

Thermal Behavior of Poly(acrylic acid)–Poly(vinyl pyrrolidone) and Poly(acrylic acid)–Metal–Poly(vinyl pyrrolidone) Complexes

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ABSTRACT: Thermal analysis (TGA and DTA) of samples of PAA, PVP, PAA–PVP complexes, containing different weight fractions of PAA and ternary polymer–metal–polymer complexes, were studied. The activation energy parameters for the thermal degradation were also calculated. The study of the effect of FeCl_3 , NiCl_2 , and $\text{Ni}(\text{NO}_3)_2$ on the TGA and DTA curves of the complexes showed that the decompositions are dependent on the concentrations and the na-

ture of the metal ions. The DTA traces of PAA–PVP complex containing FeCl_3 , NiCl_2 , and $\text{Ni}(\text{NO}_3)_2$ showed that the treatment of the complex with these metal ions causes considerable changes in the thermal decomposition of PAA–PVP complex. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4049–4057, 2006

Key words: poly (acrylic acid); complexes; FTIR

INTRODUCTION

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are analytical experimental techniques that investigate the behavior of the substance as a function of temperature. These techniques are widely employed in both scientific and industrial domains, and their ability to characterize, quantitatively and qualitatively, huge varieties of materials over a considerable temperature range has been pivotal in their acceptance as analytical techniques. Over the last two decades, the study of the thermal behavior of various polymers, such as poly(acryl amide), poly(acrylic acid), and poly(methacrylic acid), and the catalytic effect of metal ions on the thermal decomposition of these polymers has been a subject of interest for a number of researchers.^{1–7} The combined technique FTIR–TGA has been used to study the thermal properties of PAA doped with metal clusters such as Au, Cu, and Zn.⁷ Till the present time a little is known about the thermal behavior of the polymer–polymer and ternary(polymer–metal–polymer) complexes, although other techniques, e.g., FTIR spectroscopy and electrical conductivity have been used to study the formation, structure, and properties of some of these complexes.^{8–11} The main objective of this study is to investigate the process of complexation of poly(acrylic acid)–poly (vinyl pyrrolidone) and poly(acrylic acid)–

Metal–poly(vinyl pyrrolidone) complexes by using the thermal analysis TGA and DTA.

EXPERIMENTAL

Poly(vinyl pyrrolidone) (PVP) was obtained from Sigma Chemical Co. (average mol. wt. 360,000). Poly(acrylic acid) (PAA) was obtained from Nisso Shoji Co. (Japan). The polymers were used as received without further treatment. A solution from each polymer, PAA and PVP, was prepared by dissolving the polymer in distilled water with the concentration of 1 g/100 mL and each solution was then stirred to ensure complete dissolution. Mixtures from the two polymer solutions with different PAA weight fractions (WF_{PAA}) were prepared by mixing the two solutions in the appropriate proportions. Just after mixing the two solutions complete precipitation or phase separation took place without any further treatments. The precipitates were then filtered, washed with distilled water, and air-dried over three days at room temperature. The complexes were further dried at 60°C in a drying oven until a constant weight is maintained. The dried samples were then ground in ball mixer mill. The samples were sieved and a suitable particle size was used.

The solutions of PVP treated with transition metal chlorides FeCl_3 , NiCl_2 , and $\text{Ni}(\text{NO}_3)_2$ were added to PAA, which was achieved by dissolving a certain weight of polymer (0.5 g) in fixed volume of distilled water (50 mL) and homogenated by stirring for 2 h. The precipitates were then filtered, washed with distilled water, and air-dried over three days at room

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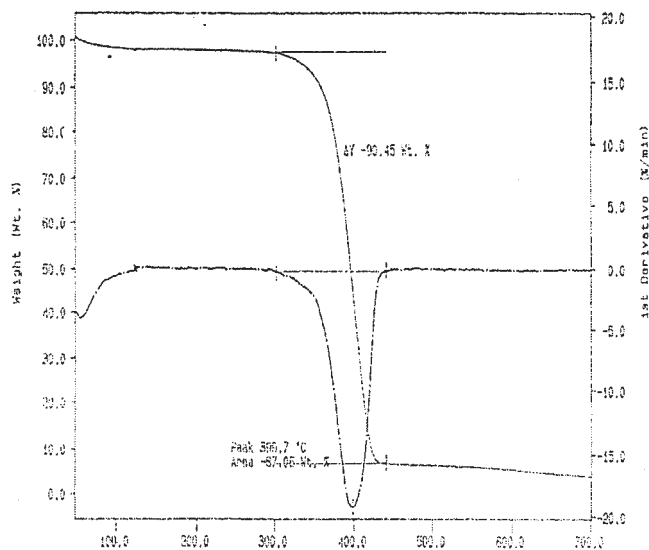


Figure 1 TGA and DTG curves of PVP.

temperature. The complexes were further dried at 60°C in dry oven until a constant weight was maintained.

All the TGA and DTA traces included in this study were obtained using a computerized Perkin-Elmer 7 Series Thermal Analysis system.

A dynamic dry N purring gas atmosphere at a constant rate of 50 cc/min for DTA and 30 cc/min for TGA, 0.1 μ g to 10 mg of the powdered sample (90–250), heating rate of 10°C/min, and α -AL₂O₃ as a reference material were maintained for all the DTA runs.

