Thermochimica Acta, 65 (1983) 9–17
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYSIS OF POLYMER BLENDS AND COPOLYMERS BY COUPLED THERMOGRAVIMETRY AND AUTOMATIC TITRATION

SHIRLEY G. FISCHER and JEN CHIU

Polymer Products Department, E.I. DuPont de Nemours and Company, Inc., Experimental Station, Wilmington, DE 19898 (U.S.A.)

(Received 17 November 1982)

ABSTRACT

A technique coupling automatic titration to thermogravimetry is described. The amount of a selected component in the volatiles produced under precise heating conditions in a DuPont 951 thermogravimetric analyzer is quantitatively determined with a Radiometer recording titration system. With the combined information on temperature, weight loss and chemical compositional changes, the stability and degradation mechanism of a sample are conveniently studied. Of particular interest is the use of such a technique to analyze polymer blends and copolymers in complex systems. Examples will be given to illustrate the various features of this application.

INTRODUCTION

Thermogravimetry (TG) has been widely used for polymer stability studies. Frequently, compositional analysis of polymer systems can also be made on the basis of weight losses in various temperature ranges and under various atmospheres. However, definitive determination of the composition or structure and establishment of decomposition mechanism or kinetics rely on the use of ancillary techniques such as GC, IR, MS, etc. coupled to TG [1–7]. Another useful but often neglected technique for this purpose is to couple titrimetry to TG in order to selectively and quantitatively determine certain components in the TG effluence.

Some studies utilizing this concept have been reviewed by Paulik and Paulik [8]. Investigations of ammonia evolution in zeolites [9,10] and transition metal amine chlorides [9] are representative of more recent applications of this technique. However, it has not been widely exploited in the analysis of complex polymer systems.

Mey-Marom and Behar monitored the elution of HBr continuously as a function of temperature with a bromide ion-selective electrode during the decomposition of a brominated polymer [11,12]. On-line titration was not utilized.

0040-6031/83/$03.00

Some work on poly(vinyl chloride) (PVC) was reported by Carel [13,14]. In one study [13], both the effluent and residue were examined for total chloride content in order to determine the effectiveness of ingredients added to promote chloride retention in the residue. Effluent gases were trapped and titrated. Additionally, recent work by Carel and co-workers [14] involved coupling TG to an AutoAnalyzer® for fraction collection and subsequent fraction analysis via another AutoAnalyzer® equipped with an ion-selective electrode. Continuous monitoring of the analyte was not performed.

This work describes the analysis of several polymer blends and copolymers by monitoring a specific component evolved under precise temperature and flow conditions with an on-line automatic titrator. Precision and accuracy determinations will also be presented.

EXPERIMENTAL

A DuPont 1090 thermal analyzer is used in conjunction with a DuPont 951 thermogravimetric analyzer (Wilmington, DE) which is coupled to a Radiometer RTS 822 recording titration system (London Co., Cleveland, OH). A schematic diagram of this coupled apparatus is shown in Fig. 1. The DuPont 1090 and 951 are used in the conventional fashion to obtain weight loss as a function of temperature. However, a quartz sample boat is used instead of the original platinum pan in order to reduce catalytic reactions of

