# A thermogravimetric method for assessing the substantivity of polymer films on dentally relevant substrates

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**Abstract** A thermogravimetric (TG) method is described for evaluating the substantivity of multi-functional polymeric materials that may be used as protective coatings for teeth. Applied to poly(butyl methacrylate) and poly(octadecyl methacrylate) film structures deposited onto model tooth surfaces from aqueous latex formulations, the method shows that while the latter polymer exhibits little substantivity, the former may be a suitable candidate material for dental-care applications.

**Keywords** Dental care · Thermogravimetry · Substantivity · Tooth coatings

## Introduction

Dental caries, dentine hypersensitivity and dental erosion are all extremely common, but preventable conditions [1, 2] that are often attributable to dietary lifestyle. The impetus behind the search for new and improved anti-sensitivity actives and for innovations in prophylactic approaches is provided by the estimated 8–30% of the adult population who suffer from sensitive teeth [3, 4]. One approach to treating dentine hypersensitivity or to inhibiting its development involves the application of polymeric dental coatings [5]. The underlying rationale for treatment is that a substantive continuous coating occludes dentinal tubules, thereby preventing transmission of the thermal or mechanical stimulus required to elicit a pain response. For prevention, the presence of a robust substantive coating may limit hard tissue erosion and/or mechanical wear that might otherwise result in dentine exposure. Other performance criteria that may be relevant to the practical utility of polymeric dental coatings include their resistance to staining and to microbial binding. Key to all of these functions, however, is the ease with which the materials can be delivered as coherent films of predetermined substantivity under the protean conditions of the oral environment. There is, therefore, considerable interest in the development of readily accessible models that assess the substantivity of tooth coatings. Of particular interest are materials that can be deposited as low-surface-energy film structures [5, 6].

The low-surface-energy approach to preventing bacterial colonisation is underpinned by the DLVO theory of colloid stability [7, 8]. Under certain physiologically relevant conditions, van der Waals' interactions between a low-surface-energy coating and prospective bacterial colonisers are minimised, with the result that the net interaction energy becomes repulsive over relatively large distances [9]. Many low-surface-energy polymers have been synthesised and tested in a range of situations for their resistance to bacterial adhesion, with comb-like alkyl and perfluoroalkyl poly(acrylate/methacrylate)-based structures showing particular promise [10, 11].

In this study, thermogravimetry is used to evaluate the substantivity of two readily accessible poly(alkyl methacrylate)s, namely poly(butyl methacrylate), PBMA, and
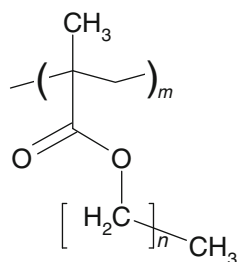
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poly(octadecyl methacrylate), POMA, Fig. 1. At 37 °C, the physiologically relevant temperature at which the in vitro experiments were conducted, both polymers are well above their softening point. As is the common practice for early in vitro studies, calcium hydroxyapatite (HA) has been employed as a synthetic mimic for human enamel [12].

## Materials and methods

### Pellicle formation on hydroxyapatite

Whole human saliva (20 mL, generated by chewing Parafilm to stimulate flow) was collected and centrifuged (8000 rpm, 10 min, 4 °C) to remove food and cell debris; sodium azide ($NaN_3$, 0.4 g $L^{-1}$) was added to the supernatant to prevent bacterial growth. A salivary pellicle was deposited onto HA beads (80 μm, BioRad, UK, 2 g) by incubation with freshly prepared supernatant (2 h, 37 °C). The pellicle-coated HA (pHA) beads were rinsed in deionised water (vortex mixing) to remove excess saliva, dried (37 °C, 24 h) and stored under dry air.