RESULTS AND DISCUSSION

The decomposition profiles and associated first derivative curves of PVP are shown in Figure 1. This figure gives clear evidence that PVP has a greater thermal stability up to 302°C when decomposition begins. The weight loss due to degradation of this material begins around 302°C. Beyond this temperature the rate of weight loss decreases continuously because of the complex char forming mechanism.

The activation energy parameters for the thermal degradation were calculated using Dharwadhar and Kharkhanawala's modified eq. (4).

$$\ln\{\ln(1 - \alpha) - 1\} = \frac{E^*}{RT_1^2} \times \frac{100}{(T_2 - T_1)} Q + C$$

where α is the weight loss at a particular temperature; E^* is the activation energy; $Q = (T - T_s)$, where T is the temperature under consideration and T_s is the maximum decomposition temperature; C is a constant; R is the gas constant; T_1 and T_2 are the initial and final decomposition temperature. The relation be-

tween $\ln\{\ln(1 - \alpha)^{-1}\}$ and Q values is shown in Figure 2. The calculated value of activation energy is 12.5 kcal/mol.

A typical dynamic TGA spectrum of PAA is shown in Figure 3, which clearly shows that there are three decomposition regions. The first decomposition region starts at 156.8°C and stops at 225.3°C, with a maximum decomposition rate at 196.89°C. The area of this peak is 5.366 wt % and the weight loss is 8.419 wt %. The second decomposition region begins at ~225.3°C and ends at 301°C, with a maximum decomposition rate at 270.93°C. The area of the second decomposition region is 7.617 wt % while its weight loss is 17.74 wt %. The third decomposition region starts at 301°C and stops at 476.1°C, with a maximum decomposition rate at 372.36°C. The area of this region is 47.37 wt % and the weight loss is 55.87 wt %.

The thermal degradation of PAA shows three separate decomposition regions. The first region may be due to a minor decarboxylation reaction. The second decomposition stage is mainly due to anhydride formation. The third region is the thermal degradation for the corresponding polyacrylic anhydride.

The values of $\ln\{\ln(1 - \alpha)^{-1}\}$ were plotted against corresponding Q values in Figure 4 for PAA. Activation energy (E^*) was calculated from the slope of the straight line.

The calculated values of the activation energies for the decompositions are 0.70 kcal/mol for decarboxylation reaction, 1.06 kcal/mol for anhydride formation, and 3.97 kcal/mol for thermal degradation of polyacrylic anhydride, respectively.

The thermogravimetric decomposition curves and associated derivative curves of samples of PAA-PVP complexes containing different weight fractions of PAA, namely 0.8, 0.5, and 0.2, are shown in Figures 5 and 6 (as examples).

It was noticed that the PAA-PVP complex with 0.8 WF_{PAA} exhibits a three steps decomposition profile, the last two being unresolved and dissemble only on the derivative curve as a peak around 409.5°C with lower temperature shoulder around 374.75°C. The

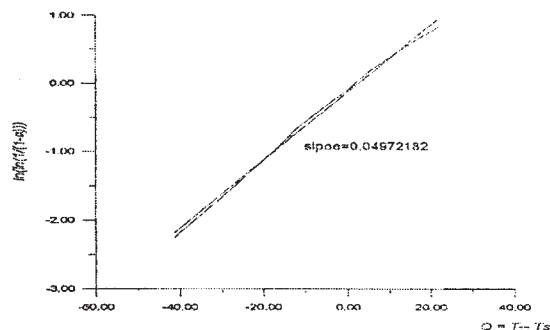


Figure 2 The relation between the values of $\ln\{\ln(1 - \alpha)^{-1}\}$ against corresponding Q values for PVP.

