The Application of Thermogravimetric Analysis to an Electrophoretically Deposited Polymer Coating

Synopsis

An electrophoretically deposited poly(vinylidene chloride)–poly(vinyl chloride) and epoxy ester coating has been shown to provide adequate protection for Be-Cu from hostile environments. The data presented show that thermogravimetric analysis can be readily applied for drying analysis and quality control of the polymer ratio.

INTRODUCTION

Electrophoretically deposited coatings of poly(vinylidene chloride)–poly(vinyl chloride) (P) and epoxy ester (E), in mixtures ranging from 50/50 to 70/30 (w/w) P/E, provide adequate protection for Be-Cu from, "hostile" environments. A study of the drying rates at various temperatures and a quality control procedure for ratio analysis of the coating were necessary. In both cases, thermogravimetric analysis (TGA) proved suitable as the analytical technique.

TGA can be defined as the continual or frequently repeated measurement of weight or weight changes of a sample while it is subjected to a temperature program.[1] In both studies, the weight was continuously monitored, but the temperature program varied. For the quality control procedure, the temperature was increased from ambient at a constant rate, and weight was followed as a function of temperature. To study the drying rates, isothermal conditions were used, and weight was monitored as a function of time.

EXPERIMENTAL

Mixtures of 50/50, 60/40, and 70/30 P/E were prepared. A few 85/15 P/E mixtures were also tried. A portion of each mixture was dried in an oven at 110°C. The remainder was used to coat copper wire. The latter samples were dried in a forced-air oven for 4 hr at 70°C, and the coatings were stripped from the copper for use. Samples of the individual polymer suspensions were also dried.

Because previous experiments have shown a nominal 60/40 P/E mixture to be the best in providing the protection for which this coating was developed, only the 60/40 mixture was used in the drying rate study.

Data were collected on the du Pont Model 950 thermogravimetric analyzer. Scan rates were 15°C/min (a few at 10°C/min) in a 1-lpm N_2 atmosphere at sensitivities of 2 mg/in. of chart paper (one sample at 1 mg/in.). Isothermal measurements at 60°, 80°, and 120°C were run at the same sensitivity with the time base at 1 in./min. The isothermal data was analyzed and fitted using an IBM System/360 Model 44.

One further item should be noted. The ratios to which these suspensions were mixed are nominal. They do not account for weights measured to the nearest gram or for variations in the solids content of each suspension.

RESULTS AND DISCUSSION

Quality Control Procedure

The poly(vinylidene chloride)–poly(vinyl chloride) began to show a sharp weight loss at just less than 200°C. The slope of the curve lessened at 250°C but did not completely level off until ~700°C. A 27.6% residue remained corresponding to the 28% residue listed for poly(vinylidene chloride).[2]

