OFFICE MEMORANDUM

MICHIGAN
DEPARTMENT OF STATE HIGHWAYS

June 26, 1969

To: R. L. Greenman
Engineer of Testing and Research

From: L. T. Oehler

Subject: Application of Thermoanalytical Techniques to Highway Materials. Research Project 69 G-169. Research Report R-699.

This report has been prepared for your information by W. L. Frederick as a brief review of the Laboratory's status concerning thermal analysis. It includes a general discussion of the theory, a review of work performed by E. I. du Pont de Nemours and Company on our samples, and recommendations for using thermal analysis in highway research. The pertinent portions of the DePont report are cited, along with our comments about them.

Thermal analysis observes and measures the changes in properties that materials undergo as they are subjected to systematic changes in temperature. Many properties of materials change as the sample is subjected to a thermal program. This makes thermal analysis a very powerful and versatile tool (ASTM has a sub-committee on thermal analysis). Some of the changes that can be observed are:

1. Changes in physical state: melting, sublimation, and evaporation or boiling.

2. Phase changes in the crystal structure of the material.

3. Chemical reactions.

4. Absorption or desorption of gases.

5. Rate of change of the above processes.

6. Changes in size (determine coefficient of expansion).

7. Changes in viscosity.

8. Changes in electrical conductivity.

Three modes of operation are generally employed to monitor properties of a sample during thermal analysis.

1. Differential scanning colorimetry (DSC), indicates the temperature at which physical or chemical changes occur during a temperature program and measures the amount of heat, in calories, that the sample liberates or absorbs during such changes. An older technique, differential thermal analysis (DTA) detects the same phenomena as DSC but does not measure the amount of heat involved. Crystal phase changes such as those at the glass transition temperature, dehydration, decomposition, oxidation, vaporization of components, and chemical reactions are detected and their heat quantities measured. Samples under 0.5 gram are used. Figure 1 shows the type of recorder trace obtained.

2. Thermogravimetric analysis (TGA) continuously records the weight of a sample during temperature programming, where the temperature may exceed 2,000 F. Thus, processes such as dehydration, decomposition, oxidation, and vaporization can be followed with ease. Samples under 0.5 gram are used. Figure 2 illustrates the type of data obtained.

3. Thermomechanical analysis (TMA) determines penetration, expansion, or contraction parameters of a sample while temperature is varied in a systematic manner. The samples used are only 0.4 in. maximum dimension. The instrument probe which contacts the sample is attached to a movable core in a variable transformer. Change in sample size, or penetration of the probe into the sample, moves the transformer core and produces a voltage change which is recorded. Thus, unless penetration is being determined, a smooth curve is obtained with a slope that indicates the thermal expansion coefficient of the sample.

On June 27, 1968, samples of five materials were sent to Dr. G. W. Miller of the Du Pont Instruments Applications Laboratory in Delaware to determine the applicability of thermal techniques to the analysis and quality control of highway materials. These samples consisted of:

1. Four samples of preformed neoprene highway joint seal, containing approximately 50 percent neoprene and varying amounts of plasticizers, fillers, and carbon black, labeled A, B, C, and D. These samples were from different suppliers and showed differences in physical properties.

2. Four samples of ground hardened concrete to determine whether thermal methods could measure their cement content. Two samples, J-7 and K-8, were prepared with blast furnace slag aggregate, the other two, 6 and 4, contained gravel aggregate.

3. Three samples of paving asphalt from different sources, to see how thermal methods might be applied to durability studies. These were labeled 35, 1, and 10.

4. Two samples of hot-pour bituminous joint sealer, labeled PP and 183, for analysis of adulterants such as cured ground scrap rubber and sand.

5. Two samples of polyethylene resin, labeled 180 and 193, for density (degree of crystallinity) measurement using thermal techniques.

Dr. Miller forwarded his results on December 31, 1968. His data clearly show that thermoanalytical techniques can be effectively applied to highway materials, although some of the material in the Du Pont report is over-simplified and tends to be misleading.

Du Pont's results are given below, followed in each case by a commentary by the Research Laboratory staff.