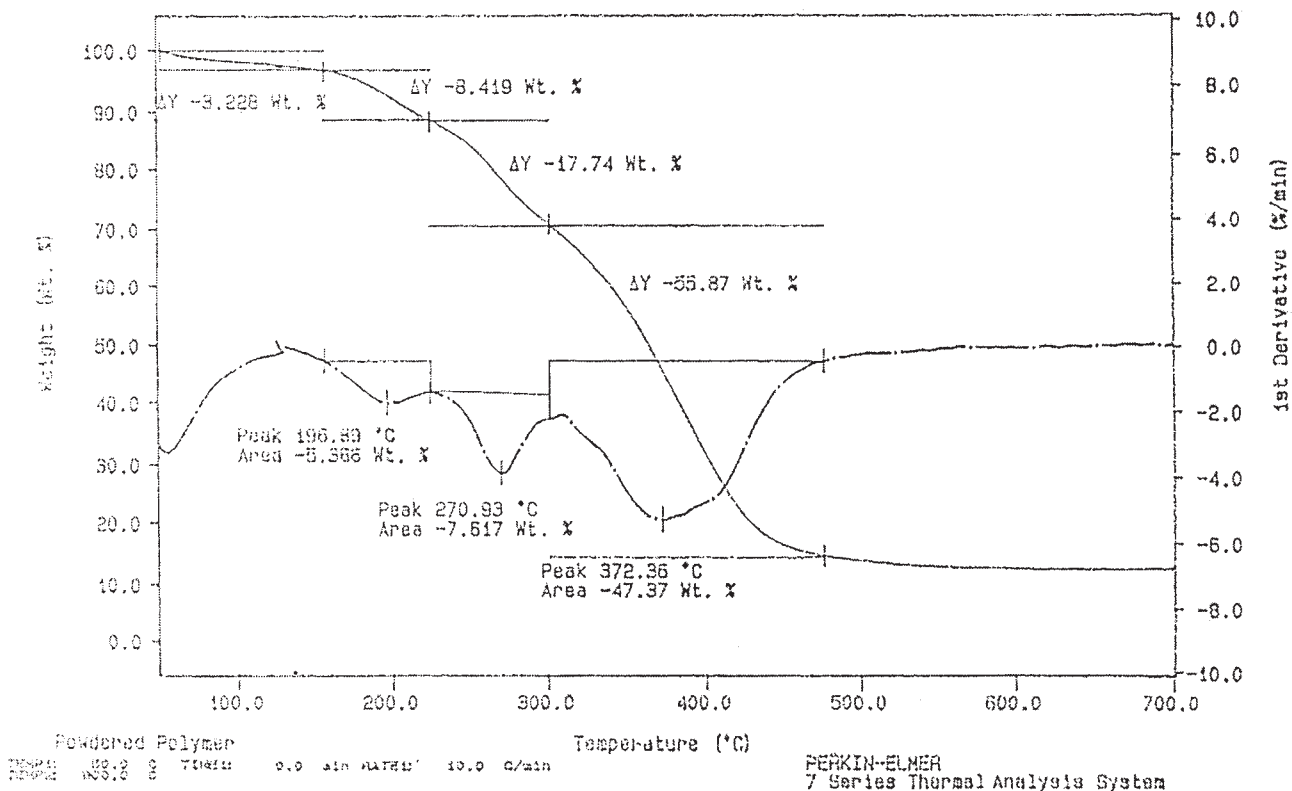


Figure 3 TGA of PAA.

first step occurring at around 245.09°C is of interest because it exhibits a profile distinct from those of the constituent PAA and PVP. Also, this step cannot be considered as a simple summation of the two components decomposition, i.e., for the PAA-PVP physical mixture. On the contrary, this step denotes some form of interaction of the two components.

Decreasing the weight fraction of PAA to 0.5 shifts the temperature of the first step from 245.09°C to

lower value at 237.33°C and the second step from 374.75°C to higher temperature at 387°C and shifted the third step from 409.05°C to higher temperature at 412.07°C. Continued decrease of WF_{PAA} to 0.2 shifted these peaks to 241.57, 381.13, and 417.57°C, respectively (Fig. 6).

The DTA curve of PVP in Figure 7 also shows two endothermic peaks around 93.53 and 423.87°C: the former is due to the evaporation of the absorbed water and the latter is due to the decomposition of PVP. Table I gives the activation energy of PAA-PVP complexes containing different weight fractions of PAA.

The DTA trace of PAA in Figure 8 shows two endothermic peaks around 90.77 and 234.02°C. The first is due to the evaporation of the adsorbed water, which could not be removed completely on drying, while the second peak corresponds to the decomposition of PAA.

The DTA traces of the complex prepared from solution containing various weight fractions of PAA, namely 0.2, 0.5, and 0.8, are shown in Figure 9. From this figure, it is evident that the main decomposition of the complex containing 0.2 weight fraction of PAA is at a considerably higher temperature (263.78°C) than that of the main decomposition of PAA. Another two endothermic nadirs are observed at 350 and 419.53°C.

The main decomposition of the complex of 0.5 WF_{PAA} is observed at the same temperature. On the

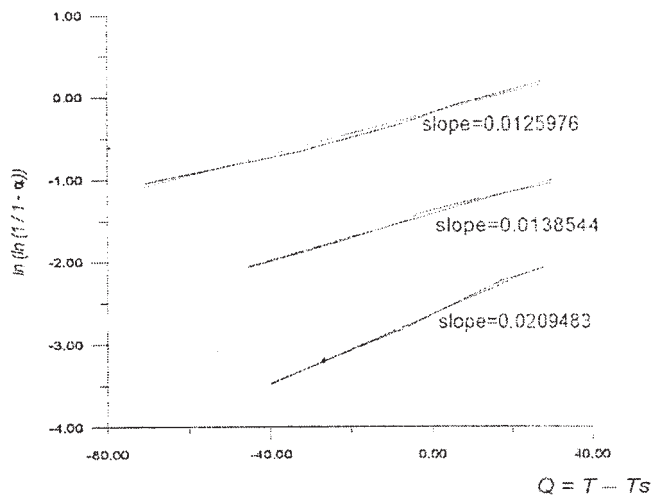


Figure 4 The relation between the values of $\ln[\ln(1 - \alpha)^{-1}]$ against corresponding Q values for PAA.

