVF_2 system.
Figure 15. DSC thermograms of 20% PVAc/80% PVF₂ and 80% PVAc/20% PVF₂ blends.
Figure 16. DSC thermograms of 40% PVAc/60% PVF₂ and 60% PVA/40% PVF₂ blends.
Figure 17. DSC thermograms of 50% PVAc/50% PVF$_2$ blend.
FTIR

Polymer Blends of PMA/PVAc System

Shown in Figure 18 are the spectra of the homopolymers of poly-(methyl acrylate) and poly(vinyl acetate). The peak at 2352 cm\(^{-1}\) in the PVAc is the C=O asymmetric stretch of carbon dioxide from the air; it is an impurity in this polymer. Figures 19 to 21 show the spectra of the experimental and coadded blends for the 20/80, 50/50 and 80/20 PMA/PVAc ratios. Also shown in these figures are the difference spectra of the experimental blends and the homopolymers. The final difference spectra are magnified by a factor of four in order to differentiate the baseline from the residual positive peaks.

The spectrum of each coadded blend is overlapped on top of each corresponding experimental blend. The spectra of the coadded blends for the various compositions were obtained by using the appropriate percent ratios of the homopolymers. The digital subtraction of the spectra of the homopolymers from the spectrum of the experimental blend was done as follows: (i) the C=O stretching frequency of the PMA at 1167 cm\(^{-1}\) was used as the correct subtraction parameter to subtract out PMA and, (ii) PVAc was subtracted from the residual blend by using a C-H symmetric blending frequency of PVAc at 1376 cm\(^{-1}\). The use of these two peaks minimize the error of oversubtraction of the homopolymers from the blend.
A. overtone of the carbonyl stretch; B. CH₃ asymmetric stretch; C. CH₂ asymmetric stretch; 
D. CH₂ symmetric stretch; E. C—O stretch; F. CH₃ 
asymmetric bend; G. CH₃ symmetric bend; I. methyl ester 
CC(—O) -- O stretch; J. out-of-plane CH₃ bend; K. CH₂ rock 
(Peak values from ref. 26)

A. CH₃ asymmetric stretch; B. CH₂ asymmetric stretch; 
C. C—O asymmetric stretch for \(^2\text{CO}_2\text{(impurity)}\)  
D. C—O stretch; E. CH₃ asymmetric bend; F. CH₃ symmetric 
bend; G. acetate CC(—O) -- O stretch; I. out-of-plane CH₃ bend 
(Peak values from ref. 26)

**Figure 18.** FTIR spectra of pure poly(methyl acrylate) and pure poly(vinyl acetate).
Figure 19. FTIR spectra of 20/80 PMA/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Figure 20. FTIR spectra of 50/50 PMA/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Figure 21. FTIR spectra of 80/20 PMA/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Polymer Blends of PVF₂/PVAc System

Figure 22 shows the spectra of the homopolymers of poly(vinyl acetate) and poly(vinylidene fluoride). As described for the PMA/PVAc system, the spectra of the coadded blends for all compositions were obtained by using the appropriate percent ratios of the homopolymers. The digital subtraction was done by first subtracting the spectrum of PVAc from that of the experimental blend using the C=O stretching frequency at 1739 cm⁻¹. Finally, the PVF₂ spectrum was subtracted from the residual blend using the C-H out-of-plane vibration at 882 cm⁻¹ as the correct subtraction parameter. The spectra of the experimental and coadded blends and those of the differences for 20/80, 50/50 and 80/20 ratios are shown in Figures 23 to 25.
A. CH₃ asymmetric stretch; B. CH₂ asymmetric stretch;
C. C=O asymmetric stretch for \(^2\)CO₂ (impurity)
D. C=O stretch; E. CH₃ asymmetric bend; F. CH₂ symmetric
bend; G. acetate CC(=O)--O stretch; I. out-of-plane CH₃ bend
(Peak values from ref. 26)