The epoxy ester shows a small (<1%) weight loss at ~120°C, with a major weight loss occurring at 270°C. This leveled off past 400°C with less than a 3% residue remaining. In time, at 1000°C, both residues burned off completely.
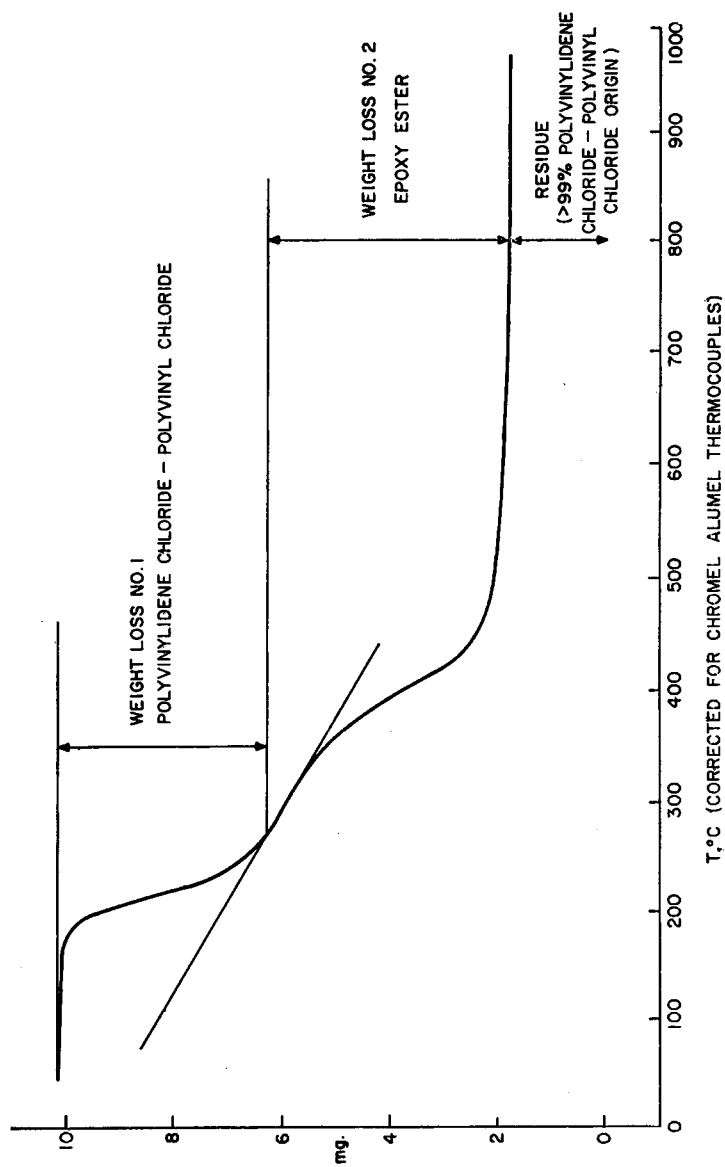
Fig. 1. Thermogram of 60/40 poly(vinylidene chloride)-poly(vinyl chloride)/epoxy ester coating.
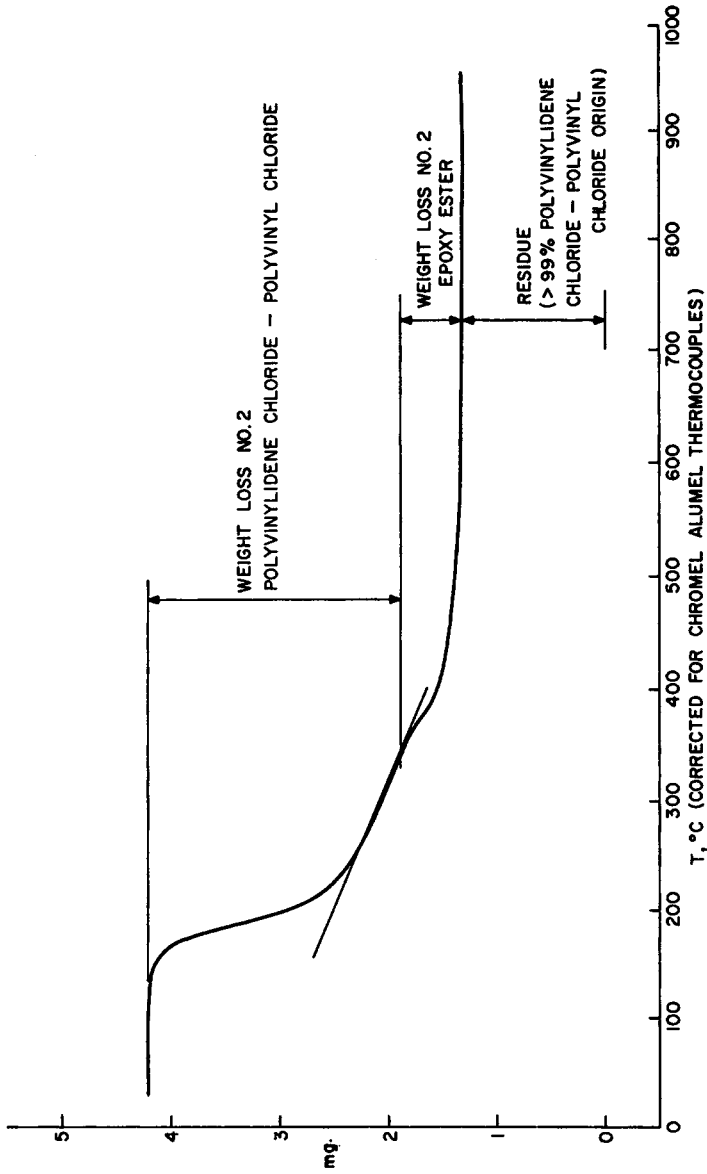
Fig. 2. Thermogram of 85/15 poly(vinylidene chloride)–poly(vinyl chloride)/epoxy ester coating.

