# Transition-Metal Coordination for Complexing Poly-(vinyl chloride)-Polyurethane Blends

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## SYNOPSIS

Binary blends of poly(vinyl chloride) (PVC) and polyether polyurethane (PU) containing divalent transition metal ($Zn^{2+}$) have been prepared by solution blending. The physical and mechanical properties of the blends are studied utilizing differential scanning calorimetry (DSC), thermogravimetry (TG), and tensile testing. The DSC results showed a high degree of molecular mixing of the two polymers. The glass transition temperatures ($T_g$) of the blends exhibited one major $T_g$ whose position on the temperature scale is raised with increasing levels of PVC. The blends yielded stress–strain behavior similar to reinforced elastomers at low PVC, but at high PVC contents, they exhibited increased elongation. The latter materials showed well-developed yield points, stress whitening, and necking. Cold drawing was exhibited by the materials under tension. The tensile strength and Young's modulus were enhanced as the PVC content was increased.

## INTRODUCTION

Studies on polymer blends have received considerable industrial and academic attention in recent years. Although the structure of polymer blends and composites are quite complex and not fully understood, polymer blends and composites are being widely used due to their desirable properties. The polymer blends are noted by their characteristic behavior resulting from the microphase-separated structure. The phase separation in polymer blends is induced by the immiscibility between their constituent polymers.[1-6] For enhancement of the compatibility of given polymer pairs, various attempts have been made. One of the attempts was made by the introduction of attractive interaction between the components.[7-10] An example is of ionomer blends, in which the Coulombic interactions enhance the miscibility of the components. Another example is of polymer pairs capable of forming an interpolymer complex by a certain specific interaction between the constituent polymers.[10,11]

Blends of PVC with various types of polyurethane have gained considerable technological value and have been studied by several investigators.[12-14] This present work is concerned with the bulk interpolymer complexes formed through the specific interaction of divalent transition-metal-neutralized polyurethane carboxylate (thermoplastic elastomer) with PVC (thermoplastic glassy polymer). Here, we report the synthesis, thermal, and mechanical properties on these coordination chemistry-based polymer blends. The motivation of this study was to form complete or at least more compatible blends.

## EXPERIMENTAL

### Materials

The commercial PVC used in this study was additive free, supplied by Merck, purified by a twofold precipitation from tetrahydrofuran into methanol, and dried under vacuum to a constant weight. Molecular weights ($M_n = 45,000$, $M_w = 78,000$) were determined in tetrahydrofuran at 25°C by gel permeation chromatography (GPC). Poly(tetramethylene oxide) (PTMO, DuPont De Nemours Co.) of 1000 molecular weight was dehydrated under vacuum at 70°C for 10 h. $N,N$-Dimethylformamide (DMF, Merck) was vacuum-distilled over calcium hydride

before use in the polymerization reaction. Tolylene diisocyanate (TDI, Merck) utilized a mixture of the 2,4- and 2,6-isomer of 80 and 20%, respectively. 2,2-Bis(hydroxymethyl) propionic acid (HMPA, Aldrich Chemical Co.) was 99% pure. Tetrahydrofuran (THF, Fluka), zinc acetate, and stannous octoate (Merck) were used as received.

## Synthesis

### Preparation of Polyurethane Anionomer (PUA) Block Copolymer

The segmented polyether polyurethane-containing carboxylic groups was prepared by a two-step condensation reaction. Polyurethane (PU) prepolymer at 11.20% NCO content (determined by the di-$n$-butylamine titration method[15]) was prepared by reacting three equivalents of TDI with one equivalent of PTMO. The NCO-terminated PU prepolymer was dissolved in DMF at a 45% solids (w/w) concentration. A solution of HMPA was prepared in DMF (55% w/v). The HMPA solution containing 0.15% catalyst (stannous octoate) was added to the stirred NCO-terminated PU prepolymer solution in several portions at 70–75°C to obtain the linear PU-containing carboxylic acid groups. The reaction was continued in the same temperature range until the NCO content reached zero as evidenced either by titration or when the IR peak of NCO had disappeared. Molecular weights ($M_n$ = 38,000, $M_w$ = 96,000) were determined in 0.5% THF at 25°C by GPC.

A stoichiometric amount of zinc acetate solution was added after determining the concentration of carboxylic groups containing linear PU solution by removal of the solvent. The neutralization reaction was carried out at 70°C until no further increase in viscosity was observed. The sample film was made by solution-casting on an aluminum mold that was previously treated with a releasing agent. The resulting sample film was heated in an oven at 65°C for 6 h and then at 80°C for 10 h. The film was further dried under vacuum at 80°C for 24 h.