A. C—H stretch; B. CF₂ stretch; C. out-of-plane
C—H bend; CH₂ rock
(Peak values from ref. 26)

Figure 22. FTIR spectra of pure poly(vinyl acetate) and pure
poly(vinylidene fluoride).
Figure 23. FTIR spectra of 20/80 PVF<sub>2</sub>/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Figure 24. FTIR spectra of 50/50 PVF₂/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Figure 25. FTIR spectra of 80/20 PVF$_2$/PVAc: (Top) experimental and coadded blends, (Bottom) the difference spectra.
Discussion

Miscibility in polymer-polymer systems generally requires the existence of a strong molecular interaction complex between the polymers. This complex is a result of exothermic interaction, such as a dipole-dipole or hydrogen bonding, between the functional groups on the component polymers.\textsuperscript{26-29} Although the DSC does not have the capability of detecting the existence of molecular interaction complexes, the FTIR does have such capability in blends involving polar compounds.

In the infra-red sense, if the component polymers are immiscible in a blend, the individual polymers would not recognize the existence of the other polymer. Therefore, it should be possible to digitally subtract the spectrum of one of the pure component polymers from the spectrum of the blend using an appropriate weighting factor. The residual spectrum thus obtained should be the same as the spectrum of the other polymer.\textsuperscript{29-34} However, molecular interactions in miscible blends may result in band shift, band broadening or intensity change of some of the absorption bands associated with one or both of the component polymers. In such cases, the residual spectrum obtained by digital subtraction of the spectrum of either one of the component polymers will be different from the spectrum of the other.

In these studies, a transparent film was obtained for each composition of the PMA/ PVAc system. The DSC measurement gave single sharp Tgs in all the compositions. These observations suggested that this
system is miscible in all proportions. This finding is in agreement with what Hughes and Brown found in their torsional modulus studies of this system.

The FTIR spectra (Figures 19 to 21) show some changes in the intensity of the peak in the coadded and the corresponding experimental blends. The peak intensities of the following bands, 2957, 1436, 1376, 1167, 1026, 945, 831 and 602 cm\(^{-1}\), in the 20/80 PMA/PVAc experimental blend are either higher or sharper than their corresponding peaks in the coadded blend. For both blends there are overtones of C=O stretch at 3455 cm\(^{-1}\); these overtones resulted from the carbonyl peak. As the ratio of PMA is increased in the blends, the intensity changes between the experimental and the coadded blends become less obvious in some regions of the spectra. However, there are still distinct changes in the intensity of the peaks between bands of 1376 cm\(^{-1}\) and 831 cm\(^{-1}\) (Figures 20 and 21). These changes indicate that there are some molecular interaction complexes involved in these blends.

Before discussing the difference spectra of this system, it seems fit to first do a theoretical prediction of the type of interaction expected for this system by inspecting of the functional groups of the polymers. The two polymers have carbonyl in the ester or acetate groups. The carbon attached to the double bond oxygen of one polymer would be expected to form a dipole-dipole interaction with the oxygen double bond of the other polymer. This dipole-dipole bond, will be
very weak because the bond formed by the two sets of carbon oxygen are chemically equal. Hydrogen bonding interaction would not be expected for this system because these two polymers do not fully meet the requirement of such bonding.

On digitally subtracting the PMA from each experimental blend the remaining spectrum, though almost identical with that of the PVAc, has a frequency shift in the 1436 cm\(^{-1}\) band (Figures 19 and 20) and a peak broadening in the 80/20 PMA/PVAc ratio. Subtraction of the PVAc from each of the residual experimental blends left some positive and negative peaks in the spectra of the 20/80, 40/60 and 80/20 compositions. The difference spectra of the 50/50 and 60/40 ratios are without positive peaks. The positive peaks in the 80/20 are fairly strong, especially the bands at the 3004-2849 cm\(^{-1}\). Also observed in the 20/80 and 80/20 is a significant peak shift in C=O stretch.

These spectral differences suggest that there are molecular interaction complexes in some compositions of the PMA/PVAc system. This interaction complex, which might be due to dipole-dipole, seems to materialize at a much higher ratio of one component to that of the other. However, the interaction seems much stronger when the PMA is at a higher ratio. Also, the strong band at the 2849-3004 cm\(^{-1}\) in the 80/20 seems to suggest the involvement of other forms of bonding interaction resulting from the methylene and the carbonyl group. The finding of interaction in some compositions of this system is in
contrast to the result of Nandi et al. as discussed previously.

