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Quantitative thermogravimetric analysis of starch contents in several polymer systems [a]

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Abstract

The use of TGA to measure accurately the starch content in plastic materials has been show to be an effective method for rapid quantitative determination of this difficult-to-determine additive. Starch content is essential to the issue of biodegradability and accurate methods of analysis are key to product performance. The described TGA method works well for the resin types tested except in the case of EVA. Accurate calculated weight losses due to starch alone might be achievable by first determining a correction factor due only to the first observed weight loss of EVA, and then subtracting this factor from the total observed weight loss calculated between 200 and 370°C. The best correlated results were observed for starch levels above 2% and up to 30% loadings in LDPE. Better correlations between theoretical and actual levels might be observed with slower temperature increases during the thermally programmed cycles, but the described test results in this paper strongly support the use of TGA for the rapid and accurate analysis of starch content in polymer systems.

INTRODUCTION

Biodegradable and photodegradable plastics have been actively pursued as possible solutions to the solid waste dilemma. Although the effectiveness of such material is currently under debate, products are still being marketed and sold and claims are still being made.

Plastics require between 6% and 22% starch concentrate in order to be classified as "biodegradable". However, the ability to monitor such levels is currently restricted to enzyme digestions or limited to infrared analysis, with poor quantitative correlations.

The goal of this paper will be to establish an analytical method for the quick, accurate and reliable quantitative determination of corn starch content in plastics independent of polymer type. The thermal behavior of starch alone in various polymer systems will be accurately measured by thermogravimetric analysis techniques with a high degree of accuracy and reproducibility.

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EXPERIMENTAL MATERIALS

Instruments used

Mettler TC10A TA processor (control unit); Mettler TG50 with thermobalance; Epson FX-85 printer/plotter.

Standard preparation

A known amount of starch and resin was added to a standard Brabender mixer and allowed to mix for ≈ 4 min to insure homogeneity. The sample was then removed and pressed flat between two pieces of polyester film for easy handling.

METHOD DEVELOPMENT

Pyrolysis of a standard starch was first carried out in a compressed air atmosphere (Fig. 1). This was then followed by another analysis of starch carried out using an inert nitrogen (N_2) gas atmosphere at 35–550°C and a compressed air atmosphere from 550 to 850°C (Fig. 2). This gas change is made using an automatic value switch-over so that the dynamic test is not interrupted.

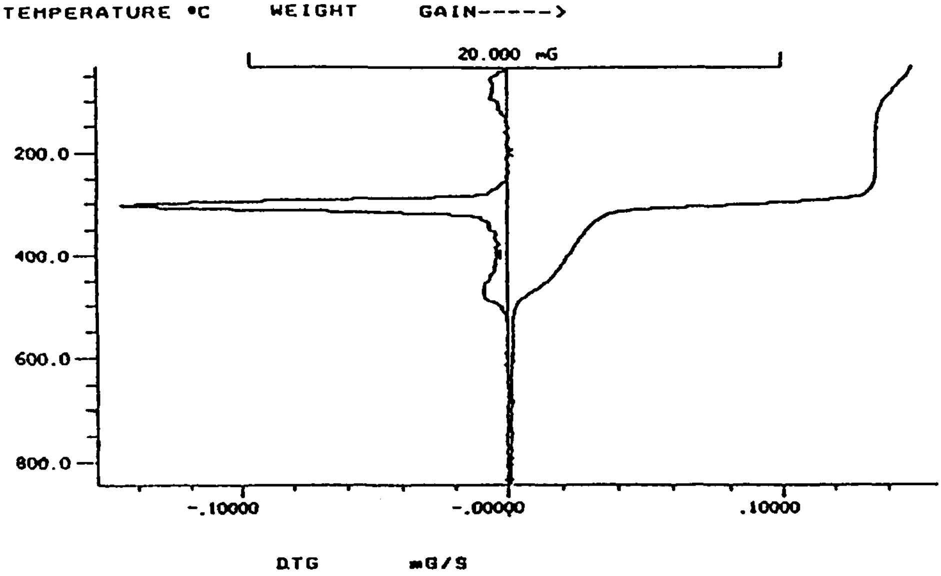

Fig. 1. TGA curve of starch run in a compressed air atmosphere.