### Polymer latex formation

The supplies of PBMA and POMA (respective average molar masses 337,000 and 170,000; surface energies of emulsion-deposited film structures 28.8 mJ $m^{-2}$ and 17.6 mJ $m^{-2}$; glass transition temperatures, $T_g$, ca. 20 °C and ca. −100 °C) were from Sigma-Aldrich, Gillingham, UK or from Schnelldorf, Germany. POMA, supplied as a solution in toluene, was precipitated from cooled methanol (liquid nitrogen bath) and re-dissolved in petroleum ether, subsequent removal of which (rotary evaporation) afforded the polymer as a solid mass. Nuclear magnetic resonance (NMR) spectroscopy experiments (deuterated chloroform; Jeol GSX instrument operating at 100 MHz ($^1$H) or at 400 MHz ($^{13}$C)) confirmed that this material was free from organic solvent.

Emulsions (28 g $kg^{-1}$) were prepared by adding dropwise (ca. 2 min) solutions of polymer (PBMA 450 mg in diethyl ether, 3 g; POMA 450 mg in petroleum ether, 3 g) to aqueous sodium dodecyl sulphate (SDS; 5.0 g $kg^{-1}$,

15 mL) under sonication (Ultrasonic Processor, amplitude 37%, 3 min following addition). In order to facilitate the removal of the organic solvent, the latex that formed was transferred into a five-necked reaction flask thermostatted to 5 °C above the boiling point of the organic solvent. Stirring was maintained for a duration of 4–6 h, with an aliquot (ca. 0.5 mL) of deionised water being added to the vessel after the first 30 min. After cooling to room temperature, a further aliquot of water was added to compensate for any loss due to evaporation (final mass of aqueous latex = 15.45 g). Particle-size analysis was performed using a Coulter N4 PLUS Analyzer. For dry mass determinations, the aqueous phase was removed by centrifugation (4000 rpm, 5 min).

### Polymer coating of hydroxyapatite

The HA beads (100 mg; pellicle-free or pellicle-coated) were added to an aqueous polymer latex dispersion (400 μL; PBMA or POMA, 2.8 g $L^{-1}$) and subjected to vortex mixing (2 min). The coated HA beads were separated from the supernatant by centrifugation (13,200 rpm, 60 s), washed (up to ×6) with deionised water (900 μL; vortex mixing, 60 s; separation by centrifugation) and dried in air (37 °C, >12 h). All the samples were prepared in duplicate.

### Thermogravimetric analysis

Polymer-coated HA beads and untreated controls were subjected to thermogravimetric analysis (TGA Q50 with TA advanced software v4 TA Instruments Analyzer). Samples (ca. 10 mg, aluminium pans) were heated (nitrogen atmosphere; furnace purge flow rate = 60 mL $min^{-1}$, balance purge flow rate = 40 mL $min^{-1}$) from room temperature to 500 °C at 10 K $min^{-1}$.

## Results and discussion

In order to prepare dentally relevant formulations, two poly(alkyl methacrylate)s have been emulsified with 5.0 g $kg^{-1}$ aqueous SDS, yielding relatively stable latex particles with average diameters in the range 50–100 nm. The thermal characteristics of the solid polymers (PBMA and POMA) and of the corresponding latexes have been studied [13]; the control was uncoated HA. Repeat experiments have shown that temperatures were reproducible to ±0.05 K and masses to ±0.005 mg.

