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The Use of Derivative Thermogravimetry to Estimate Degree of Thermal Degradation

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ABSTRACT

It is difficult to estimate the degree of thermal degradation which has taken place in complex parts composed of cellulosics and polymeric insulation unless complete failure has occurred. There is a definite need for a parameter which can quickly and easily measure the relative degree of thermal attack on organic insulation subjected to various known environmental and processing conditions. This paper reports preliminary work using derivative thermogravimetry to perform this function. Derivative thermogravimetric analysis (TGA) was used to produce a value, TGA Index, related to the peak height of the major TGA derivative signal. This TGA Index was found to correlate with the copper number of insulating paper measured after thermal degradation. The application of TGA Index to evaluation of polymer degradation after thermal shock, water absorption, and accelerated UV attack is also discussed. Finally, preliminary studies on the use of derivative TGA to evaluate coatings exposed to various outdoor environments around the country are reported.

INTRODUCTION

Thermogravimetry (TG) or thermogravimetric analysis (TGA) has been used for many years to study degradation processes in polymers. Reaction mechanisms and kinetics have been elucidated in this manner, and accelerated aging tests have been developed which use TGA to predict relative thermal stability of a wide range of materials. Because thermogravimetry is such a versatile tool in the study of degradation processes themselves, it was the logical method to explore evaluation of a related phenomenon, the state of degradation.

The rationale for our initial experiments can be summarized as follows. Thermogravimetry involves the dynamic measurement or weight changes in a sample as a function of temperature. A TGA run on a sample of fresh material will usually exhibit weight loss steps corresponding to various stages in the degradation of the original substance plus weight losses corresponding to secondary reactions of the initial degradation products. At any given temperature T_x, the rate of weight loss is a function of the amount of original material remaining and the nature and relative amounts of degradation products present.

If one now submits a sample of the fresh material to thermal degradation and runs another TGA experiment on the degraded material, the rate of weight loss at T_x is still a function of the amount of original material remaining and the activity of the degradation products. However, we know that there is less of the original material present since some prior breakdown has taken place. If the primary breakdown products of degradation are relatively inert, they will exert a dampening effect on the rate because of dilution effects, and the result will be a slowing of the rate of weight loss. If, however, the major breakdown products are reactive, an increase in their concentration due to prior degradation could very well lead to an increase in the rate of weight loss for the degraded specimen. Either way, a definite change in rate of weight loss should be observed in degraded material.

EXPERIMENTAL

Figure 1 illustrates a typical weight loss curve obtained with organic electrical insulating materials. The most sensitive point at which to choose T_x would be at the maximum rate of weight loss. Unfortunately, in the conventional thermogram, this corresponds to the point at which the curve is changing direction at the greatest rate and reproducible measurements are very difficult to make. However, if one records the time derivative of the weight loss against temperature

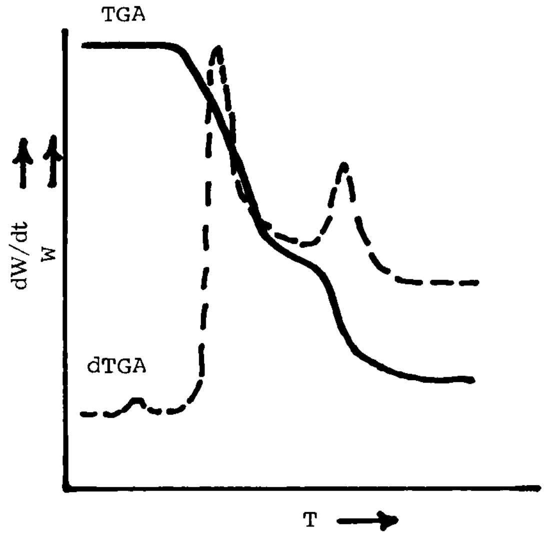

FIG. 1. Typical thermograms of cellulose insulation.

instead of weight loss, a curve similar to the dashed line in Fig. 1 results. The point of maximum rate of weight loss is now displayed as the maximum of a well-defined peak. This maximum is easily measured and is quite reproducible.

For this work, a Du Pont Thermal Analyzer with a Du Pont 950 Thermogravimetric Analyzer was used to produce the primary TGA curve. The output from the thermobalance was processed by a Cahn Time Derivative Computer and the dTGA curve was then recorded on a Houston X-Y recorder. Sample size was generally between 2 and 6 mg.

