

*Dedicated to Prof. Edith A. Turi in recognition of her leadership in education*

## **APPLICATION OF TGA/DTA/MS TO THE HISTORIC PRESERVATION OF STONE**

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### **Abstract**

The combined technique TGA/DTA/MS, thermogravimetric analysis/differential thermal analysis/mass spectrometry, has been used, in conjunction with other analytical techniques, FTIR, SEM, XRD, and optical microscopy, to analyze a specific patching material that had become seriously discolored on its surface after being used to repair a historic stone pillar at Bethesda Terrace in Central Park, New York in the 1980s. The stone patch was found to contain a polyacrylate binder which was associated with the discoloration.

**Keywords:** DTA, mass spectrometry, PMMA, polymethacrylate, preservation, stone, TGA

### **Introduction**

During the preservation interventions at historic structures, it is frequently necessary to reintegrate missing stone for aesthetic and/or structural reasons. When the missing part cannot be easily replaced with the same stone material, artificial stone formulations are used. These formulations, similar to traditional mortars, have a mineral binder plus an inert aggregate. To improve adhesion to the stone, organic resins, such as polyvinyl alcohol or acrylics are frequently added.

At Bethesda Terrace in Central Park, New York, several patches, which were applied during the 1980's restoration of this site, developed a disfiguring black coloration on the surface or around the edge of the stone-patch interface [1] (Fig. 1). No records were available to indicate whether or not a polymeric resin binder had been used with the patching formulation.

The excellent track record of acrylic resins in conservation, in particular that of the methyl acrylate-ethyl methacrylate copolymer, suggested that, if a binder had been used, the formulation for this particular patching material may have included a resin which through aging under outdoor conditions could produce a blackened surface residue. The cause of this problem is currently under investigation. Records of the original patching material used were not available. The thermal analysis tech-

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**Fig. 1** Stone pillar at Bethesda Terrace, Central Park, New York, showing discoloration of a patch at the base

nique of TGA/DTA/MS [2], together with XRD, SEM, FTIR and optical microscopy, has been applied to the surface and bulk of the patch to help determine the origin of the discoloration. In this paper we discuss the thermal analysis testing performed to date on the subject material and exemplars of standard acrylic polymers and patching material, for comparison.

## Experimental

Samples of the subject sandstone patch, a) a scraping from the exterior surface which contained the black residue, referred to as 'black patch' and b) a sample from the interior of the patch 2–3 mm below the surface, referred to as 'patch interior', were subjected to TGA/DTA/MS using a TA Instruments Model 2960 SDT coupled to a Fisons Quadrupole Mass Spectrometer through a heated capillary interface [3, 4]. The standard procedure was to heat a sample, 20–40 mg, from room temperature to 1200°C at 20°C min<sup>-1</sup> under an atmosphere of nitrogen (99.999%) and collect mass spectra in the 'Log. Histogram' mode in the range 1–200 amu.

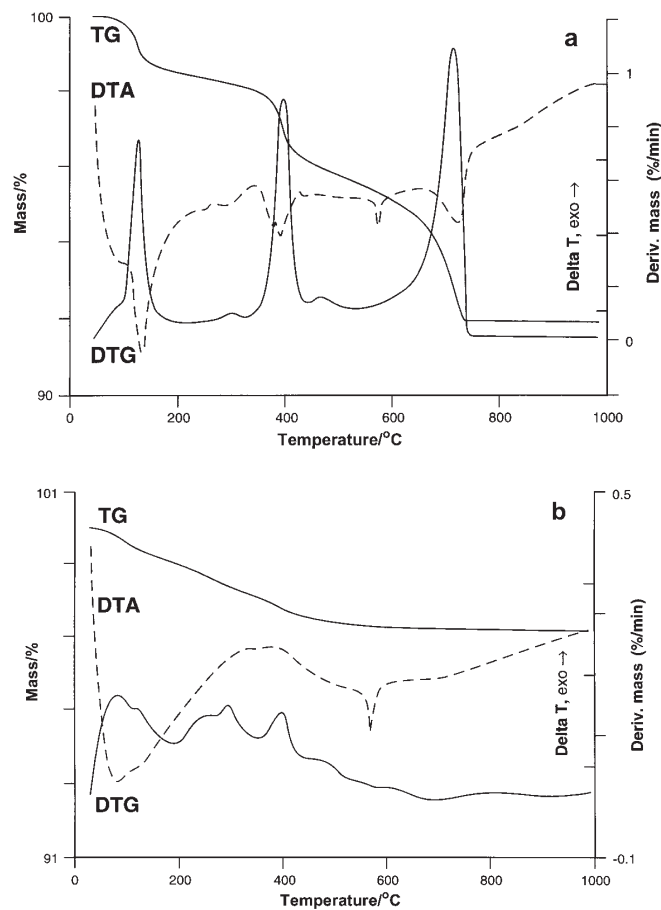
For comparison purposes, the following materials were examined: PMMA, pure polymethylmethacrylate, of two different molecular masses, 4.6·10<sup>4</sup> (Polysciences Inc.) and 3.9·10<sup>5</sup> (Pressure Chemicals Inc.); Acryloid B72 (Rohm & Haas), a copolymer of methylacrylate and ethylmethacrylate; a commercial product, Custom SYSTEM 45 (Edison Coatings), an acrylate-based patching material which was made up at 5:1 patching material: emulsion ratio and allowed to set for periods of 3 and 20 h prior to testing; and Custom SYSTEM 45 part A, pure acrylate emulsion, and part B, patching material [5].