The thermogravimetry (TG) and derivative curves (DTGs) have revealed the degradation characteristics of solid polymers, Fig. 2a, and of latexes, Fig. 2b; thermoanalytical data are shown in Table 1. Powdered samples of
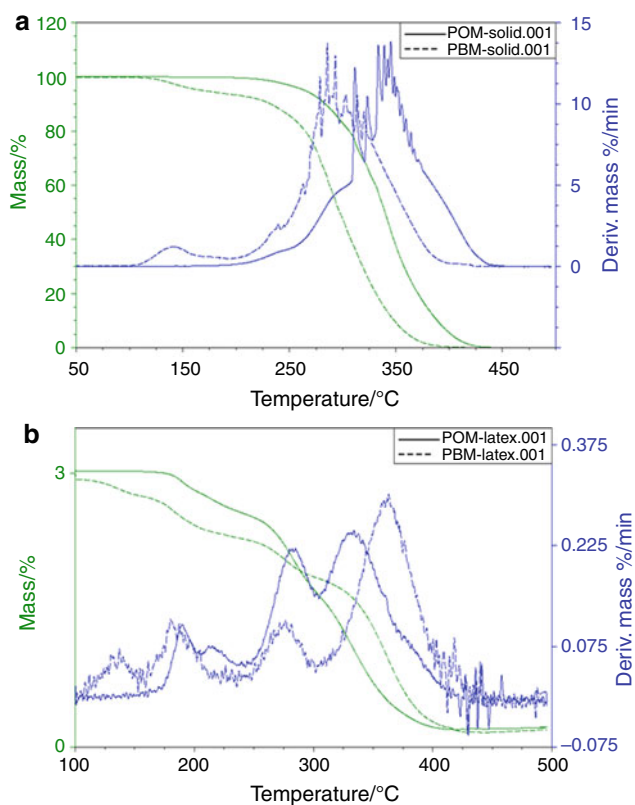
**Fig. 2** Thermal analysis curves and derivative curves (10 K min$^{-1}$ under nitrogen at 60 mL min$^{-1}$) for **a** powdered samples (ca. 10 mg) of PBMA (*dashed line*) and POMA (*solid line*) and **b** latex samples (ca. 10 mg) of PBMA (*dashed line*) and POMA (*solid line*). The mass loss due to the vaporisation of 'free' water (20–100 °C, 97%) is not shown

PBMA and of POMA show no degradation up to 105 and 180 °C, respectively, and from the DTG profiles the main degradation steps are similar. Since the residual masses at 500 °C are ca. 0.05%, the polymers have been completely degraded/volatilised well below this temperature. Any residual mass may reflect incomplete decomposition, experimental error, or the presence of non-volatile impurities in the samples. Solid PBMA exhibits a stepwise degradation profile, with two pronounced steps: The first (105–155 °C) corresponds to a mass loss of about 6.0%, and may have arisen from trapped volatile material, possibly water. The main degradation step (194–425 °C) accounts for 93.9% of the total mass loss; DTG shows that overlapping thermal events occur within this step. The POMA TG curve is dominated by a single degradation step (185–451 °C) which DTG shows to be a sequence of three overlapping events. The profiles are similar to those exhibited by solid PBMA, but are displaced to higher temperatures.

The mass loss profiles and the corresponding derivative traces obtained from the PBMA and POMA latexes show sequences of degradation steps that extend, respectively, over the ranges 105–450 and 160–450 °C. The DTG of the PBMA latex is characterised by four well-defined steps; the fine features that characterise the main step of the degradation profile of the solid polymer are not visible. The DTG from the POMA latex also reveals a four-step degradation process, but in this case, there is considerable overlap between both the first two steps and the last two steps; the main step of the degradation profile is again featureless. As with samples of the pure polymer, the first step in the degradation of PBMA latex is attributed to its relatively strong association with water. The first step in the degradation of the POMA latex and the second step in the degradation of the PBMA latex (DTG$_{max}$, respectively, 190 °C and 180 °C; Table 1) are attributed to water strongly bound to SDS. Since pure SDS melts at 206 °C,

**Table 1** Thermal degradation characteristics of PBMA and POMA (nitrogen atmosphere)

| Polymer | Step | Temperature range/°C | DTG$_{max}$/°C | Residue mass loss/% |
|---|---|---|---|---|
| PBMA (solid) | II | 105–155 | 141 | 6.0 |
| | | 194–425 | 290 | 93.9 |
| PBMA (28 g kg$^{-1}$ latex) | IV | 105–155 | 137 | 0.18 |
| | | 155–240 | 180 | 0.46 |
| | | 240–300 | 277 | 0.42 |
| | | 300–450 | 363 | 1.70 |
| PBMA (coating) | | | 365 | |
| POMA (solid) | I | 185–451 | 345 | 99.93 |
| POMA (28 g kg$^{-1}$ latex) | III | 162–240 | 190 | 0.45 |
| | | 240–300 | 282 | 0.83 |
| | | 300–451 | 334 | 1.53 |
| POMA (coating) | | | 345 | |