RESULTS

The dashed curve in Fig. 1 illustrates the typical time derivative weight loss curve obtained with insulating paper. Three maxima are observed, a small peak at 30 to 40° C, a large peak at 335 to 340° C, and a third peak of variable size centered at about 440° C.

The derivative traces in Fig. 2 show the basis of the method. After aging for 16 hr at 200° C, cellulose insulation is degraded to the point where the major weight loss on thermogravimetry, the one whose derivative signal peaks out at 340° C, has been greatly retarded. The

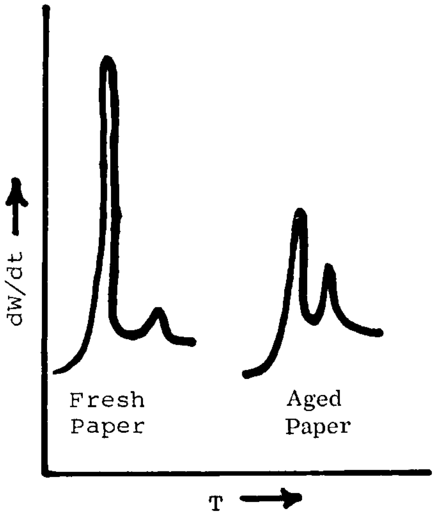

FIG. 2. Comparison of fresh and aged paper (16 hr at 200°C).

quantitative measurement of this rate retardation is what we are relating to prior degradation. The value which we have labeled as TGA Index is defined as the height of this peak in inches of chart paper divided by the original sample weight, T.I. = h/w.

Table 1 summarizes the results of a reproducibility study on fresh paper and pressboard. The individual values recorded in Table 1 were obtained over a period of several weeks so that the precision calculated is a reasonable estimate of the precision likely to be encountered over the time span of a single series of experiments. With both pressboard and paper the relative standard deviation is less than 10%. This is a reasonable precision for the type of measurement being made.

The next question to answer is whether these curves obtained by thermogravimetry correlate with any of the more traditional methods for estimating thermal degradation in insulation. With cellulose, one of the tests widely used is copper number.

Copper number has been used for many years to evaluate paper insulation. In theory, copper number denotes the number of scissions formed by aging. In practice, the reagent reacts more or less selectively on ketone and aldehyde groups. It is a very useful test, especially when used in conjunction with acid number.

The bow in the curve of Fig. 3 is caused by the fact that the TGA Index is a double-valued function with respect to copper number. The index rises slowly as aging proceeds at low temperatures. This may represent a small improvement in properties due to loss of loosely

TABLE 1. Reproducibility of TGA Index Values

	h/w Values of 60% manila/40% kraft paper	h/w Values of 100% kraft pressboard
	3.41	3.71
	3.54	3.34
	2.86	3.53
	3.54	3.88
	3.02	3.16
	3.74	3.68
	3.65	3.62
$\overline{X}$	3.39	3.64
S	0.33	0.31
Range	3.06 to 3.72	3.33 to 3.97
$\overline{X}$/S, %	9.7	8.5

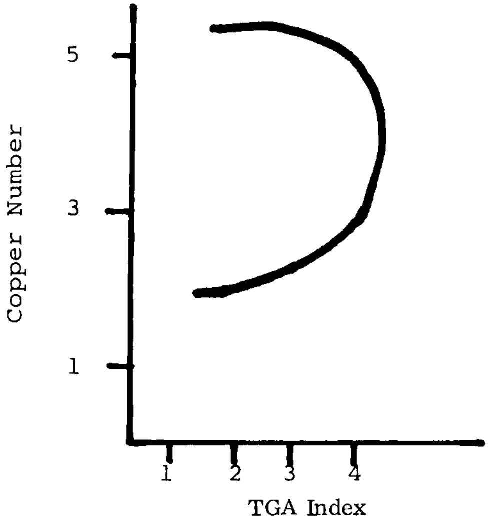

FIG. 3. Copper number vs TGA index for insulating paper.

bound water. As the aging temperature is increased, a point is reached at which the index rises sharply; this corresponds to the region of greatest increase in copper number and so it must be considered to be the point where serious degradation has begun. In contrast to copper number, which slowly approaches a limiting value of 6 or 7 as degradation proceeds, the TGA Index reaches a maximum and then drops off very sharply to quite low values for completely charred paper.