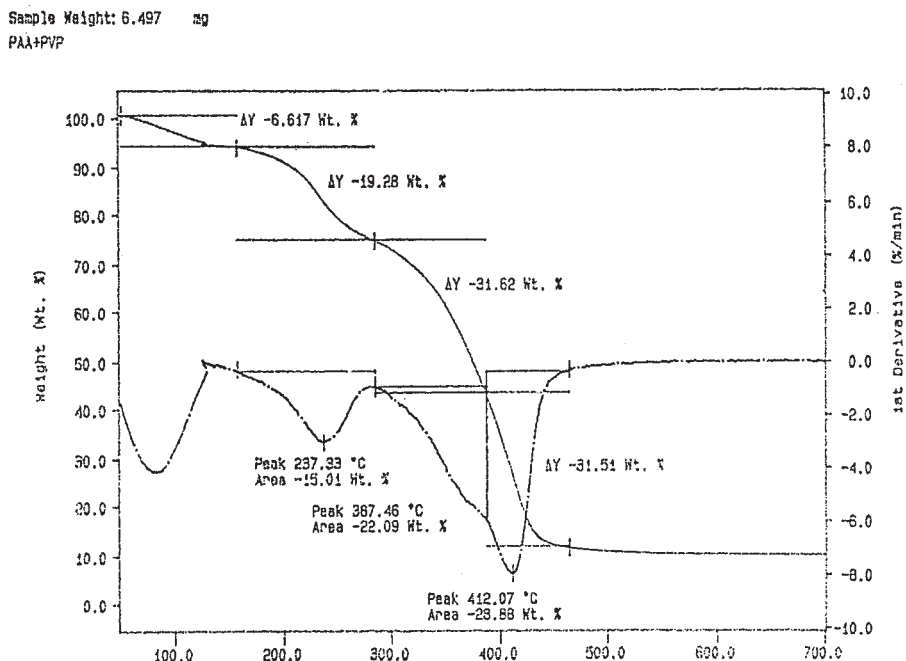


Figure 5 TGA of PAA-PVP complex containing weight fraction of PAA, namely 0.5.

other hand, this decomposition in the DTA curve of the complex of 0.8 WF_{PAA} appears at considerably lower temperature (234.75°C).

Examination of the thermal curves of PAA, PVP, and their complexes reveals that considerable differences are found between the curves of the individual components and that of the complex. This means that the DTA trace of the complex cannot be considered as a simple summation of these two component's traces. But the DTA trace of the complex gives strong evidence that some form of interaction between the two

polymers took place. This result confirms the results reported by TGA measurements.

The TGA and associated DTG curves of PAA-PVP complex (0.5 weight fraction) and the complexes containing 10 and 20% w/w Fe^{3+} are shown in Figures 10 and 11. From the thermal curves of these samples considerable differences are found between the Fe^{3+} free and Fe^{3+} containing complexes.

The DTG curve of the complex with zero metal ion content shows three decomposition at around 237, 387, and 412°C with the weight losses 19.28, 31.62, and

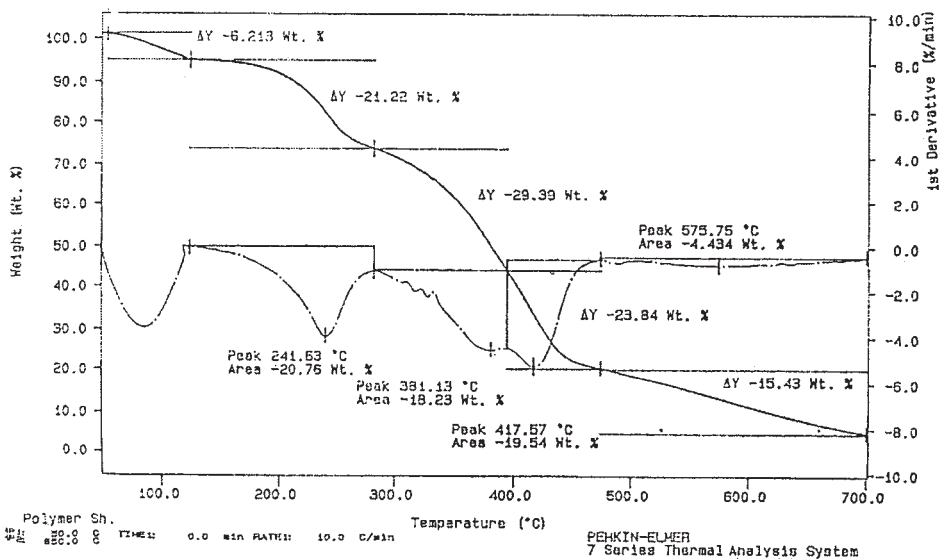


Figure 6 TGA of PAA-PVP complex containing weight fractions of PAA, namely 0.2

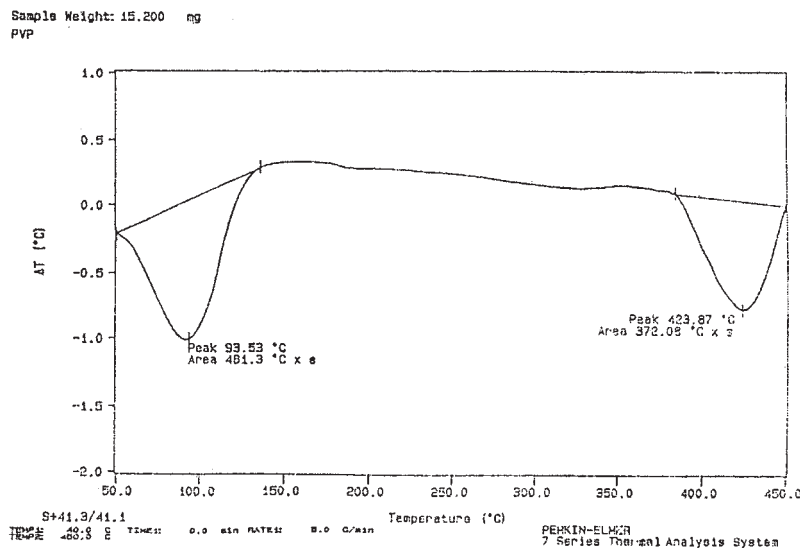


Figure 7 DTA of PVP.

31.51, respectively. The decompositions of the Fe^{3+} containing complexes, however, are at different temperatures and weight losses. For the sample containing -10% Fe^{3+} , the decomposition are around 240, 337, and 397°C with the weight losses 18.37, 11.09, and

30.08 wt %, respectively. Increasing the concentration of Fe^{3+} into 20% w/w shifted the temperature of the decomposition to 237, 356 and 404°C with the weight losses 19, 18, and 23 wt %, respectively.