The intervals are determined from DTG and represent events of vaporisation determined from the inflection points and, where possible, temperature onset points for vaporisation of each material
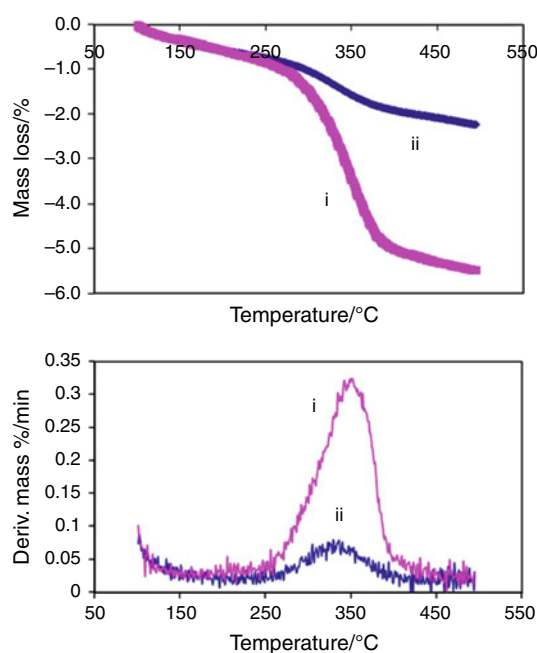
the corresponding second and third steps (DTG$_{max}$: 282 °C, 277 °C; Table 1) may be explained in terms of the SDS component (ca. 180 g L$^{-1}$) of the latex formulations. For both latex formulations, the final step corresponds with the main, polymer-related, degradation event. In the degradation of poly(methyl methacrylate), PMMA, the sole product is monomer [14, 15]. However, larger ester groups in the poly(alkyl methacrylate)s may also degrade to methacrylic acid and to structures derived from the corresponding side chains, such as monomeric alkyl acrylates and alcohol mixtures containing methanol, ethanol and propanol [15, 16]. The thermal stability of methacrylic homopolymers depends on specific chemical features such as branches, cross-links and end-groups [13].

The TG of uncoated HA samples (pre-dried as for coated samples) shows mass losses of 0.9–1.1% over 25–105 °C and of 0.93–1.04% progressively over 100–500 °C. In previous reports, progressive losses of up to ca. 4% over 25–500 °C have been attributed to desorption of strongly bound water, and the onset of the thermal decomposition of HA has been observed at ca. 800 °C [17, 18]. Therefore, the TG trace for uncoated HA, showing small mass losses due mainly to the displacement of adsorbed water, has been subtracted from the corresponding traces for polymer-coated HA samples shown in Figs. 3 and 4. Further, the average mass loss of 0.49% from heating uncoated HA over 240–450 °C has been subtracted from each of the corresponding values for polymer-coated samples (Table 2).

The TG of polymer-coated samples shows mass losses of 0.8–1.1% over 25–105 °C, with some exceptions (labelled * in Table 2), incomplete pre-drying of which has led to substantial mass losses (up to 40%) over this range. Traces of TG and DTG (105–495 °C) for polymer-coated samples show mass losses of 4–5% due mainly to the displacement of polymer over 240–440 °C (PBMA, Fig. 3) and 250–400 °C (POMA, Fig. 4). The temperatures for
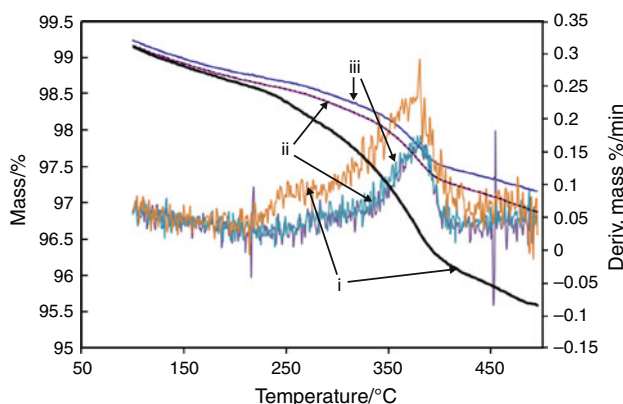