Since we were fairly successful in evaluating the thermal degradation of cellulose by derivative thermogravimetry, we decided to investigate the utility of this technique with other materials and other modes of degradation. The example we chose was a poly(vinyl chloride) powder coating we had been evaluating.

We ran derivative thermogravimetry experiments on fresh coating and coating after exposure to three separate environments. The first test was a simple immersion in water at 38°C for 14 days. The second was a thermal cycle test in which the temperature was cycled from -23 to 130°C twice a day. The coating was examined after 10 cycles. The third test is an UV/condensing moisture test conducted in a QUV cabinet made by the Q-Panel Co. The coating was examined after 1469 hr of UV exposure.

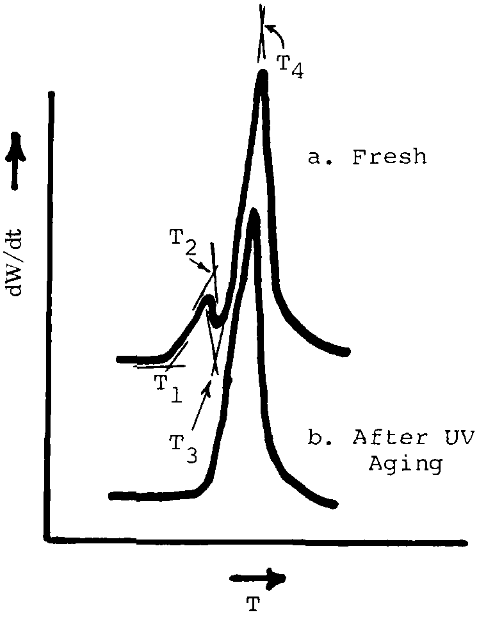

FIG. 4. Comparison of fresh and UV-aged PVC coating.

TABLE 2. DTGA Results on PVC Powder Coating

Treatment	h/w, T_1	h/w, T_2	h/w, T_3	h/w, T_4
Fresh	0.16	0.42	0.51	2.3
After 14 days at 38°C in water	0.18	0.44	0.60	2.2
After 12 cycles of -10° to 266°F	0.08	0.23	0.41	2.4
After 1469 hr UV exposure in QUV cabinet	0.30	-	0.62	1.9

A typical derivative TGA trace of the fresh PVC formulation is shown in Fig. 4. Measurements were made at the four indicated temperatures, which in the case of fresh material were 249, 255, 266, and 278°C, respectively. A summary of the TGA Index values obtained is given in Table 2. The water immersion test revealed no changes in gloss or Sward rocker hardness, and essentially no change in the DTGA results either. No cracking, embrittlement, or loss of adhesion was observed after the thermal cycling test, but the h/w values of T_1 and T_2 dropped to half of the original value, suggesting that some physical change has occurred in the material. After exposure to 1469 hr of UV radiation, one might expect some serious changes in the formulation to have taken place, but all that is observable is a moderate amount of chalking. The DTGA results indicate drastic changes however, the peak associated with T_2 disappearing entirely, as shown in Fig. 4.

One may postulate that the rate processes involved with T_1 and T_2 are associated with more volatile components of the formulation. The lower TGA Index values for T_1 and T_2 observed after thermal cycling can then be explained by assuming the more volatile fragments have been removed at the high temperature end of the cycle. The more drastic changes observed after UV exposure can be related to the degradation of the main PVC polymer itself, which results in a lowered TGA Index for T_4. The volatile breakdown products then provide the rationale for the doubling of the T_1 rate. The disappearance of the T_2 rate maximum may be due either to the complete reaction of a specific formulation component responsible for T_2 or it may be due to the merging of the T_2 maximum with rate maxima produced by primary and secondary degradation products. These postulated mechanisms can be readily checked by further work, but it is clear that the derivative TGA method described here can serve as a sensitive indicator for many types of degradation.