The effect of $NiCl_2$ and $Ni(NO_3)_2$ on the TGA and DTG curves of the complexes was also taken into account. Figure 12 shows the TGA and DTG curves of PAA-10% $NiCl_2$ -PVP. It was found that Ni^{2+} ions cause striking changes in the temperatures of decomposition and their corresponding weight losses. This is due to the physical properties of metal ion.

TABLE I
Activation Energy of PAA-PVP Complexes Containing Different Weight Fractions of PAA

WF _{PAA}	Activation energy (kcal/mol)		
	1st decomposition	2nd decomposition	3rd decomposition
0.8	1.25	1.56	4.32
0.5	1.18	2.06	4.33
0.2	1.06	1.67	3.17

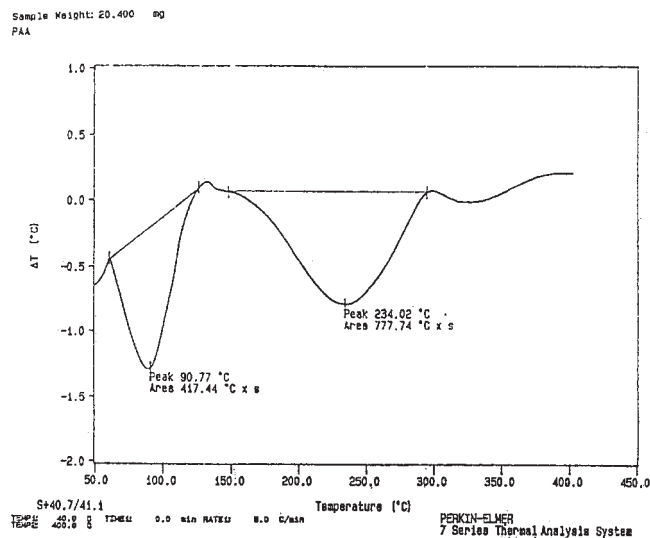


Figure 8 DTA of PAA.

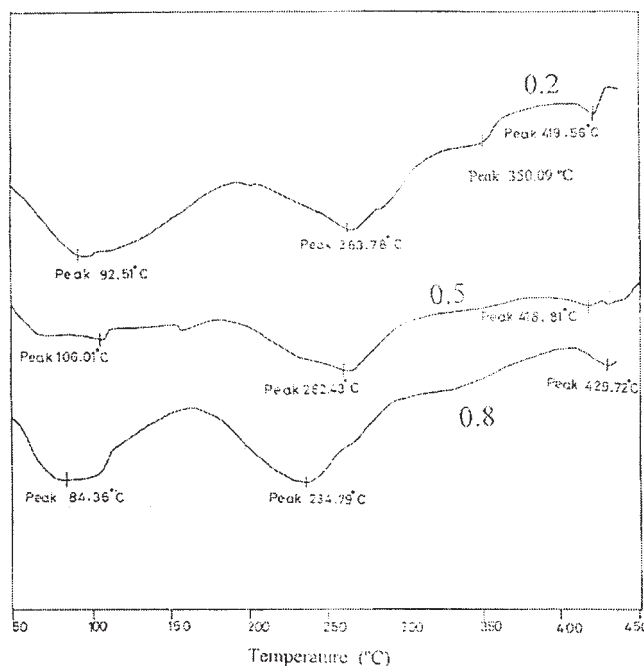


Figure 9 DTA of PAA-PVP complexes at different WF_{PAA}.