Patch samples were also examined by XRD (Rigaku Geigerflex), FTIR microscopy (Nic-Plan), and optical microscopy (Olympus).

## Results and discussion

Reflection mode optical microscopy showed that the black layer on the surface was very thin, uniform and shiny and did not appear on top of quartz particles, identified by XRD, that protruded through the surface. It appeared only in the regions believed to contain polymeric materials derived from organic binders.

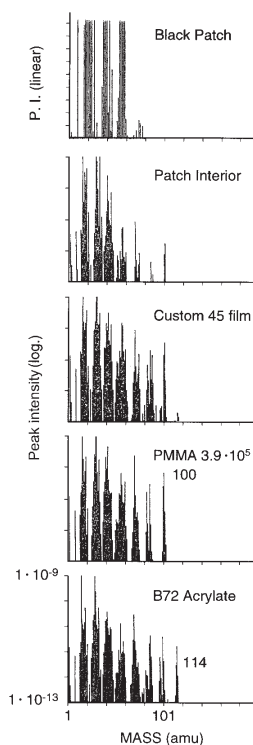
Figure 2 shows the comparison of the TGA/DTA data between the patch interior and exterior, black patch, samples of the patching material at Bethesda Terrace. Of



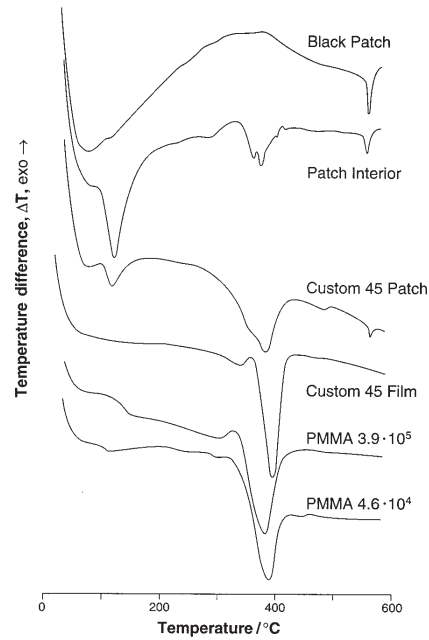
**Fig. 2** Combined TG/DTA of stone patch interior. Sample size, 24.5 mg, heating rate  $20^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$  (a). Black patch from sample exterior. Sample size, 23.8 mg, heating rate  $20^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$  (b)

particular interest is the organic component that was evolved between 200–600°C. In the interior sample of the patch there was only one predominant mass loss regime between 206–535°C. This occurred with a maximum in DTG at 398°C and a total mass loss of ~3.0% in this range whereas the black patch had a total mass loss of only ~1.8% in the range 184–620°C and was accompanied by three small maxima in the DTG, at 248, 295 and 396°C. This indicates that the organic product on the surface is of totally different composition from that in the bulk. Note also the difference in character of the bound water, peak maximum at 120–125°C, and carbonate decomposition at 720–730°C, from calcite crystals that were also identified by XRD. The latter components of the patch were confirmed by mass spectrometry with evolution of H<sub>2</sub>O and CO<sub>2</sub>, respectively.