A. Concrete characterization

Du Pont reported:

> "Two samples were prepared using different kinds of aggregate and varying quantities of cement. The concrete was studied by using the Du Pont 950 TGA, and the thermogravimetric curve used to identify the components of the concrete. Bound water from texture elements was lost at temperatures up to 300° C and water from the dehydration of calcium hydroxide occurs near 400° C. The calcium carbonate in the mortar dissociates above 600° C.
>
> Sample J-7 -- Blast Furnace Aggregate
>
> 2.3 % water from texture elements
> 0.6% water from calcium hydroxide
> 5.2% carbon dioxide from calcium carbonate
>
> Sample 4 -- Gravel Aggregate
>
> 2.7% water from texture elements
> 0.6% water from calcium hydroxide
> 1.2% carbon dioxide from calcium carbonate
>
> The thermogravimetric analyses of concrete using two different aggregates illustrate the similarity in the loss of water, but there was a pronounced difference in the amount of CO_2 lost from the $CaCO_3$."

Comment:

Although the method apparently cannot be used to determine cement content, we found Du Pont's application of the method and interpretation of the results to be very good.

B. Preformed Neoprene Highway Joint Seals

Du Pont reported:

"The 941 Thermomechanical Analyzer was used in the expansion mode to detect the differences in expansion coefficient (α L) among samples. Several transitions were found in both samples, but there was a difference in the expansion coefficient.

Samples A and D were identical materials from the same manufacturer, whereas sample C was obtained from a different supplier. Sample A was found to be unsuitable since it showed a low elongation at rupture. This type of behavior is usually associated with larger amounts of crystallinity or crosslinking. The linear coefficient of expansion will be lower for more crystalling or crosslinked rubbers, and this behavior is reflected in Table I.

TABLE 1

Linear Expansion Coefficients, in/in/^{o}C

Sample	20-30^{o}C	40-60^{o}C
A	1.8×10^{-4}	1.4×10^{-4}
C	1.7×10^{-4}	20.3×10^{-4}
D	1.7×10^{-4}	18.9×10^{-4}

Hence, one could predict from an easy measurement of linear expansion in the temperature use range of the neoprene that the material which fails is too crystalline. A numerical threshold for product assurance can be set, so that all incoming materials can be readily examined. In this case, materials showing α L greater than 15×10^{-4} in/in/^{o}C (40-60^{o} C) will be acceptable."

Comment:

The information supplied to Du Pont by the Research Laboratory did not indicate that samples A and D were identical. Another sample (B) was also submitted but no data for this sample appear in the Du Pont report. Finally, even though TMA has done a good job of pin-pointing differences among these three samples, the data are not a sufficient basis for establishing a quality control limit. Further study, however, might prove linear coefficient of expansion to be an excellent quality control procedure for neoprene joint seal.

C. Hot-Pour Bituminous Joint Seals

Du Pont reported:

"The Thermogravimetric Analyzer was used to analyze for adulterants such as cured, ground, or scrap rubber and sand. The joint seals containing scrap rubber will expand more than those containing sand, and the degree of changes in expansion will depend upon the amount of each therein (TMA). However, TGA studies can yield qualitative information on the contents of each contaminant. The following analyses were deduced from the TGA (in air). The decomposition of these composites in air will show the initial loss of the asphalt, followed by the degradation of the crosslinked rubber and sand.

Sample	%Asphalt	%Rubber	%Sand
183	65	30	5
PP	70	28	2

Hence, component analysis can be easily accomplished by TGA analysis."

Comment:

The third sentence in the Du Pont paragraph indicates qualitative information will be obtained, but quantitative data are presented for the joint seal samples. Further, it is not possible to evaporate asphalt with no decomposition of rubber. The asphalt and rubber will both char and burn-off as temperature increases. Sand will not degrade at all under these conditions. Although such sealers can be studied effectively by TGA, these results are of dubious value.

D. Polyethylene Densities

Du Pont reported:

"The density of a semi-crystalline polymer can be related to both the heat of fusion and the linear coefficient of expansion. Examining two samples of polyethylene of different densities by Differential Scanning Calorimetry and Thermomechanical Analysis readily showed the difference.