Sample Weight: 2.786 mg

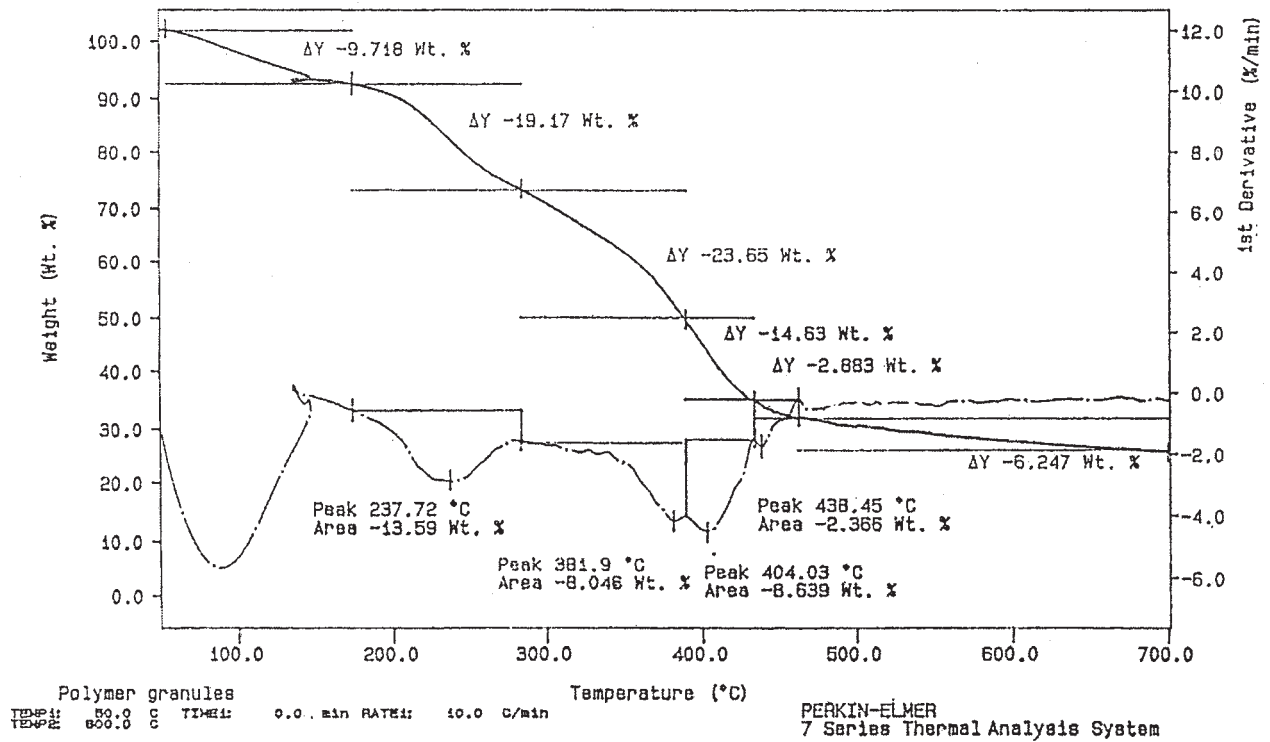


Figure 10 TGA of PAA-20% FeCl₂-PVP complex.

Sample Weight: 9.239 mg

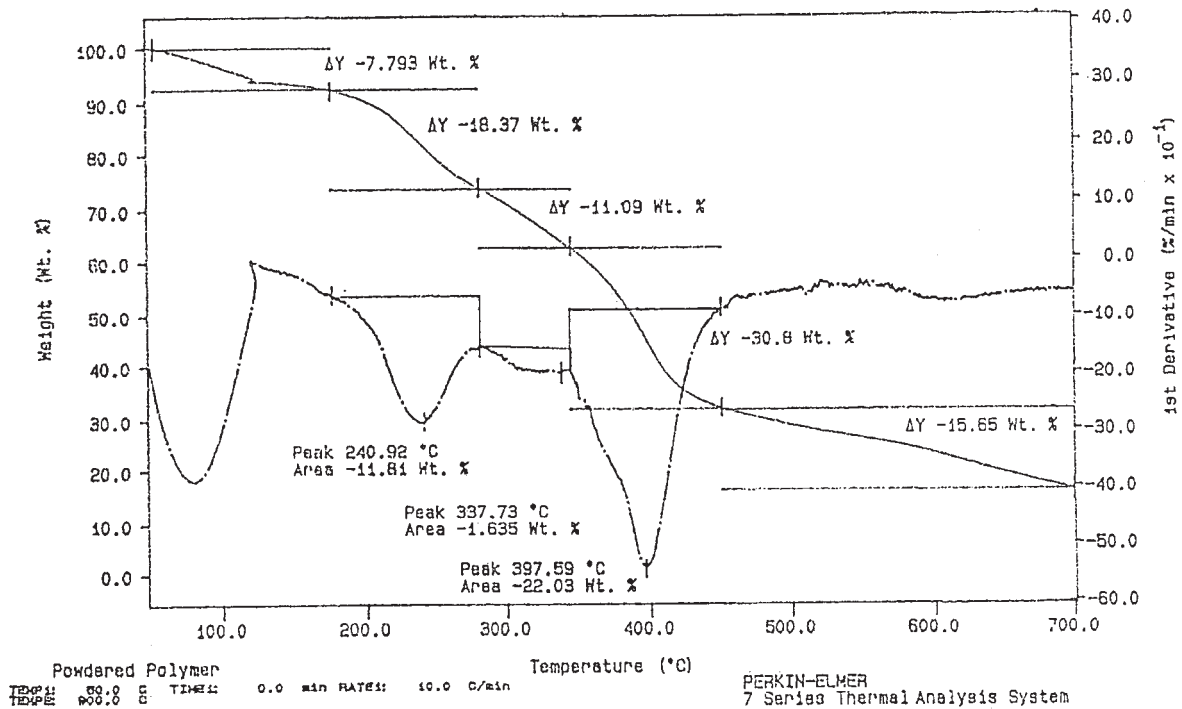


Figure 11 TGA of PAA-10% FeCl₃-PVP complex.