### Preparation of Polymer Blends

The binary polymer blends were made by mixing PUA solution in DMF and PVC solution (approximately 20% w/w) in THF. The homogeneous solution was degassed at room temperature to remove any air bubbles. The degassed polymer solution was casted on an aluminum mold and the resulting films were treated as previously described. The following compositions given in terms of weight ratios of com-

ponents were studied: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100. The first numeral denoted the weight percent of PVC.

## Methods of Measurements

Differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), and derivative thermogravimetry (DTG) were performed on a DuPont Thermal Analyzer 2000 system in combination with a standard DSC cell and TG-951. Measurements were made at a heating rate of 20°C/min in an atmosphere of dry nitrogen at a flow rate of 100 mL/min. The glass transition temperature ($T_g$) was taken as the midpoint of the transition.

Uniaxial stress–strain experiments were obtained using a table model Instron tensile testing machine at room temperature, with a crosshead speed of 5 cm/min and a gauge length of 3.25 cm. Samples were cut with an ASTM 412 Die.

## RESULTS AND DISCUSSION

### Thermal Analysis

DSC scans of homopolymers and polymer-blend series materials are shown in Figure 1. Results for all the materials are summarized in Table I. The $T_g$'s of the PU phase shifts toward higher temperatures as the PVC content is increased. Since, the molecular structure of PUA prepared with TDI mixture differs primarily with regard to the symmetry of the
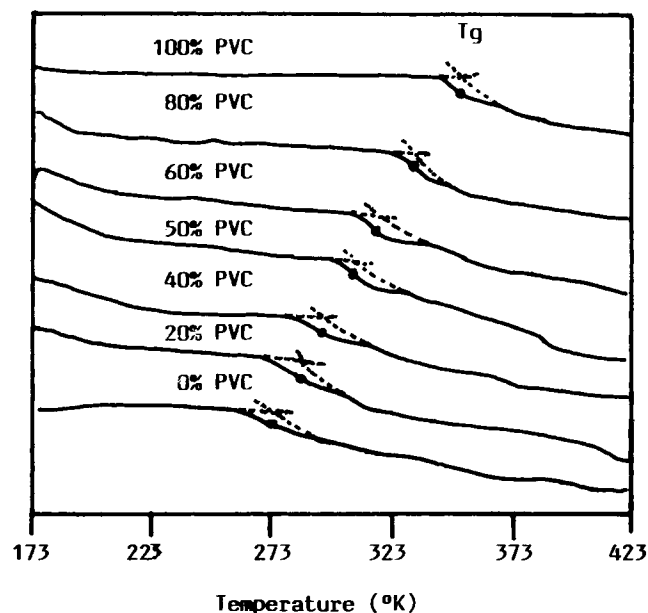


**Figure 1**   DSC curves for blends of PVC and PUA.

**Table I  Glass Transition Temperatures ($T_g$) of PVC–PUA Blends**

| Composition (wt % PVC) | $T_g$ (D) K (by DSC) | $T_g$ (A) K[a] (calc) | $\sigma$[b] |
|---|---|---|---|
| 100 | 351 | — | — |
| 80 | 332 | 332.6 | 0.0018 |
| 60 | 315 | 316.0 | 0.0317 |
| 50 | 309 | 308.4 | 0.0019 |
| 40 | 296 | 301.0 | 0.0169 |
| 20 | 288 | 287.0 | 0.0035 |
| 0 | 275 | — | — |

[a] Average: $T_g$ (A) $= W_1 T_{g_1} + W_2 T_{g_2}$; $W_1$ and $W_2$ are the weight fractions of PVC and PUA, respectively.

[b] The quantity $\sigma$ was calculated by the following equation: $[T_g$ (D) $- T_g$ (A)$]/T_g$ (A) $= -\sigma/1(1 + \sigma)$.

diisocyanate linkages. The mixture of TDI isomers contains a high proportion of the asymmetrical isomer, 2,4-TDI, which can result in head-to-tail isomerization within the PUA structure. 2,4-TDI, which can result in head-to-tail isomerization within the PU structure. The amorphous character of the hard

segments containing the isomeric TDI units, and both the carboxylic and methyl side groups of HMPA, may result in considerable intermixing of this phase with the soft segment (PTMO). These hard segment–soft segment interactions can produce restrictions on the relative mobility of the PTMO segments and increase the $T_g$ of PU.[16–18] Also, this intermixing enhances the interactions among zinc cations, oxygen atoms of PTMO segments, and chlorine atoms of PVC through ion–dipole interactions.