TABLE 3. One Year Outdoor Weathering Results dW/dt

	Peak temperature (°C)			Peak height (mV)		
Location	Alkyd 1	Alkyd 2	Acrylic	Alkyd 1	Alkyd 2	Acrylic
Control	380	334	346	0.63	0.73	0.85
Mild Industrial	374	329	393	0.55	0.70	0.85
Hot dry	354	326	307	0.54	0.55	0.78
Hot moist	317	335	382	0.52	0.50	0.60
Severe industrial	357	324	375	0.47	0.59	0.86

By the same token one would expect the derivative TGA procedure to be quite helpful in evaluating the effects of outdoor weathering. We presently expose organic coatings to four separate locations around the country considered to be, respectively, mild industrial, hot dry, hot moist, and severe industrial environments. A sampling was made of three coatings which had been exposed for 1 year, and Table 3 summarizes the TGA data we obtained from them.

The first point to note is that the two alkyds act similarly, both yielding lower peak heights and lower peak height temperatures after exposure. The fact that the TGA degradation rate drops suggests that the products of weathering breakdown are inert, perhaps even inhibitive, with respect to subsequent thermal degradation. Because the peak temperatures also drop, one can further surmise that the weathering breakdown products are lower molecular weight fragments of the original formulation.

Let us assume that, for alkyd systems at least, the greater the drop in peak height, the greater the weathering degradation. Certainly, such an assumption must be verified by correlation with definitive property data and, moreoever, will depend entirely on the physical property chosen for correlation. But we expect our TGA method to perhaps show degradation trends before they are apparent by other means, and a 1-year exposure is really not enough to expect discernible changes in good coatings by traditional methods. So let us bypass the problem of correlation for now and see what we can extract from the data shown.

If one does make the aforementioned assumption, it is clear that alkyd formulation # 1 performs about as expected with mild industrial and hot dry environments affecting the coating the least; the hot, moist environment affecting the coating a little more; and the severe industrial environment causing the most serious degradation. The peak temperature drops show the same trend except that the hot, moist location exhibits a much lower peak temperature than the severe industrial site, which actually shows up better than the hot dry location. A possible explanation for this is that the hot moist location is also located near the ocean and is subjected to a certain amount of salt spray. This undoubtedly leads to the presence of metallic salts on the surface of the coatings, and these salts may well catalyze the TGA degradation reactions.

In contrast, the peak heights for alkyd formulation # 2 suggest that the hot, moist temperature is the most degrading. Even the hot, dry environment gave a lower peak height than the severe industrial site. The fact that both warm climate sites exhibited the most attack suggests that alkyd formulation # 2 is temperature sensitive, and further tests should be conducted before the coating is ever used in hot climates. The peak temperatures for alkyd formulation # 2 show that a slight catalytic effect has occurred at all of the sites except at the hot, moist site. This is in direct contrast to the results from the first alkyd formulation, and while it can be rationalized, any explanation should really await the results of further experimentation.

The third example is an acrylic coating. The attack of either industrial environment on the acrylic is not evident after a year's exposure. Both hot weather sites, on the other hand, show evidence of having affected the acrylic coating, the moist site doing the most damage. The apparent severity of the two warm climate sites may be due to the higher temperatures, but most likely it is the increased incident UV radiation because of the additional sunlight at these sites that is responsible for the attack.

This particular acrylic was chosen for inclusion because it demonstrates anomalous temperature effects. The coating panels exposed at both industrial sites and at the hot, humid site exhibit increased peak temperatures over the control, suggesting that cross-linking may be the primary reaction taking place. However, the panels from the hot, dry site show a considerable drop in peak temperature, suggesting disruption of polymer chains as the major route. Further work is needed to clarify this situation, but the mechanism of acrylic degradation at these outdoor sites is obviously more complex than one would expect at first glance.

CONCLUSIONS

The cellulose and polymer studies reported suggest that the derivative TGA method may be applicable to a wide variety of aging and processing conditions. The advantage of the TGA Index approach is that by tailoring aging conditions to approximate known processes, a simple, fast, effective method for post-mortem estimates of thermal attack on insulation can be developed for the monitoring and evaluation of many plant processes.

Bearing in mind the constraints on this approach, we can draw the following conclusions:

1. TGA Index, as defined above, is a very useful parameter for evaluating, after the fact, the degradation, thermal or otherwise, suffered by polymers.
2. The TGA Index has a precision of 5 to 10% in estimating degree of thermal degradation.
3. For cellulose insulation, TGA Index correlates with copper number in evaluation of thermal degradation.
4. TGA Index shows promise as a fast, sensitive monitor for early detection of degradation under natural and artificial weathering conditions.