Sample	Heat Content, Cal/g.	Linear Expansion (70-80 ^{o}C) in/in/ ^{o}C
180	21.8	3.8×10^{-4}
193	45.7	2.8×10^{-4}

Hence, both the larger heat requirement for polymer fusion and the lower linear expansion coefficient clearly show sample 193 to be more crystalline (higher density), and sample 180 a lower density polyethylene."

Comment:

The above is an excellent application of thermoanalytical techniques.

E. Paving Asphalt

Du Pont reported:

"Three samples of paving asphalt which showed differing behaviors in weathering and abrasion were examined with the Du Pont 941 Thermomechanical Analyzer in the expansion mode. Their characteristics were:

Sample No.	Abrasion	Weatherability
1	Good	Good
35	Poor	Good
10	Poor	Poor

The data obtained were:

Sample No.	Softening Point, ^{o}C	Expansion Slope, in/^{o}C -50 to -30^{o}C
1	+10	.015
35	+ 4	.016
10	- 6	.049

The abrasion characteristics of a material relate to its phase changes and softening temperature, for a material which softens significantly below its use temperature should exhibit more flow and apparent abrasion than the same material which has a higher viscosity at that use temperature for the same force of abrasion. Usually, the higher softening point is a function of greater crystallinity which will not allow the material to flow as readily as one which has less crystallinity.

Weatherability can be related to the crystalline content of many polymeric substances. Usually, organic polymers appear to weather because they increase in crystalline content. Hence, Sample 10 is much less crystalline than Samples 1 and 35, judging from the considerably smaller expansion slopes. Hence, the larger the expansion slope, the less crystalline content and the poorer weathering characteristics.

Comment:

Thermal analysis has been shown, by this limited number of samples, to

be an excellent method for detecting differences among asphalts. The softening points reported are due to a phase transition not related to the customary ring and ball softening point method for asphalts. Realistically, these data for three samples indicate only that differences have been found in properties of asphalts; properties that have not been previously determined by the Department.

Du Pont's first paragraph after the data are given is a general statement that could have been made with no data at all. It attempts to make a little data look good. We actually find that running the abrasion test at lower temperatures, which increases crystallinity, leads to poorer abrasion resistance.

The Du Pont comment on weatherability is also tailored to fit meager data. Asphalt cannot reasonably be called an organic polymer. Even though poor weatherability correlates in this instance with a large expansion slope, we have no proof that sample No. 10 increases in crystallinity during weathering.

In addition to the applications pointed-up by the samples analyzed at Du Pont, members of the Research Laboratory staff suggested the following, after reviewing the Du Pont results:

1. Apply differential scanning colorimetry and thermogravimetric analysis to detect expansive material in open hearth slag.

2. Study the hydration of portland cement paste and the binding of various forms of water in concrete.

3. Delineate the changes in neoprene joint seals that occur during heat aging tests and ozone exposure.

4. Study the rate of cure and degree of cure of epoxy resin systems and characterize cured epoxy resins that exhibit different tensile strengths, flexibility, and bonding properties.

5. Study the loss of plasticizer and other additives from neoprene joint seals and plastic water stop during field exposure and laboratory tests, such as heat aging.

6. Define the crystallization behavior of neoprene joint seal at low temperature to develop an acceptance test.

7. Determine the brittle temperature of traffic cones as an acceptance test.

The Du Pont data show four or five specific applications of thermoanalytic techniques for highway materials, and Laboratory staff members have suggested seven more. These eleven specific applications supplement the many potential applications described in our proposal for an HPR project, which was presented in 1968. Therefore, we recommend that the equipment for an HPR project to apply thermoanalytical techniques for characterization and acceptance testing of highway materials be included in the 1970-71 budget of the Research Laboratory Section. It will not be possible to obtain this equipment if the stringencies of the 1969-70 budget are repeated in 1970-71.

