

Thermogravimetric Behavior of Starches

BENJAMIN CARROLL AND JOHN W. LISKOWITZ¹

Thermogravimetric analyses have been performed with a precision of about $\pm 0.2\%$ on granular starches, starch fractions, modified starches, and mechanical starch mixtures. No feature of the thermogram could be related quantitatively to any functional group or structural aspect of the starch, although some general qualitative relationships were observed. The lack of a precise quantitative correlation appears to be caused by the presence of trace substances, especially inorganic materials, which may occur naturally

or be added during the processing of the starch product. However, a gravimetric thermogram may be used to "fingerprint" and thus empirically identify a starch sample. In some cases, the components of simple mechanical mixtures may be determined quantitatively. The modification of a starch resulting from prior heat treatment or chemical treatment such as carboxylation markedly lowers its thermal stability and alters thermograms accordingly.

Several years ago, carbohydrates were reported to be characterized by differential thermal analysis (DTA) curves and distinct variations had been observed between the amylose and amylopectin fractions of starch (2). This work has been repeated. Although naturally occurring carbohydrate polymers yield a wide variety of thermal curves, it was not possible to ascribe any feature of the DTA starch thermogram to a functional or structural aspect of the carbohydrate.

An early comparison of the thermograms obtained by DTA and thermogravimetric analysis (TGA) revealed that the latter method was more precise and that finer details could be observed partly because the conventional use of a reference substance such as Al_2O_3 for DTA is not required for TGA. The present authors found that the presence of Al_2O_3 had a pronounced effect in lowering the thermal stability of starch and tended to level out fine differences among closely related starches. The interesting area of TGA of starches is the 250° to 350° C. temperature range.

The effect of gradual chemical modification of a starch such as carboxylation was investigated. Carboxylation lowered the stability of the starch, but a series of samples of known degree of carboxylation revealed no strict systematic trend. This result may be due to the fact that in the carboxylation of starch other variables may be introduced such as changes in micellar aggregation, ash content, etc. In the case of branching, the effects of this structural difference revealed no special qualitative effect. The source of the starch seemed critically important. The differences in the thermograms, though extremely reproducible, were due in part, at least, to the effects of trace quantities of impurities in these products. For example, the presence of a trace quantity of butanol in an amylose fraction (the sample having been dried previously in vacuo for 18 hours) was sufficient to alter its thermogram radically (Figure 1). Extensive washing with methanol was required as a pretreatment to remove traces of butanol in starch fractions. Prob-

ably the naturally occurring phosphate content of a starch also exerted a marked effect on thermograms.

Two types of samples, however, appeared to show systematic trends on a TGA curve and, as a result, TGA indicates possible promise for control purposes in these cases. Progressive heat treatment of a starch gradually lowers its thermal stability. Also, simple mechanical mixtures of similar starches seem to yield thermograms that are a superposition of the thermograms of the individual components.

Apparatus and Reagents

Two macrothermobalances were used in this investigation, the Testut and the Ainsworth automatic recording balance, Model AV-AU-1. Commercial literature describing the latter instrument is available. Most thermograms, particularly those requiring the highest accuracy, were run on the Ainsworth. The Testut instrument is a magnetic transmission type continuously recording instrument which operates on the chainomatic principle.

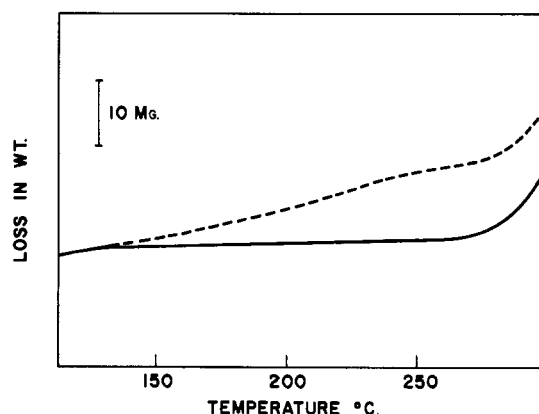


Figure 1. Effect of trace quantity of butanol (less than 1%) on thermogravimetric curve of corn amylose (14SSP) between 150° and 270° C. under atmospheric pressure

— Corn amylose washed six times with anhydrous methanol
--- Unwashed sample of corn amylose
Initial sample weight = 300 mg.
Heating rate = 5°/minute
Washed and unwashed samples previously dried at 60° C. in vacuo for 18 hours

Chemistry Department, Rutgers—The State University, Newark, N.J.

¹ Present address, Research Division, American Radiator and Standard Sanitary Corp., New Brunswick, N.J.

A Marshall testing furnace provided with Nichrome windings was used for the pyrolysis. Thermocouples of Chromel-Alumel were found satisfactory for temperature measurements, which were recorded on a millivoltmeter. Values were checked occasionally with a Leeds & Northrup K-2 potentiometer. The thermocouples were used to measure and monitor the furnace temperature. In the latter case, a Model JSG-2 Gardsmann pyrometric stepless controller was programmed to provide a linear heating rate of 5° C. per minute.