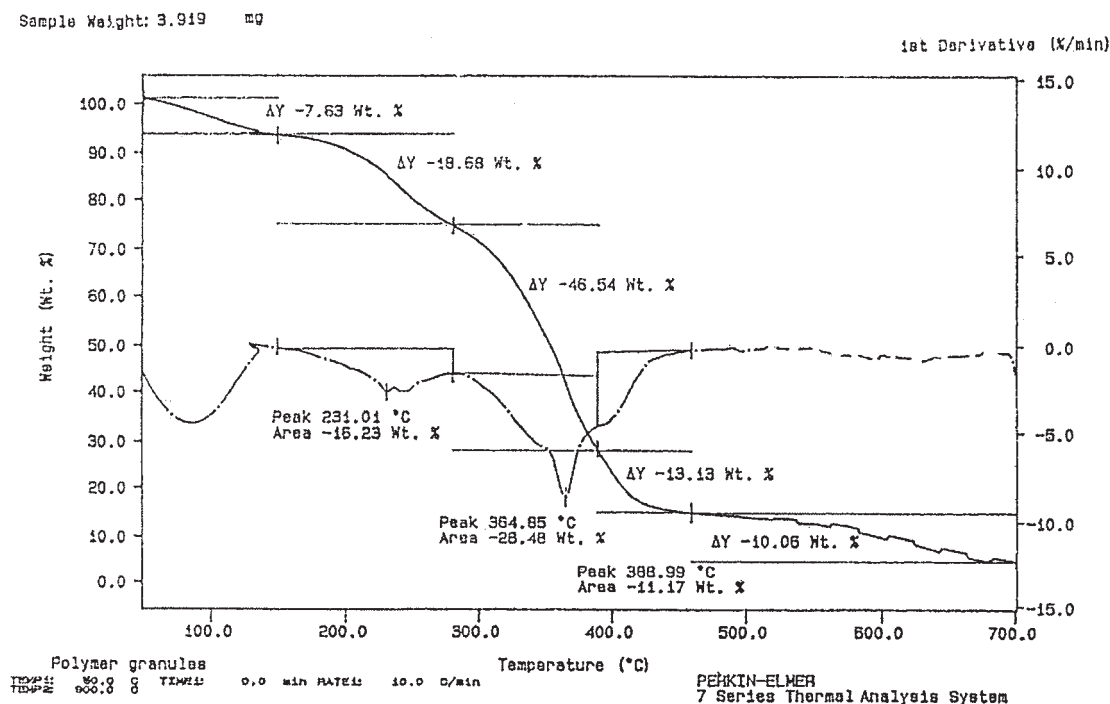


Figure 12 TGA of PAA-10%NiCl₂-PVP complex.

As far as the present results are concerned, it can be established that Fe³⁺ and Ni²⁺ ions cause considerable quantitative changes in the thermal behavior of PAA-PVP complex. In the presence of the ions, the decomposition temperatures are shifted and the corresponding weight losses are lowered.

It is worthwhile to take into account that metal ions have a specific effect on the thermal stability of organic materials; they can either stabilize the system or even catalyze the thermal decompositions.

Obviously, the concurrent reactions taking place during the decomposition are dependent on the concentrations and nature of the metal ions. The calculated values of activation energy of decomposition of these components are given in Table II

The DTA traces of PAA-PVP containing 10% w/w and 20% w/w Fe³⁺ are shown in Figure 13. It is clear from this figure that the DTA trace of the ion-free

complex, with zero metal ion content, shows an endothermic peak at 262.13°C corresponding to the decomposition of the complex. The DTA peak of the main decomposition of Fe³⁺ containing complexes, however, is at slightly lower temperature (254.65°C). No essential influence of the Fe³⁺ concentration was found.

The same complex was reacted with different concentrations of NiCl₂ (10%, 20% w/w). Results obtained on the products are shown in Figure 14. It can be seen that the presence of NiCl₂ with 10% (w/w) shifted the main decomposition of the ion free complex into higher temperature at about 276.84°C, while the presence of NiCl₂ with 20% (w/w) affects the thermal behavior of the complex. The most striking effect is that the originally one-step thermal decomposition becomes bimodal. The temperature of the first step is at about 182.58°C and the temperature of the

TABLE II
The Calculated Values of Activation Energy of Decomposition

	Activation energy (kcal/mol)		
	1st decomposition	2nd decomposition	3rd decomposition
PAA-PVP	1.18	2.06	4.33
PAA-FeCl ₃ -PVP	1.12	0.66	2.43
PAA-2FeCl ₃ -PVP	1.04	1.06	1.45
PAA-NiCl ₂ -PVP	1.02	2.61	2.07
PAA-2NiCl ₂ -PVP	0.90	2.56	2.95
PAA-Ni(NO ₃) ₂ -PVP	1.05	2.64	3.13

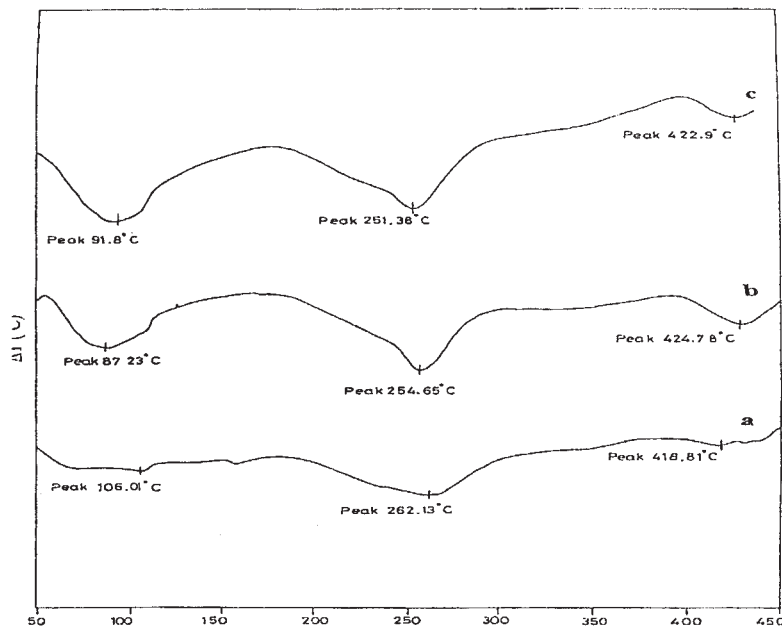


Figure 13 DTA of PAA-FeCl₃ at different concentration (a) PAA-PVP, (b) 10%, and (c) 20% FeCl₃.

second one is at about 274.81°C. The temperature of the first step is lower by about 80°C than that for ion-free complex. The second decomposition step is shifted toward some what higher temperature.