The Gordon–Taylor copolymer equation has been applied to the $T_g$ data in this study to determine if the blends are single phase or not:[19]

$$T_{g_{12}} = T_{g_1} + [kW_2(T_{g_2} - T_{g_{12}})]/W_1$$

where $T_{g_1}$ and $T_{g_2}$ are the $T_g$ values of the pure components. $W_1$ and $W_2$ are the corresponding weight fractions, and $k$ is the ratio of the thermal expansion coefficients between the rubber and glassy states of the component polymers. For a well-mixed system, the plot of $T_{g_1}$ vs. $[(T_{g_2} - T_{g_{12}})W_2/W_1]$ will yield a
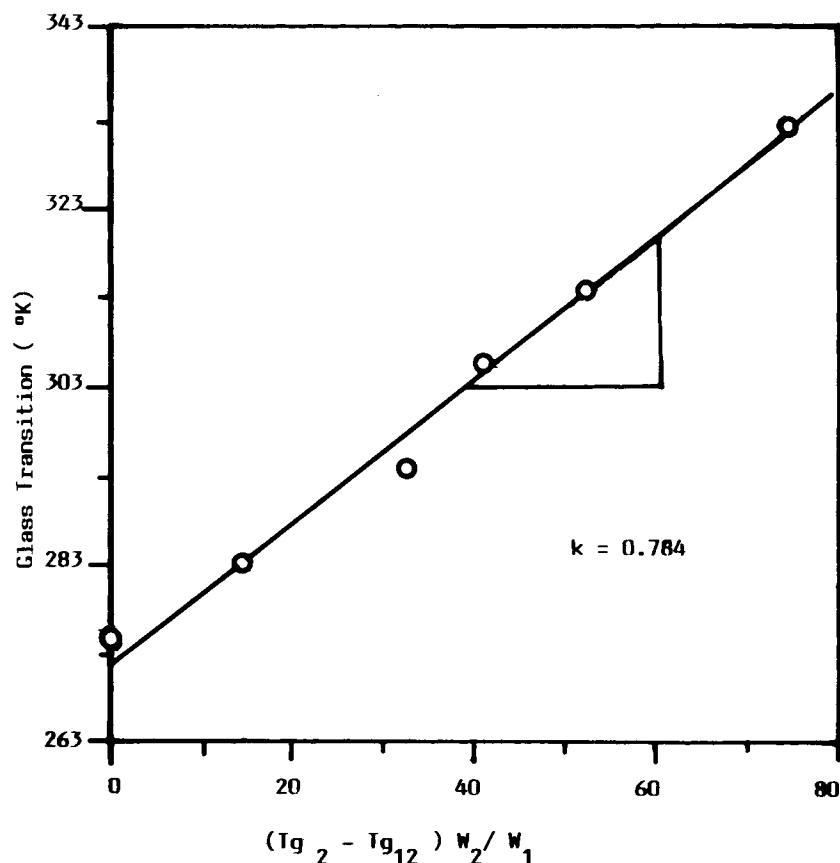


**Figure 2**  $T_g$ data for blends of PVC and PUA plotted according to the Gordon–Taylor equation.
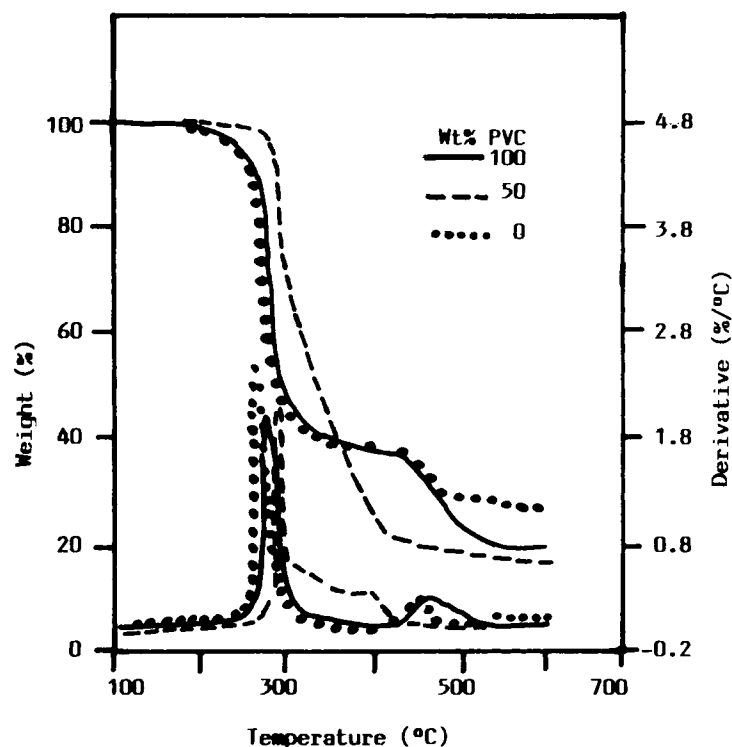
**Figure 3**   TG and its derivative (DTG) for blends of PVC and PUA.