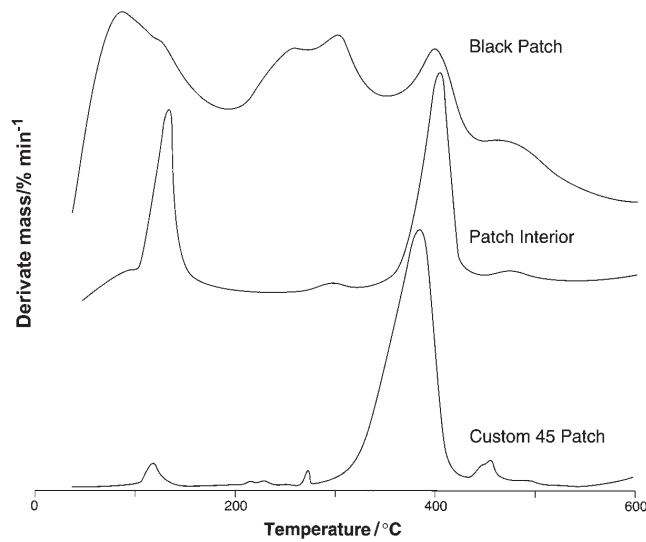
The other interesting feature observed in the DTA curves of all patching material was the sharp endotherm at approximately 575°C that had no associated mass loss. This is due to the alpha-beta phase transition in quartz and could, in principle, be used to determine the amount of sand in the patch.



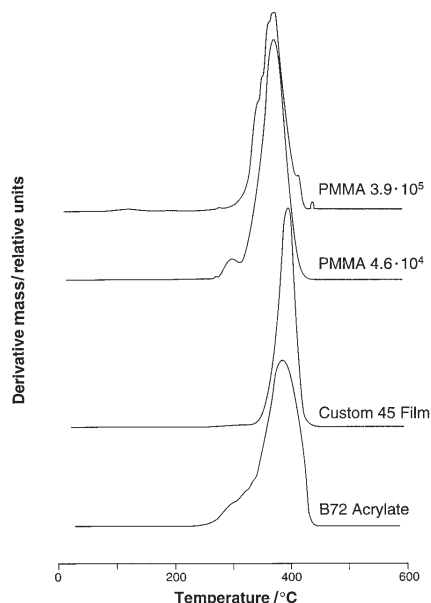
**Fig. 3** Mass spectra of volatiles detected at the maximum rate of evolution in the temperature range 200–600°C during combined TG/DTA/MS runs for the samples shown. All intensities are on a logarithmic scale, range  $1 \cdot 10^{-13}$  to  $1 \cdot 10^{-9}$ , except for the black patch which is linear ( $0$ – $10 \cdot 10^{-13}$ )



**Fig. 4** DTA curves for the samples of patching material and pure polymers as indicated. Heating rate  $20^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . Exotherms are up



**Fig. 5** DTG curves, %mass change/min vs. temperature, for black patch, patch interior and Custom 45 patch. Note that the vertical scale is arbitrary. Conditions as above



**Fig. 6** DTG curves for pure polymer samples as shown. Vertical scale is arbitrary. Conditions as above

DTA data also show striking differences between the organic components in both samples. The DTA of the patch interior organic component showed behavior consistent with that of an acrylate. This was confirmed by mass spectrometry of the volatile component at the point of maximum rate of mass loss, approximately 400°C, which showed strong similarities to the degradation pattern of both a pure sample of polymethylmethacrylate and of the Custom SYSTEM 45 acrylate, though there are slight differences in the mass spectra of each (Fig. 3). It is clearly not a co-polymeric acrylate like B72 in which one of the monomers in the co-polymer, ethylmethacrylate, can be observed in the mass spectrum at 114 amu compared to methylmethacrylate at 100 amu. Note that in these mass spectra the intensity of the black patch is shown on a linear scale ( $0-10 \cdot 10^{-13}$  ion current) whereas all others are on a logarithmic scale from  $1 \cdot 10^{-13}$  to  $1 \cdot 10^{-9}$ . This indicates that very little of the volatiles evolved from the black patch makes its way through the heated capillary tube to the mass spectrometer. The DTA of the black patch also indicates the existence of exothermic behavior in the range 200–300°C that may be due to production of  $\text{CO}_2$  and water, which could not be observed in the mass spectra due to their relatively high background concentrations.

Figure 4 shows the DTA thermal degradation patterns in the organic region of the curves for the subject material and representative pure acrylates and patching materials. Observe that the patch interior showed very similar characteristics to the Custom 45 patching material whereas the pure Custom 45 film decomposed much more

cleanly at slightly higher temperature and was qualitatively similar to the degradation of the pure PMMA films. The dependence of this shift in peak maximum with the presence of patching material makes it difficult to assign the polymeric species by this measurement alone and the simultaneous measurement of the mass spectrum is essential.