Coors porcelain crucibles were used to contain the samples during pyrolysis. A 00000 size was used for samples of 100 mg. or less. The next larger size was used for larger samples.

The corn amylose (14SSP), corn amylopectin (14SSP), potato amylose (13SSP), and potato amylopectin (13SSP) were obtained from R. J. Dimler (Northern Utilization Research and Development Division, USDA, Peoria, Ill.). The carboxylated starches were prepared by the hypochlorite oxidation process and were supplied by T. J. Schoch, Corn Products Refining Co. The corn starch and the corn yellow dextrin were supplied by the National Starch and Chemical Corp. All other chemicals used were of reagent grade.

The starch fractions, amylose and amylopectin, had been prepared by a method based on the Schoch procedure (3). Small amounts of butanol were present in the amylose fractions. After considerable trials, triturating starch fractions six times with anhydrous methanol washing was found to yield fractions which were effectively free of butanol. After the methanol washings, the samples were dried overnight in vacuo at 60° C. Thermogravimetric studies on the carboxylated starches, corn starch, and corn yellow dextrin were made without prior treatment of the samples.

Procedure

Thermogravimetric experiments were carried out under atmospheric conditions at a linear heating rate of 5° C. per minute. It was found convenient to fix the weight of a starch sample; an anhydrous basis was used. In the case of the runs on the Ainsworth thermobalance, the weight was set at 90 mg. Excellent reproducibility for the thermogram was obtained by enclosing the sample in the furnace so as to minimize convection currents. Repeated runs yielded thermograms that could be superimposed completely within the thickness of the recorded line on the thermogram; this represented 0.1 mg.

Buoyancy corrections were made by simply recording the weight change of an empty crucible as a function of the temperature, using the same conditions as prevailed during a thermogravimetric run.

Results

The results in Figure 2 show that carboxylation of a starch causes a decrease in the thermal stability of the starch. However, strict correlation between per cent carboxylation and thermal stability is lacking.

In the case of the amylose *vs.* the amylopectin starch

molecule, Figure 3 indicates that other factors must completely mask the difference in pyrolysis between a linear and branched molecule. Bryce and Greenwood found that potato amylose was less stable than the potato amylopectin fraction (1). They employed isothermal techniques and the evolution of gases, and used weight loss at 350° C. as a criterion of thermal stability. There is a crossover in Figure 3 at about 325° C. (see also Figure 6). If one uses the 350° C. temperature as the point of reference, there is agreement between the authors' results and those of Bryce and Greenwood. This points up the difficulty in generalizing on the relative thermal stability of starch fractions from a comparison of a few sets of samples.

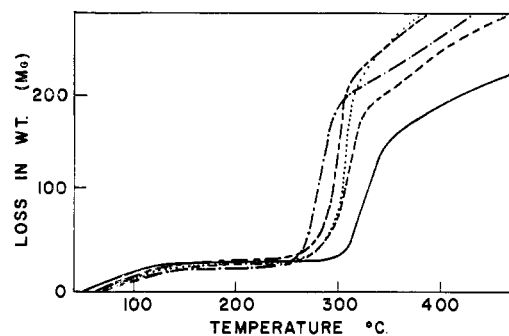


Figure 2. Effect of introducing aldehydes and carboxyl groups and shortening the chain length on the thermogravimetric curve of starch using the Testut balance under atmospheric pressure

— Corn starch
 --- 0.75% carboxylated
 ···· 0.25% carboxylated
 - - - 0.44% carboxylated
 - · - · 0.35% carboxylated
 Initial sample weight = 270.9 ± 0.4 mg.
 Heating rate = 5°/minute

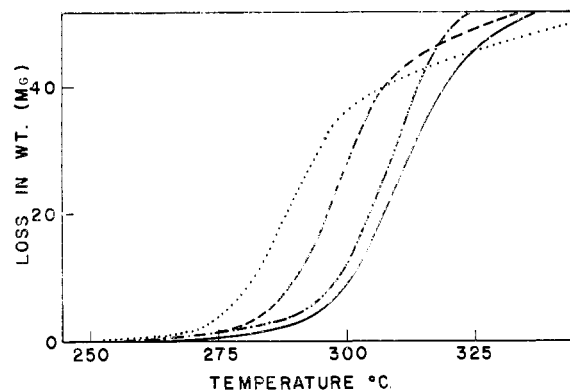


Figure 3. Composite of thermogravimetric curves of corn amylose (14SSP), corn amylopectin (14SSP), potato amylose (13SSP), potato amylopectin (13SSP) under atmospheric pressure