In Figure 15 the thermal curves of the ion-free complex and that of the complex containing 10% (w/w) of its weight Ni(NO₃)₂ are compared. It is

apparent from this figure that in the presence of Ni(NO₃)₂ the thermal decomposition is modified. The differences between the two curves are striking, and the DTA curve of the product resulting from the reaction between the complex and Ni(NO₃)₂ shows two main steps, the first is at around 243.96°C and the second at around 390.71°C.

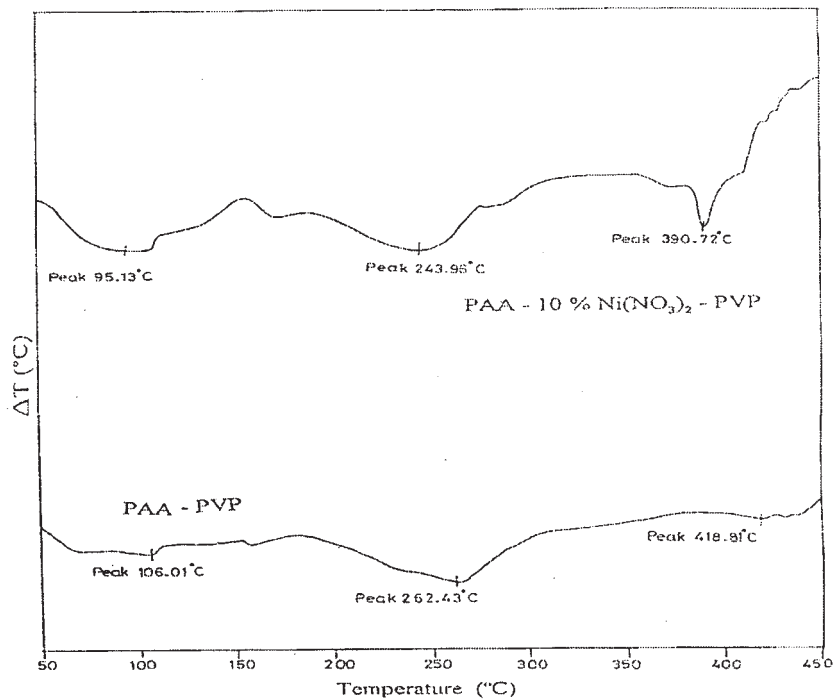


Figure 14 DTA of PAA-NiCl₂ at different concentrations (a) PAA-PVP, (b) 10%, and (c) 20% NiCl₂.

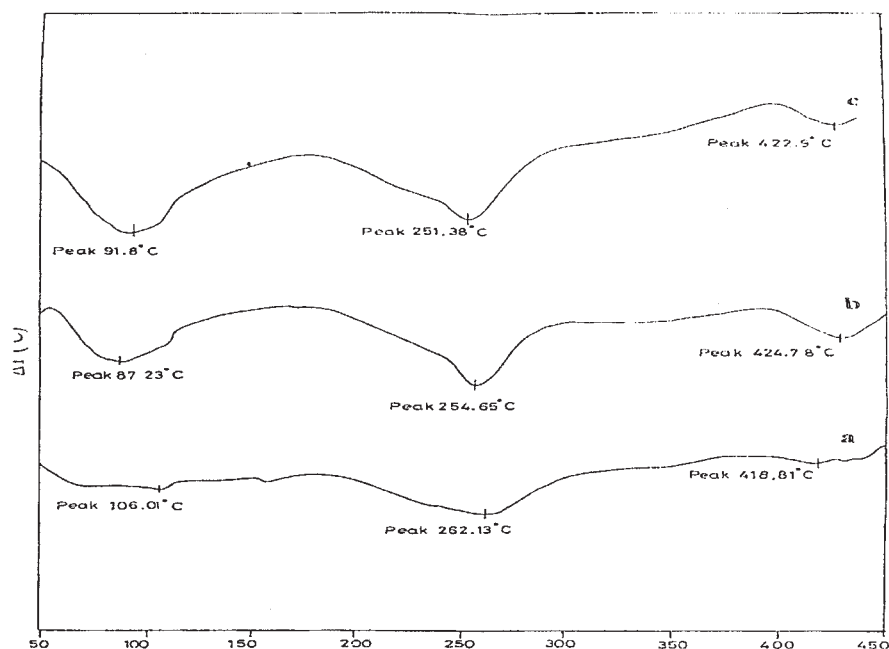


Figure 15 DTA of PAA-10%Ni(NO₃)₂-PVP.

The temperature of the first decomposition is lower by about 18°C and the second is higher by about 128°C than that for the ion-free complex.

CONCLUSIONS

Examination of TGA and DTA curves of PAA, PVP, and their complexes demonstrates that considerable differences are found between the thermal curves of the individual components and that of the complex. This means that the curves of the complex cannot be considered as a simple summation of these two component's curves. But the curves of the complex give strong evidence that some form of interaction between the two polymers took place and the thermal behavior of the complex resulting from the cooperative interactions are different from those of the constituent polymers. The complexation is generally attributed to the formation of hydrogen bonding between the PAA and PVP. The weight fraction of PAA in the solution has a clear effect on the thermal behavior of the complex. Moreover it was concluded that Fe³⁺ and Ni²⁺ ions cause considerable changes in the thermal behavior of

PAA-PVP complex. The magnitude of these changes depends on the physical properties of the metal ions.

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