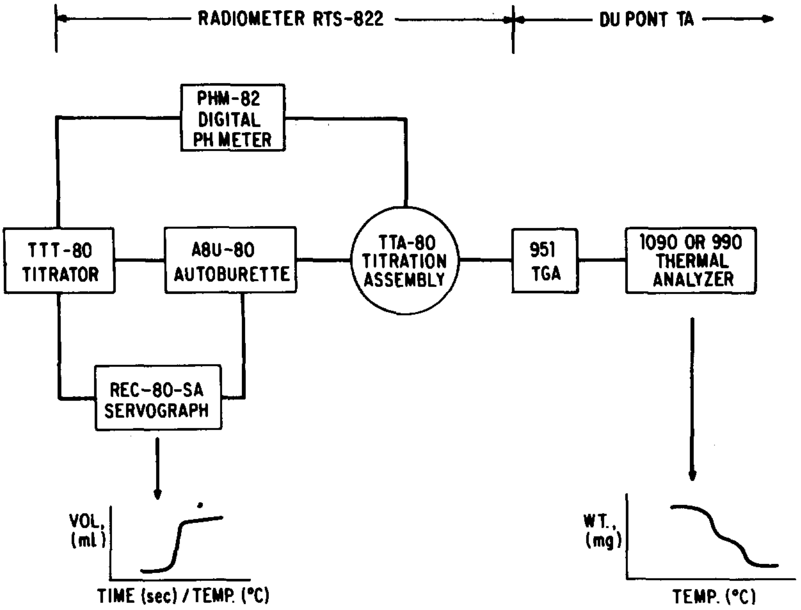

Fig. 1. Schematic diagram of a coupled TG–titration system.

some evolved products. The effluent gas from the TG is interfaced to the titration cell, where the sensing electrodes and autoburette are situated. The autoburette delivers titrant to the cell as required. This is sensed by the electrodes connected to the pH meter. The volume of titrant added as a function of time or temperature is recorded by the servograph.

The core of this instrument, where interfacing occurs, is highlighted in Fig. 2. The TG effluent delivery tip consists of a quartz tube with a female 12/5 spherical joint which is connected directly to the end of the TG quartz furnace tube. The neck of the delivery tip is bent at a right angle and tapered to a capillary of 1/8 inch diameter. After intensive studies on various sizes, this diameter has been found to provide optimum recovery of most eluted components. The vertical length is approximately 4½ inches and is inserted directly into the sample inlet of the titration cell. A gas flow of 100 ml min^{-1} is recommended.

Standard saturated calomel (Radiometer Model No. K4040) and glass (Radiometer Model No. G2040C) electrodes and double junction (Orion Research, Inc. Model 90-02-00) reference and chloride-ion selective (Orion Research, Inc. Model 94-17A) electrodes are used.

Typically, heating rates of 10–15°C min^{-1} are used. However, for samples containing a higher analyte concentration, such as homopolymers, a slower heating rate (2°C min^{-1}) is utilized to attain complete recovery.

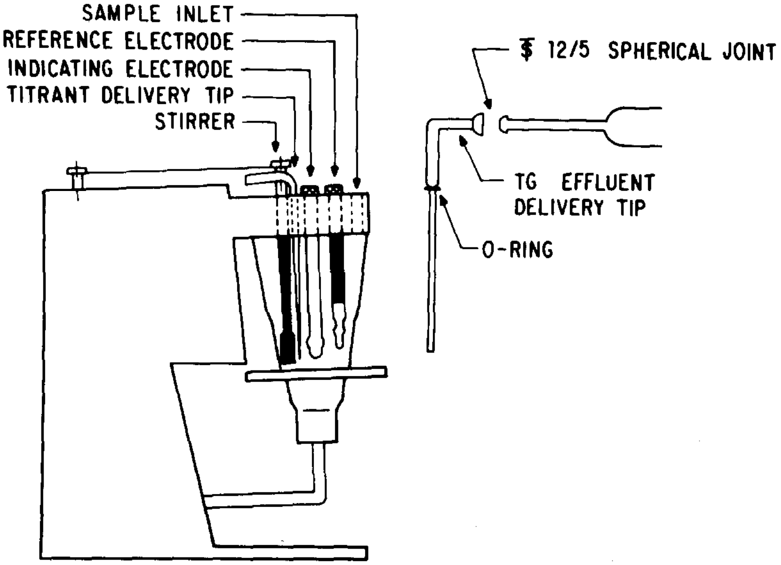

Fig. 2. Interface of the TG–titration apparatus.