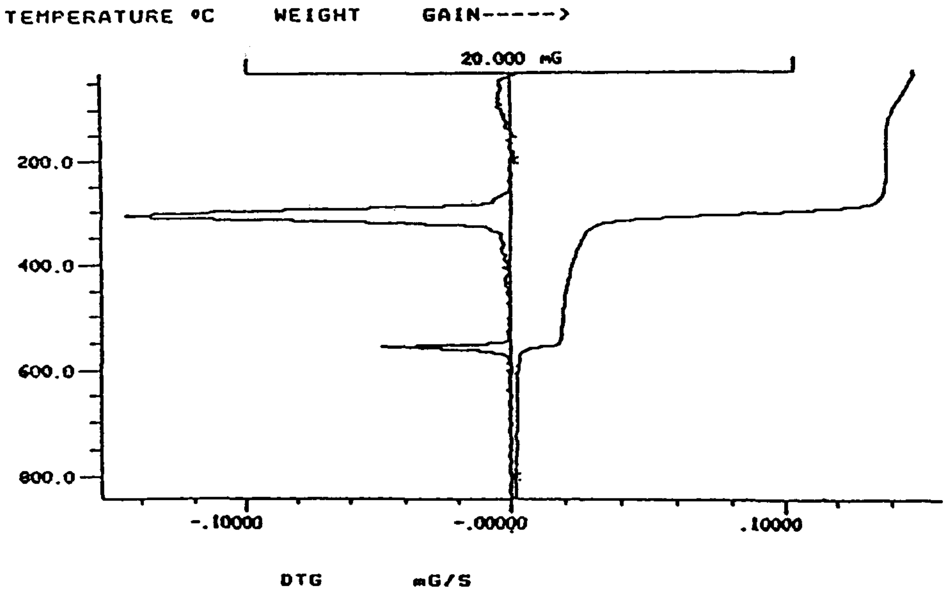

Fig. 2. TGA curve of starch run in a nitrogen atmosphere from 35 to 550 °C and in a compressed air atmosphere from 550 to 850 °C.

Various resins were evaluated to determine the temperature range at which complete decomposition occurs. The resins included in this study were polypropylene–polyethylene copolymer (CoPP), high density polyethylene (HDPE), low density polyethylene (LDPE), high impact polystyrene (HIPS) general purpose polystyrene (GPPS), and a polyethylene–vinyl acetate (EVA) that is 9% VA. The range of decomposition for five out of the six resins evaluated was found to be from approximately 350–550°C (Fig. 3). The gas phase change at 550°C allows the second starch peak to be read as the third step in the TG curve without interference from the resin (Figs. 4, 5 and 6) at all the starch loadings tested.

Infrared analysis of known blends were run on a Perkin–Elmer Model 1760 FT–IR instrument. An attempt was made to develop a method for analysis of starch using FT–IR. The development of a method was hindered by the fact that at elevated levels of starch, samples become too opaque (film thickness was 100 μm), thus cutting down the transmission of the beam.

CONCLUSIONS

Method

A sample is placed in an open porcelain crucible and weighed in a nitrogen (N_2) atmosphere. A dynamic test is started at 35°C and run up to 550°C. Without interrupting the test, a gas change is made from N_2 to

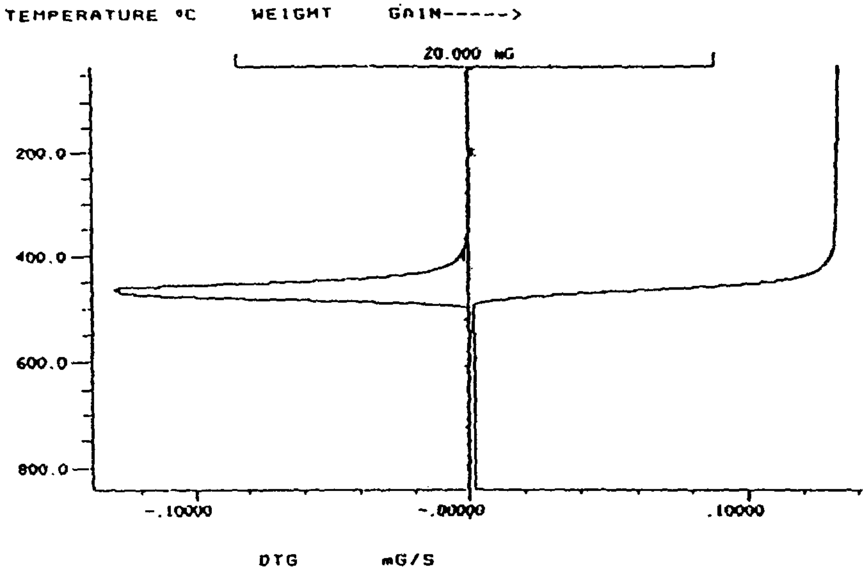

Fig. 3. TGA curve of LDPE run in a nitrogen atmosphere from 35 to 550 ° C and in a compressed air atmosphere from 550 to 850 ° C.

compressed air at 550°C. The test is continued to the end temperature of 850°C. The heating rate is 20 K $\min^{-1}$ for the entire test.