The composite curves for samples containing >30% epoxy ester appear similar to the one shown for a 60/40 mixture in Figure 1. Weight losses for the components were measured as indicated. The major portion (>95%) of the loss past 270°C is attributable to the epoxy ester. This loss can be used for measurement of the P/E ratio of the electrophoretically deposited coatings.

A slight deviation from this procedure, as indicated in Figure 2, is necessary for samples containing low amounts of epoxy ester (i.e., the 85/15 mixture). In these samples, it was found that a major portion of the loss from ~250° to ~300°C is attributable to the polyvinylidene chloride-polyvinyl chloride. The change in slope to the leveling off of the curve, as shown, is taken as the epoxy ester loss.

The results obtained with coated samples are shown in the following Table I and represent the averages of multiple determinations of each ratio coated on different samples. For comparisons, 43.5% epoxy ester was found in a dried 60/40 mixture, and 46.8% was found in the dried 50/50 ratio. The results in the table, therefore, agree to within ±3% (relative) of the analysis of the original suspensions. The data for polyvinylidene chloride)-poly(vinyl chloride) was obtained by combining the first weight loss with the residue.

TABLE I
Poly(vinylidene Chloride)-Poly(vinyl Chloride)/Epoxy Ester Ratios[a] As
Determined by TGA

P/E ratio	Epoxy ester, %			Poly(vinylidene chloride)–poly(vinyl chloride),[b]		
	Ave.	σ	Error[c]	Ave.	o	Error[c]
50/50[d]	47.9 ± 1.3	1.57	3.3	52.1 ± 1.5	1.8	3.5
60/40[e]	42.3 ± 0.6	0.22	0.52	58.0 ± 0.8	0.85	1.5
70/30	33.3 ± 0.9	0.81	2.4	66.7 ± 0.5	0.71	1.1
85/15[f]	14.9 ± 0.6	0.6	4.0	85.1 ± 0.6	0.6	0.8

[a] Nominal values of prepared suspension.

[b] Obtained by adding weight loss no. 1 (see Fig. 1), and residue.

[c] % Error = $\dfrac{\sigma}{\text{Ave.}} \times 100$.

[d] Dried sample showed 46.8% epoxy ester; average for coated samples is within 2%.

[e] Dried sample showed 43.5% epoxy ester; average for coated samples is within 3%.

[f] Two samples only.

The slight overlap in weight losses, the small amount of residue left by the epoxy ester, and the inherent error in graphic interpretation of data all contribute to some error in the analysis. However, these results are accurate to within ±5% (relative) of the amount present and allow this procedure to be used for quality control of the coatings. Additionally, the technique is rapid (~1 hr/sample) and requires only small samples; sample sizes for this work ranged from 4 to 10 mg.