Figure 5 shows the DTG plots for the black patch and patch interior samples of the Bethesda samples compared with that of a Custom 45 patch that had been freshly prepared. The similarities in the patch interior and the fresh Custom 45 patch can be clearly observed while the black patch has a small maximum around 400°C and two new, small maxima in the range 200–300°C. No differences were observed on fresh Custom 45 patching material that had been allowed to stand for either 3 or 20 h after mixing.

Figure 6 compares the DTG plots for pure polymer samples, two PMMA samples, a Custom 45 film and a B72 acrylate film. Again these results are consistent with the organic component being a pure PMMA-type rather than a co-polymer such as B72. The mass spectrum of the Custom 45 film, Fig. 3, indicates the possible presence of a low concentration of ethylmethacrylate co-polymer that results in a slightly higher maximum temperature in the DTG and corresponds to that of B72 acrylate.

Infrared spectroscopy is also consistent with the polymer being a polyacrylate (Fig. 7), in which the FTIR spectrum of the black patch, obtained using an infrared microscope, was compared with that of a sample of methylmethacrylate in solution.

It was observed above that the presence of the acrylate in the patching compound changes the degradation pattern by both broadening the DTG peak and moving the maximum to lower temperature. This behavior prevents the assignment of these peaks from TG data alone and requires the use of other techniques such as MS or FTIR for confirmation of the polymeric species.

It was surprising to find little or no trace of acrylates in the MS of the black surface layer, though it is possible that the small DTG peak at 398°C is due to residual

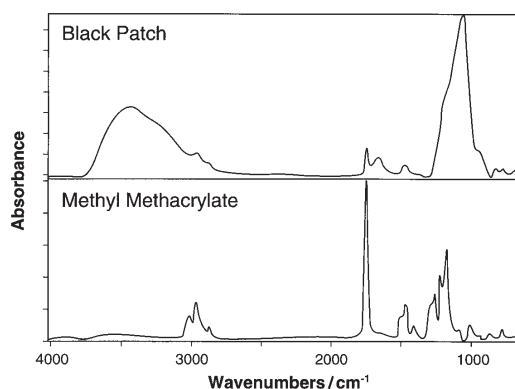


Fig. 7 FTIR spectra of the black patch and a methylmethacrylate solution obtained using an FTIR microscope

PMMA-like material. It has not been possible to determine unequivocally the origin of the black layer though several explanations can be proposed:

1. Exposure of acrylate polymer on the surface which becomes 'tacky' and causes soot or other dark air borne particles to adhere to the surface. This should burn off in the TGA under air at high temperature and show a mass loss. This has not been experimentally observed. An increase in the percentage of organic material at the surface would be expected but this also has not been observed.

2. Degradation of the polymer by a side group elimination reaction similar to that observed in polyvinylacetate, PVA, or polyvinylchloride, PVC [6], on heating which would result in conjugated backbone chains with polyacetylene-like structures that are colored and can be as black as pure polyacetylene [7]. This type of reaction would lead to a reduction in the mass of polymer remaining, as is observed experimentally. Because the patch has not been exposed to high temperatures, it is necessary to invoke a mechanism that could be carried out at ambient temperatures. This could result from a combination of UV exposure from the sun coupled with atmospheric pollutants like SO<sub>2</sub> or NO<sub>x</sub>. Since this behavior is not normally observed in commercial patching materials, it suggests here that some other impurity either in the polymer system or patching material may have contributed to this surface discoloration. One such possibility is the presence in the polymer system of a polyvinylacetate component that is frequently used at low concentration to stabilize the polymer emulsion.

## Conclusions

The patching material used at Bethesda Terrace that turned black on the surface is a synthetic stone patch that contains an acrylate binder. TGA/DTA/MS and FTIR studies indicate that it is a polymethylmethacrylate-based material with properties similar to commercially available materials and is probably a pure PMMA rather than a co-polymer.

The reason for the black discoloration at the surface has not been determined. One possible explanation involves an ingredient in the formulation, of either the acrylate emulsion or stone patching material, which facilitates a side group elimination reaction on an acrylate or, possibly, a polyvinylacetate additive, probably by chemical /UV exposure at the surface, to produce a conjugated backbone polymer that appears black.

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