RESULTS AND DISCUSSION

E / VAc Copolymer

Degradation of ethylene–vinyl acetate copolymer (E/VAc) is known to yield acetic acid essentially quantitatively as shown in the TG scan in Fig. 3a. The first step in the degradation is due to liberation of acetic acid. The second major step observed is a result of the breakdown of the polymer backbone. The weight-loss steps are well resolved and the first weight loss due to generation of acetic acid has been used to determine the VAc content [15]. However, the method would be in error if other volatiles, such as residual monomer or solvent should be released. In this case, coupled TG–titration provides precise analysis of the copolymer composition without ambiguity.

The titration curve obtained corresponding to the TG curve [Fig. 3(a)] is found in Fig. 3(b). The titrator is used in a pH stat mode, whereby an operator pre-set pH is maintained. The TG effluent gases are absorbed in dilute caustic solution in the titration cell. As the liberation of acetic acid occurs, the electrodes sense the change in pH in the titration vessel. The resulting decrease in pH is compensated by the automatic addition of standard NaOH titrant. The total amount of titrant added is a quantitative indication of the amount of acetic acid liberated, from which the VAc

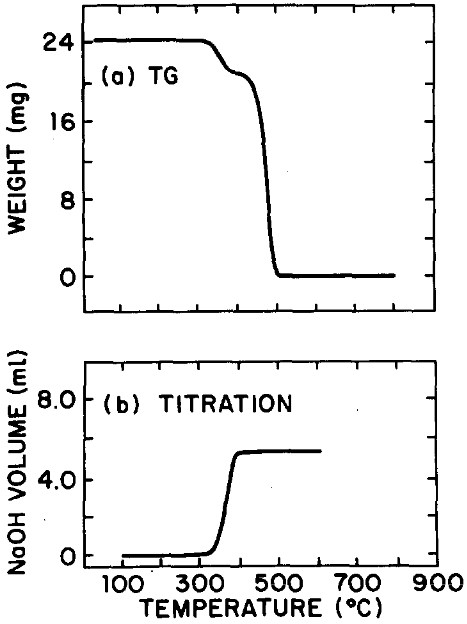

Fig. 3. Analysis of E/VAc copolymer. (a) TG scan; (b) titration curve.

TABLE 1

Accuracy of TG/titration determination of vinyl acetate

Sample	Weight % VAc	
	Nominal	TG/Titration
E/VAc [a]	8.8	8.8 ± 0.1
	19.9	20.0 ± 0.2
	39.1	39.5 ± 1.2
PVAc [b]	100.0	99.7 ± 0.8

[a] ASTM round robin.

[b] Scientific Polymer Products Inc., Ontario, NY.

concentration content can be determined. The curve obtained [Fig. 3(b)] shows the volume of titrant added as a function of temperature. Note that the titration curve shows only one step, that due solely to acid liberation, despite the two-step thermal degradation that occurs as shown by TG.

The titration results obtained from a series of E/VAc copolymer samples, used in an ASTM round robin, with varying VAc content (% by weight) are shown in Table 1 and plotted vs. those obtained by saponification in Fig. 4. The solid line delineates ideal recovery, while the points indicate actual experimental data. Excellent agreement is observed.

A study to determine precision is conducted utilizing one of the E/VAc samples. Results from this analysis are given in Table 2. A relative standard deviation of better than 1% is obtainable.

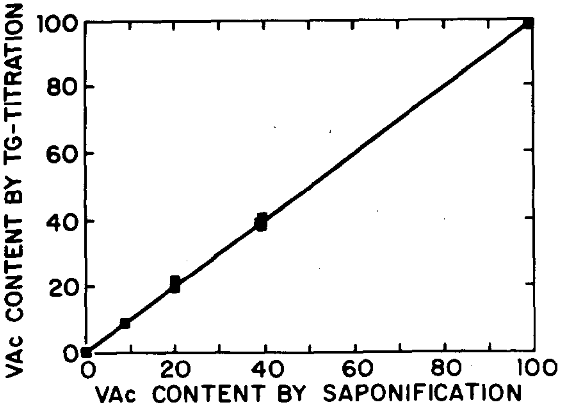

Fig. 4. Correlation between TG–titration and saponification results.