Table 1 gives the complete analysis of each TG sample, starch standard or

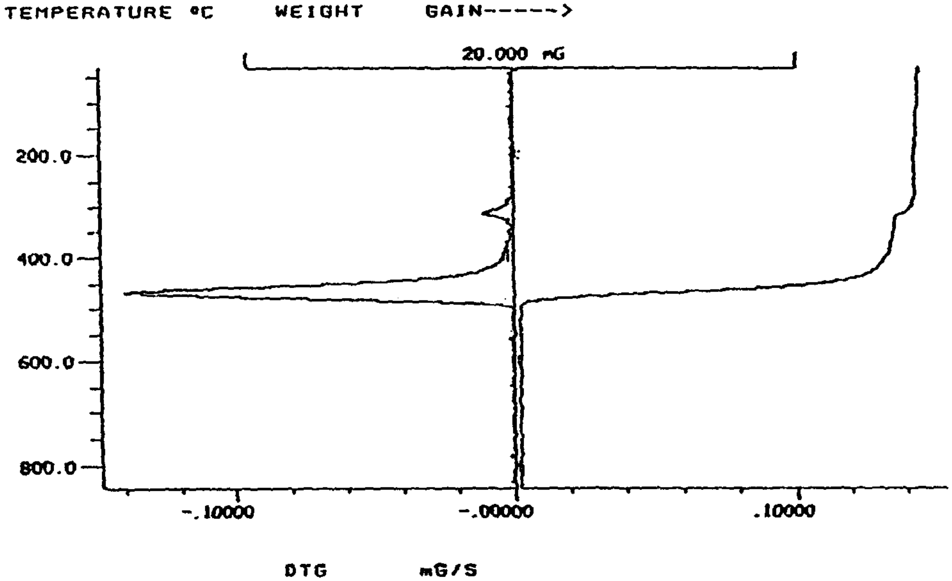

Fig. 4. TGA curve of a 6% starch standard in LDPE run in a nitrogen atmosphere from 35 to 550 ° C and in a compressed air atmosphere from 550 to 850 ° C.

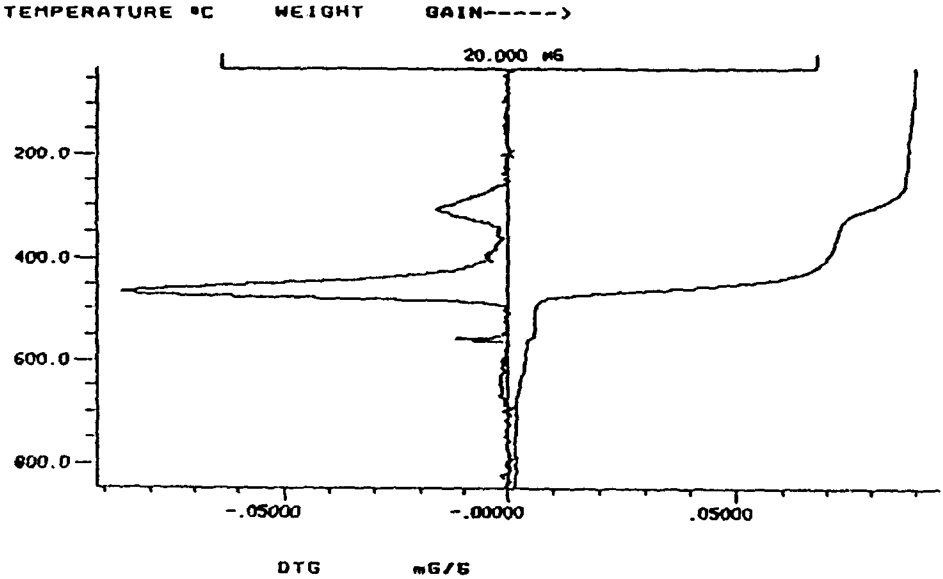

Fig. 5. TGA curve of a 20% starch standard in LDPE run in a nitrogen atmosphere from 35 to 550 °C and in a compressed air atmosphere from 550 to 850 °C.