TESTING AND RESEARCH DIVISION

L Roy T. Oehler

Engineer of Research
Research Laboratory Section

LTO:sjt

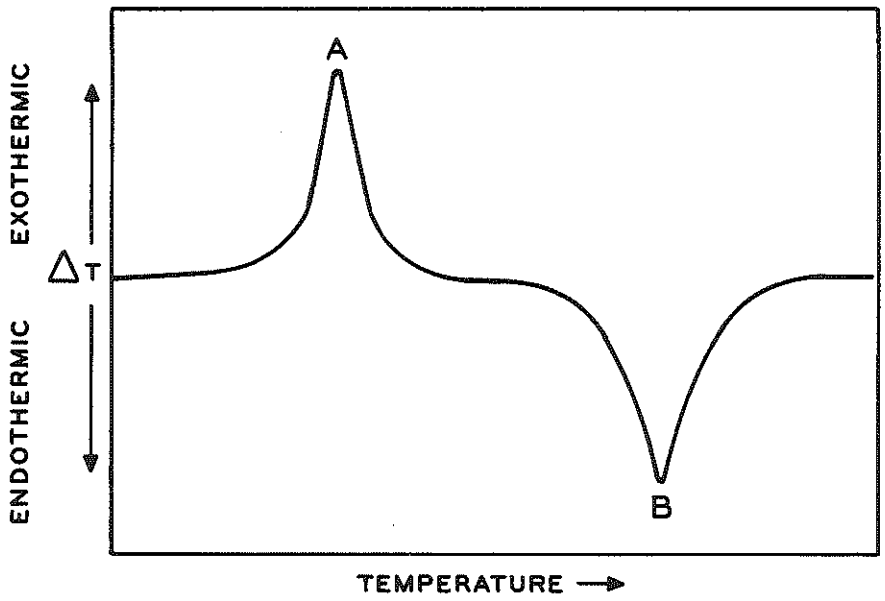

Figure 1. Difference in temperature recorded as a function of programmed environmental temperature. Peak A indicates liberation of heat by the sample due to a process such as crystallization. Peak B indicates absorption of heat by the sample due to processes such as melting or vaporization. The area under the peaks indicates the amount of heat (in calories) associated with the process.

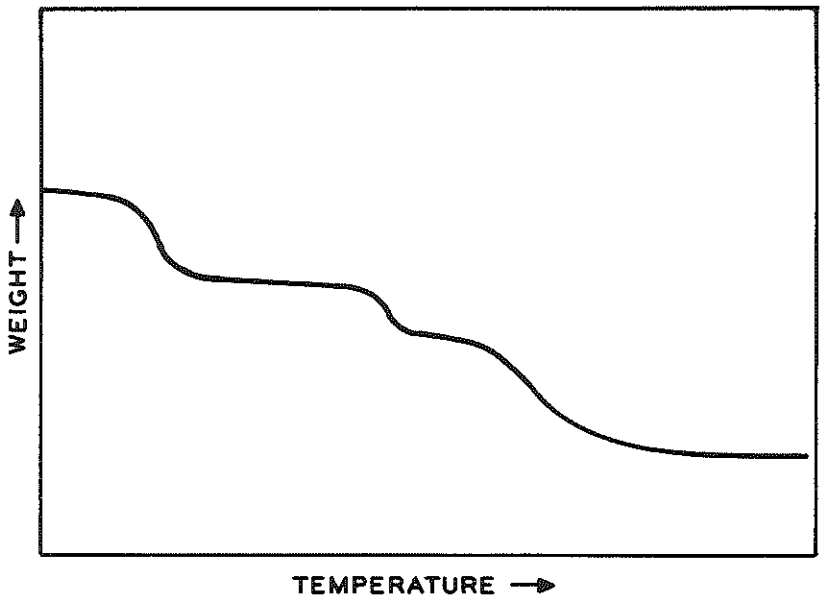

Figure 2. Typical TGA curve with weight plotted as a function of environmental temperature. In the case of a concrete sample, the low temperature weight loss would be due to water of hydration from the cement. The second weight decrease would be due to water from dehydration of calcium hydroxide to form calcium oxide. Weight loss at still higher temperature would be largely due to loss of carbon dioxide from carbonates.