Films for the PVAc/PVF2 system were slightly opaque, especially in compositions with a high ratio of PVF2. The first two scans of each blend established known thermal history for the DSC measurement. In most cases the information of these scans are not quite accurate. For this system, except for the 80% PVAc/20% PVF2 composition which exhibits a single sharp Tg, the other compositions exhibit single broad Tgs. The Tg for the PVF2 as reported by the manufacturer is 13.0°C and from the extrapolation of the least squares curves, a value of 13.5°C was obtained for PVF2. From the DSC measurement, 33.5°C was obtained for the Tg of PVAc. Between the Tgs of these homopolymers, it is quite obvious that the system exhibits a single Tg. This system, therefore, is deemed miscible in all proportion. This conclusion is in agreement with the result of Bernstein et al. as described previously.

The FTIR spectra of the coadded and the experimental blends, except for the 20% PVAc/80% PVF2, are almost identical. However, there are some significant changes in the intensity of the peaks at 1405, 1378, 1239, 1184 and 1024 cm⁻¹ in the experimental 20/80 ratio as compared to the coadded blend. This observation indicates that there are some interactions involved in this blend. On digitally subtracting the PVAc and the PVF2 from the experimental blend, band broadening was observed for the C=O and CF2 peaks. The broadening of these peaks effected
a shift of the positive and negative peaks in the difference spectra (Figures 23 to 25). These observations suggest that there is molecular interaction in this system. From the functional group, this interaction could be that of a dipole-dipole interaction effected by the C=O of PVAc and the CF$_2$ of the PVF$_2$. This conclusion is in agreement with the results of Paul et al.$^{22}$ as described previously.
CONCLUSION

Due to thermodynamic reasons polymers are generally not miscible on a molecular level. However, if two polymer pairs are miscible, miscibility is achieved through strong molecular interactions between the functional groups. Our studies show that the films of the poly (methyl acrylate)/ poly(vinyl acetate) blends are transparent. As shown by the DSC measurements, each blend exhibits a single sharp glass transition temperature intermediate between these of the homopolymers. From these observations, the PMA/PVAc system is said to be miscible.

Miscibility of PMA/PVAc blend was expected to be due to molecular interaction complexes. The FTIR data showed such evidences in some of the compositions. There were intensity changes in the spectra of the coadded and the experimental blends. On digitally subtracting the PMA and PVAc from each experimental blend, each difference spectrum showed some positive and many negative peaks, especially for the 20/80 and 80/20 compositons. The positive peaks, however, were stronger for the 20/80 and 80/20 ratio. These observations suggest the involvement of molecular interaction complexes in some of the compositions, especially at a higher percentage of PMA. From the functional groups of both homopolymers, one would expect that the interaction is that of a dipole-dipole. However, the strong positive peaks in the range of 2849-3004 cm\(^{-1}\) suggest the possibility of a second type of interaction which involves the methylene and the carbonyl of both polymers.
A slightly opaque film was obtained for each poly(vinyl acetate)/poly(vinylidene fluoride) system. The Tg for PVF2 could not be obtained from the DSC due to its high crystallinity. However, a value of 13.5°C was obtained for the Tg of PVF2 from the least squares curve. This value is quite reasonable as compared to the 13°C reported by the manufacturer. Though most of the compositions exhibit broad Tg's, they are all single, intermediate between the Tg's of the two homopolymers. From these observations, this system is said to be miscible.

Except for the 80% PVF2/20% PVAc blend, the FTIR spectra of the coadded and the experimental blends were found to be almost identical. There were significant intensity changes in the spectra of the coadded and the experimental blends. The difference spectra for each of the compositions, especially the 80/20 ratio, show a significant band shift in the C=O and CF2 peaks, indicative of molecular interaction complexes. Like the PMA/PVAc system, the molecular interaction is suggested to be that of dipole-dipole.
REFERENCES


35. Mishra, S.P.; Deopura, B.L. Polymer Comm. 1985, 26, 5.