resin run. The starch content can be calculated by adding together the two percentages obtained by evaluating the two separate steps of decomposition of the starch. The first area of decomposition occurs between 200 ° and

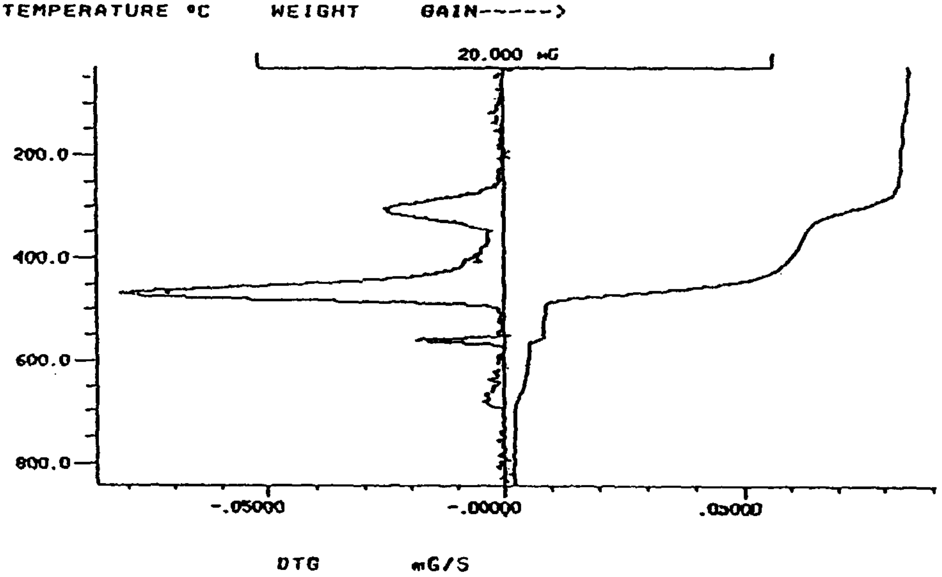

Fig. 6. TGA curve of a 30% starch standard in LDPE run in a nitrogen atmosphere from 35 to 550 °C and in a compressed air atmosphere from 550 to 850 °C.

TABLE 1

Thermogravimetric starch analysis results

Material	Starch (%)		Polymer (%)	Volatiles (%)
	200–370 °C	550–850 °C	370–550 °C	35–125 °C
HDPE			99.7	
HIPS			98.3	
LDPE			99.8	
GPPS			98.8	
EVA			97.7	
CoPP			99.5	
LDPE + 1% starch	1.4	0.5	99.2	0.2
LDPE + 2% starch	2.1	0.4	98.3	0.3
LDPE + 4% starch	4.0	0.2	96.2	0.2
LDPE + 6% starch	5.5	0.2	94.7	0.3
LDPE + 8% starch	7.6	0.1	92.5	0.3
LDPE + 10% starch	9.7	1.2	87.7	0.4
LDPE + 20% starch	17.3	3.5	76.0	0.4
LDPE + 30% starch	24.3	6.8	62.7	0.8

370°C and the second one occurs between 550° and 850°C. The resin decomposed between 370° and 550°C. The level of starch can also be calculated directly from the TG curve. In addition, any inorganic residue (i.e., ash content) can be obtained by making note of the weight of the crucible and the residue at the end of the run.

Limitations

Determination of starch content by the TGA method outlined above works remarkably well for five of the six resins evaluated. The exception occurs when the base resin is EVA. This resin's decomposition occurs in two

TABLE 2

Test results correlations

Starch content (%) (theoretical)	Starch content (%) (experimental)
1.0	1.9
2.0	2.5
4.0	4.2
6.0	5.7
8.0	7.7
10.0	10.9
20.0	20.8
30.0	31.1

weight steps instead of the one weight step observed for the five other resins. The first weight loss occurs at approximately 370°C, which interferes with the first weight loss step of the starch.

The best correlations between the theoretical data and the method results were obtained between 2% and 30% starch loadings (Table 2). Approximately 95% recovery of the starch standards was obtained in this region. Higher starch loadings resulted in lower recovery (i.e., accountability) when the starch levels exceeded 30%. It is very probable that by changing the heating profile the recovery at the higher loadings would be better, but the overall analysis time would be increased.

ACKNOWLEDGMENTS

The assistance of Mr. D. Sloan is greatly appreciated in manufacturing the standards used in this work.