straight line with a slope of $k$ and an ordinate intercept of $T_{g_1}$.

The $T_g$'s for the PVC–PUA systems have been plotted vs. $[(T_{g_2} - T_{g_{12}})W_2/W_1]$ in Figure 2. The figure shows that the Gordon–Taylor equation fits for the PVC–PUA blends quite well. The ordinate intercept is 270 K, which is the observed $T_g$ of the PUA, and $k = 0.784$. Noticeably, the extrapolated $T_{g_1}$ agrees with the experimentally determined $T_g$ of

the PUA component. We can thus conclude that ion pair–dipole interactions of the type utilized here are sufficient to achieve miscibility in the present system.

The $T_g$ values in the third column in Table I are calculated from the DSC data using the copolymer equation

$$1/T_g = W_1/T_{g_1} + W_2/T_{g_2}$$

**Table II   TG and DTG Results of PVC–PUA Blends**

| Composition (wt % PVC) | Weight Loss (wt %) at Temperature (°C) (TG) | | | Decomposition Temperature (°C) (DTG) | |
|---|---|---|---|---|---|
| | 300 | 400 | 500 | First | Second |
| 100 | 51 | 62 | 76 | 280 | 467 |
| 80 | 58 | 61 | 71 | 265 | 465 |
| 60 | 56 | 65 | 75 | 269 | 464 |
| 50 | 59 | 68 | 77 | 275 | 460 |
| 40 | 14 | 40 | 84 | 286 | 426 |
| 20 | 40 | 72 | 79 | 281 | 384 |
| 0 | 31 | 75 | 82 | 289 | 392 |

**Table III   Tensile Properties of PVC–PUA Blends[a]**

| Composition (wt % PVC) | Ts (MPa) | | E (%) | $\epsilon_y$ (MPa) |
|---|---|---|---|---|
| | At Yield | At Break | | |
| 100 | — | 47 | 6 | 480 |
| 80 | 37 | 35 | 120 | 377 |
| 60 | 33 | 26 | 136 | 218 |
| 50 | 20 | 23 | 185 | 134 |
| 40 | — | 48 | 288 | 72 |
| 20 | — | 30 | 388 | 58 |
| 0 | — | 20 | 544 | 37 |