Drying Rates

Initially, two weighed (after 15 min of air drying) samples of the coated 60/40 P/E mixture were dried in a forced-air oven at 60°C for 200 hr. Periodic weighings were taken during this time span. The samples were then subjected to 80°C and 120°C drying for an additional 2 hr each. The amount of water lost did not significantly increase during the additional 2 hr at 80°C. The 120°C drying caused an additional 1% loss, but changes in the coating color indicated the loss of material other than water (e.g., surfactants, etc.).
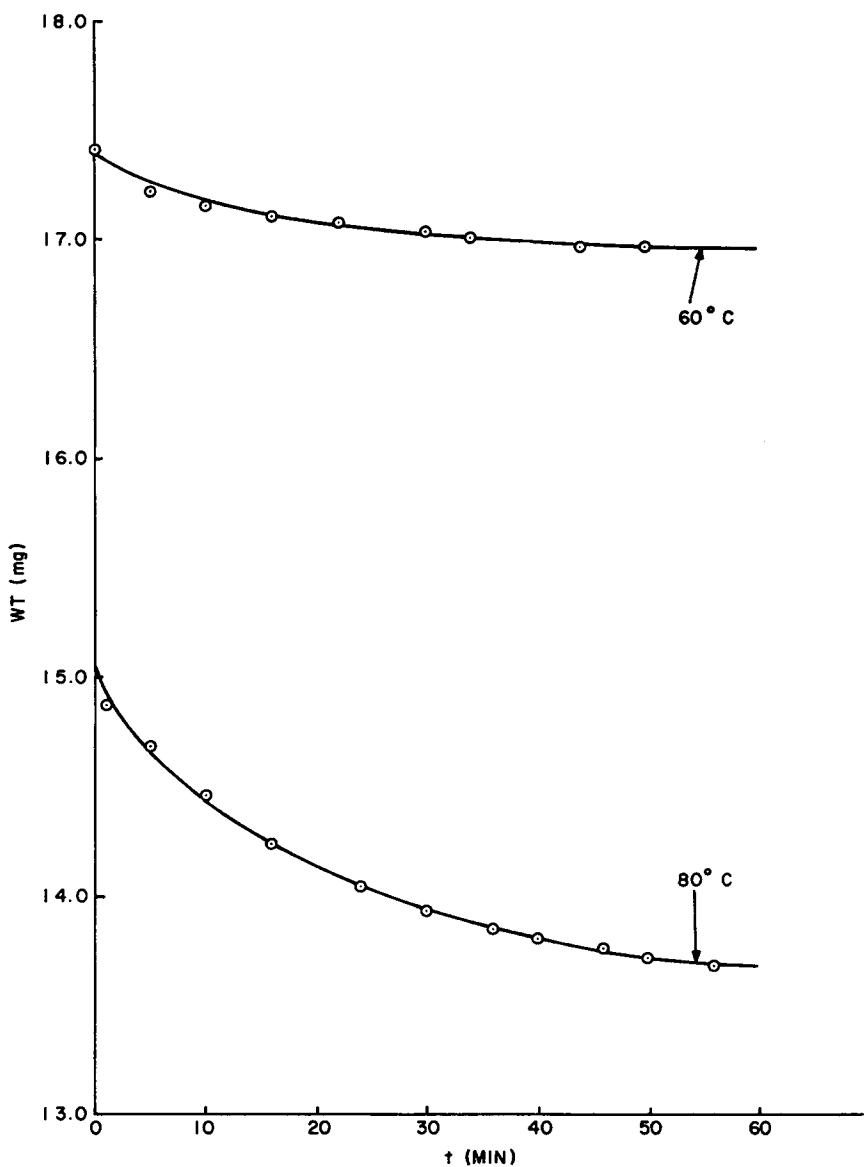
Fig. 3. Drying rate curves for 60/40 poly(vinylidene chloride)–poly(vinyl chloride)/
epoxy ester coating at 60°C and 80°C.

The 60°C data, obtained under conditions similar to those in a manufacturing situation (e.g., full-sized samples, etc.), were plotted as a function of time. The plot indicated that 2.5 to 3 hr at 60°C in a forced-air oven provided sufficient drying. However, the question arose as to whether this time could be shortened by the use of 80°C.

Isothermal TGA measurements rapidly provided this answer. Two additional samples (~10 mg each) were dried on the TGA unit at 60°C and 80°C, and weight losses were measured as a function of time. Figure 3 shows the computer-fitted data for each

sample.   The 80°C sample contained more moisture than the other, resulting in a greater percentage change based on the original sample weight.   However, the change in sample weight stopped after ~60 min, indicating that the overall drying rate is not highly temperature dependent in the 60°C to 80°C range.

CONCLUSIONS

The drying rate plots obtained by TGA measurements allow the use of the lower drying temperature (60°C), as the data indicated that the 80°C temperature does not significantly speed up the drying process.

Thermogravimetric analysis can be readily applied to the quality control ratio analysis of electrophoretically deposited polymer mixtures.   The analysis can be performed in approximately 1 hr with results obtained to better than ±5% (relative) accuracy.

References

1. P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965, p. 305.

2. Notes from Seminar on Flammability Characteristics of Polymeric Materials, Polymer Institute, University of Detroit, 1969.

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