TABLE 2

Precision of TG/titration determination of vinyl acetate

Sample no.	Weight % VAc	
	TG	TG/Titration
1	19.3	20.3
2	19.6	19.9
3	19.3	19.8
4	19.6	20.1
5	19.4	19.8
6	19.4	20.0
Average	19.4	20.0
σ	0.13	0.18
%RSD	0.67	0.90

PVAc–PVAl Blends and copolymers

Analysis of poly(vinyl acetate) (PVAc)–poly(vinyl alcohol)(PVAl) blends or their copolymers is often difficult. A typical saponification method requires hours of refluxing. The IR method is restricted to narrow ranges of VAc content [16]. The TG method is not applicable because acetic acid and water moieties are liberated in the same temperature range (Fig. 5). Here, TG coupled with titration is ideally suited to resolve this problem. One can selectively analyze for acetate content or hydroxyl content by monitoring

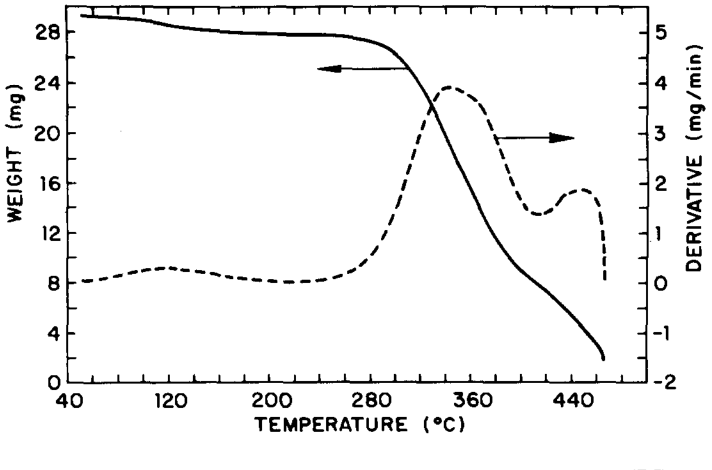

Fig. 5. Analysis of partially hydrolyzed PVAc. ———, TG curve; — — — — —, DTG curve.

TABLE 3

Analysis of PVAc/PVAl systems using TG/titration

Sample	Mole % VAc	
	Nominal	TG/Titration
PVAc + PVAl	13.5	13.4 ± 0.7
Partially hydrolyzed PVAc[a]-A	12.5	13.7 ± 0.4
B	11.7	11.8 ± 0.3
C	12.0	13.9 ± 0.8
D	12.4	12.3 ± 0.4
PVAl[b]	13.4	13.4 ± 0.7
PVAc[b]	100.0	99.7 ± 0.8
PVAl[b]	0.0	0.5 ± 0.2

[a] Experimental

[b] Scientific Polymer Products, Ontario, NY.

either acetic acid or water evolution. Some results based on the acetic acid liberation are shown in Table 3 for several partially hydrolyzed PVAc samples and a blend of PVAc and PVAl. Generally, good recovery was observed.

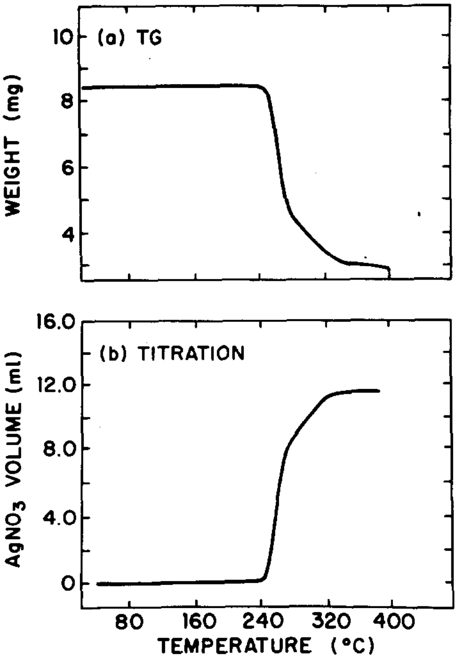

Fig. 6. Analysis of VCl/VAc copolymer. (a) TG scan; (b) titration curve with ISE.