— Potato amylose 13SSP
 --- Corn amylopectin 14SSP
 - - - Corn amylose 14SSP
 ···· Potato amylopectin 13SSP
 Samples washed six times with anhydrous methanol to remove traces of butanol
 Initial sample weight on any anhydrous basis = 90 mg.
 Heating rate = 5°/minute

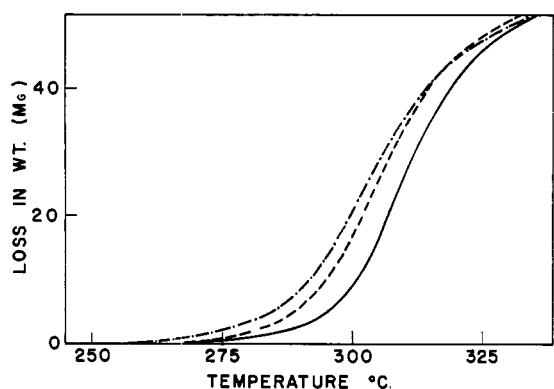


Figure 4. Effect of preheating on thermogravimetric curve for potato amylose (13SSP) under atmospheric pressure

— Potato amylose 13SSP
 - - - Potato amylose 13SSP heated for 30 minutes at 240° C.
 ···· Potato amylose 13SSP heated for 60 minutes at 240° C.
 Initial sample weight on an anhydrous basis = 90 mg.
 Heating rate = 5°/minute

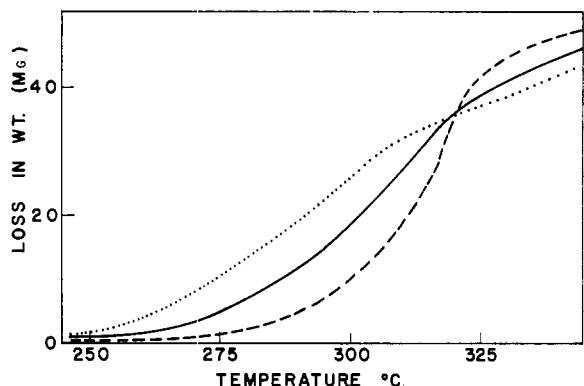


Figure 5. Thermogram for a mechanical mixture compared with thermograms for individual components

····· Corn yellow dextrin
 — 1:1 mechanical mixture of corn yellow dextrin and corn starch
 - - - Corn starch
 Initial sample weight on an anhydrous basis = 90 mg.
 Heating rate = 5°/minute, pressure = 1 atm.

Preheating a starch, or a starch fraction, lowered the thermal stability of the sample. This effect increased with increasing temperature and time of the heat treatment. The curves in Figure 4 show rather marked effects of a 30- and 60-minute heat treatment at 240° C. for potato amylose; similar results were observed for corn amylose, the amylopectin fractions, and granular starch. TGA was sufficiently sensitive to detect stability lowering in starch samples when the preheat treatment was carried out at 100° C.

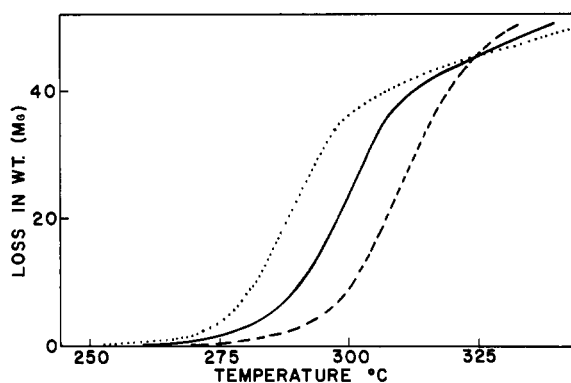


Figure 6. Thermogram for a mechanical mixture compared with thermograms for the individual components

- - - Potato amylose 13SSP
 — 1:1 mechanical mixture of potato amylose 13SSP and potato amylopectin 13SSP
 ···· Potato amylopectin 13SSP
 Initial sample weight on an anhydrous basis = 90 mg.
 Heating rate = 5°/minute, pressure = 1 atm.

Figure 5 compares the thermal stability of a corn yellow dextrin with corn starch. The qualitative effects are as would be expected. In addition, Figure 5 shows that thermal stability of a 1:1 mechanical mixture of the dextrin and corn starch may be deduced by the superposition of both thermal curves.

Nongranular starch mixtures yield thermograms which are also a simple superposition of the components of the mixture. This behavior may be seen in Figure 6. Here, the thermal curve for a mechanical mixture of potato amylose and amylopectin may be deduced from the TGA curves of the individual components.

Strongly dissimilar carbohydrates—for example, a monosaccharide and a polysaccharide—will yield thermograms for mixtures that will depart from the simple behavior of superposition. Similarity of components appears to be required to deduce the thermogram of a mechanical mixture from the TGA curves of its components.

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