[a] Ts: Tensile strength; E: elongation at failure; $\epsilon_y$: Young's modulus.
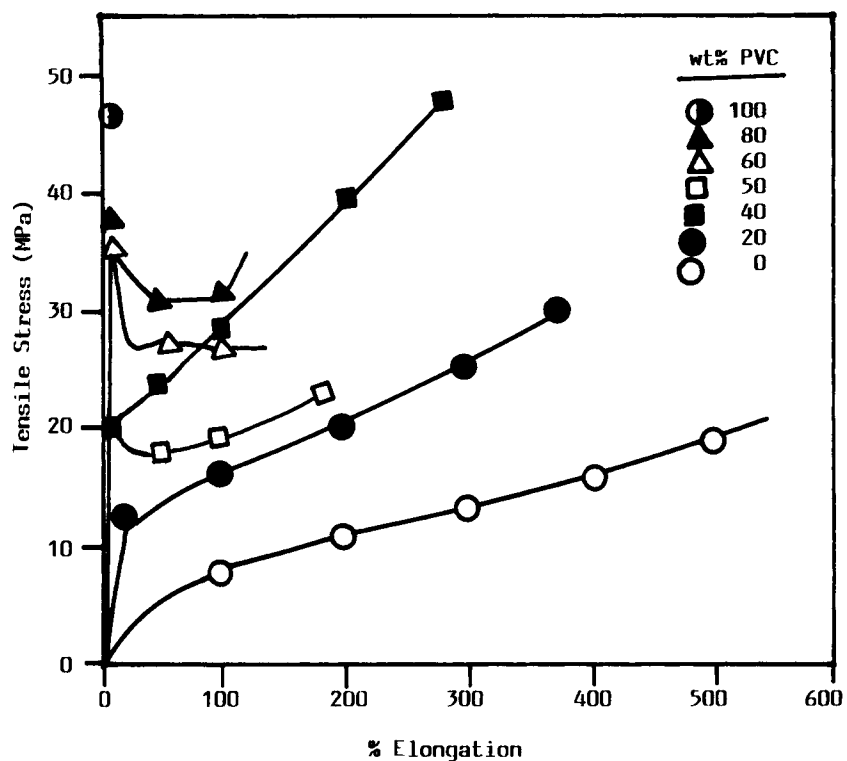
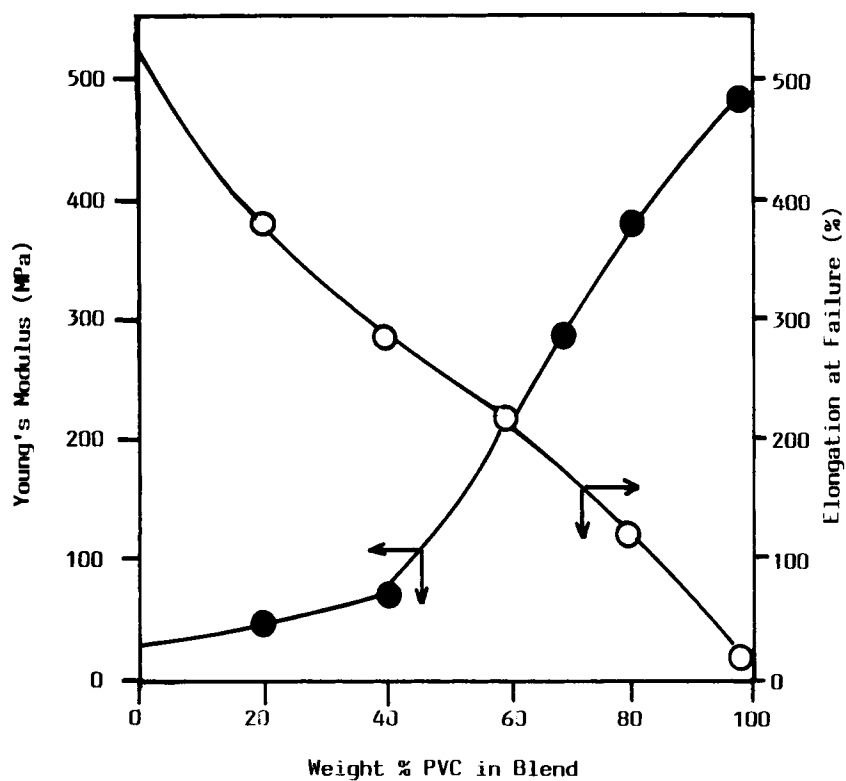**Figure 4**   Stress–strain curves for blends of PVC and PUA.



**Figure 5**   Elongation at failure and Young's modulus vs. composition for blends of PVC and PUA.

where $W_1$ and $W_2$ are the weight fraction of PVC and PUA in the blends. It is evident that the observed values of $T_g$ in the second column are similar to the calculated values. It is evident that the blends are at least significantly compatible as they exhibited only one $T_g$ whose position on the temperature scale is raised with increasing levels of PVC.

Typical results for TG and DTG for polymer blends degraded in nitrogen are shown in Figure 3. The DTG curves indicate that two main reaction stages occur during the degradation. The first reaction stage appears around 270°C and the second stage appears around 385°C. The first and second reaction stages for the polymer blends shift inward and upward between the degradation stages of homopolymers. Loss in weight of the polymer at different temperatures was determined from the respective TG analysis and is represented in Table II.

**Tensile Properties**

Figure 4 shows the detailed stress–strain behavior of homopolymers and blends. All stress–strain data are summarized in Table III. These data are an average from three runs for ultimate tensile strength, Young's modulus, and elongation at break. Stress have been calculated on the basis of the initial cross-sectional area. The samples with low PVC behave as reinforced elastomers. As the level of PVC is increased, a yield point begins to appear in the neighborhood of 50% PVC. Above this composition, all the samples show a well-developed yield point, suggesting a possible mechanism of failure by crazing. Evidence of cold drawing is exhibited by samples having an upper yield point as shown by the increase of tensile strength before failure. The corresponding elongation at break and Young's modulus showed the same trend and are given in Figure 5. The elongation at break decreases with increasing PVC content, whereas Young's modulus decreases with increasing PUA content.

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