TABLE 4

Analyses of VCl/VAc systems using TG/titration with ISE

Sample	Mole % VCl	
	Nominal	TG/Titration ISE
PVC [a]	100	99.3 ± 1.5
VCl/VAc [b]	90	90.2 ± 1.5
VCl/VAc [b]	83	85.3 ± 0.5
PVAc [b]	0	0
PVC + PVAc	92.6	90.3 ± 1.3

[a] International Standards Organization round robin.

[b] Scientific Polymer Products, Ontario, NY.

VCl / VAc Copolymers

Polyvinyl chloride (PVC) produces hydrogen chloride (HCl) quantitatively upon thermal degradation by a mechanism very similar to that of PVAc [17] and, thus, can be effectively studied by TG coupled with titration. However, HCl evolution is very rapid and a slower heating rate (2°C min^{-1}) and faster titration rate (20 ml min^{-1}) are necessary to obtain complete recovery. Ordinarily, heating rates of 10–15°C min^{-1} can be used.

With the present Radiometer system, ion selective electrodes (ISE) can be used as an endpoint detector for the titration. This provides a convenient method for analysis of vinyl chloride–vinyl acetate (VCl/VAc) copolymers. These samples produce both HCl and acetic acid during thermal decomposition, and thus, acid–base methods are not suitable. The amount of chloride liberated can be selectively titrated by standard silver nitrate solution quantitatively in the presence of acetic acid. The sample composition can then be determined. Figures 6(a) and (b) show a typical TG and ISE scan obtained for a VCl/VAc copolymer sample. Some results utilizing the ISE method are given in Table 4. The agreement between experimental and expected recovery is good.

CONCLUSIONS

The coupled TG–titration apparatus described here has been shown to be effective in polymer compositional studies utilizing both acidimetric and ion-selective electrode methods. The other capabilities of the titrator, such as redox, complexometric, colorimetric, Karl Fischer titrations, etc., could also be utilized to selectively monitor a large variety of species in the effluence of the TG.

REFERENCES

1 J. Chiu, Anal. Chem., 40 (1968) 1516.
2 J. Chiu, Thermochim. Acta, 1 (1970) 231.
3 H.G. Wiedemann, in P.D. Garn and R.F. Schwenker, Jr. (Eds.), Thermal Analysis, Vol. 1, Academic Press, New York, 1969, p. 229.
4 D.E. Smith, Thermochim. Acta, 14 (1976) 370.
5 C.A. Cody, L. DiCarlo and B.K. Faulseit, Am. Lab., 13 (1) (1981) 93.
6 J. Chiu and A.J. Beattie, Thermochim. Acta, 50 (1981) 49.
7 J. Chiu and A.J. Beattie, Thermochim. Acta, 40 (1980) 251.
8 J. Paulik and F. Paulik, in G. Svehla (Ed.), Wilson and Wilson's Comprehensive Analytical Chemistry, Volume XII, Part A, Elsevier, New York, 1981, p. 35.
9 G.T. Kerr and A.W. Chester, Thermochim. Acta, 3 (1971) 113.
10 A.B. Halgeri, M.H. Joshipura and T.S.R. Prasada Rao, Thermochim. Acta, 34 (1979) 325.
11 A. Mey-Marom and D. Behar, Thermochim. Acta, 30 (1979) 381.
12 A. Mey-Marom and D. Behar, J. Appl. Polym. Sci., 25 (1980) 691.
13 A.B. Carel, Proc. Int. Cable Symp., 27 (1978) 299.
14 J.W. Wimberley, A.B. Carel and D.K. Cabbiness, Anal. Lett., 15 (A1) (1982) 89.
15 J. Chiu, Appl. Polym. Symp., 2 (1966) 25.
16 B.B. Baker and C.E. Day, Private communication, 1980.
17 N. Grassie, in G. Geuskens (Ed.), Degradation and Stabilization of Polymers, Wiley, New York, 1975, p. 1.