Fig. 4 TG and DTG for HA with POMA coating deposited from latex: (i) as coated; (ii) after one washing. Data are normalised with respect to uncoated HA

DTG$_{max}$ correspond with those for polymer latexes (Table 1). The TG traces also show that most of the polymer has been removed by three washings. The amounts of polymer present on latex-coated HA samples have been calculated from the TG-determined net percentage mass losses.

In order to simulate the effects of saliva flow under normal physiological conditions [19], samples (100 mg) of coated HA beads have been challenged with water ('washings': vortex mixing, 300 or 900 μL over specified times). From the mass losses in TG over 240–450 °C, with allowance being made for displacement of strongly adsorbed water, residual masses after washing of adsorbed polymer, relative to the average initial deposit, have been estimated with an uncertainty of ±5%, Table 2. The proportion of PBMA removed from the HA substrate reached a plateau of ca. 75% after the third 60 s wash. It is reasonable to attribute the residual mass to a surface layer of polymer that was bound strongly enough not to be removed by washing. Reducing the volume of water for a single wash did not significantly alter the erosion of polymer by a single wash (polymer removed 41% for 900 μL, 46% for 300 μL). Extending the washing time to 2 min did result in the displacement of most of the removable polymer, but longer washing times had no significant effect (polymer removed 41% for 1 min, 69% for 2 min, 62–75% for 6 min, 66% for 30 min).

Deposition of POMA onto HA gave slightly heavier polymer films than those of PBMA (Table 2). However, a



Fig. 3 TG and DTG for HA with PBMA coatings deposited from latexes: (i) as coated; (ii) after one washing; (iii) after three washings. Data are normalised with respect to uncoated HA

**Table 2** TG data for polymer-coated HA samples subjected to various washing regimes

| Coating | Washing regime | | | Loss/mass% | | Net loss/mass% | Loss relative to unwashed samples/% |
|---|---|---|---|---|---|---|---|
| | Number of washings | Volume/μL | Time/min | 105–240/°C | 240–450/°C | 240–450/°C | |
| None | | None | | 0.68 | 0.25 | (−0.3) | |
| None | | None | | 0.36 | 0.69 | (+0.2) | |
| PBMA | | None | | 0.80 | 4.06 | 3.6 | 100 |
| PBMA | | None | | 0.81 | 3.96 | 3.5 | 97 |
| PBMA | 1 | 900 | 1 | 0.63 | 2.52 | 2.1 | 57 |
| PBMA | 1 | 900 | 1 | 0.65 | 2.61 | 2.1 | 60 |
| PBMA | 1 | 300 | 1 | 0.80 | 2.55 | 2.1 | 58 |
| PBMA | 1 | 300 | 1 | 0.73 | 2.22 | 1.8 | 49 |
| PBMA | 2 | 900 | 1 | 0.54 | 1.51 | 1.0 | 29 |
| PBMA* | 3 | 900 | 1 | 0.60 | 1.83 | 1.4 | 38 |
| PBMA | 3 | 900 | 1 | 0.52 | 1.36 | 0.9 | 25 |
| PBMA | 4 | 900 | 1 | 0.54 | 1.29 | 0.8 | 23 |
| PBMA | 5 | 900 | 1 | 0.54 | 1.32 | 0.9 | 24 |
| PBMA* | 1 | 900 | 6 | – | 1.69 | 1.2 | 34 |
| PBMA | 1 | 900 | 6 | 0.72 | 2.37 | 1.9 | 53 |
| PBMA | 1 | 900 | 30 | 0.59 | 1.68 | 1.2 | 34 |
| PBMA | 3 | 900 | 2 | 0.58 | 1.55 | 1.1 | 30 |
| PBMA | 3 | 900 | 2 | 0.66 | 1.63 | 1.2 | 32 |
| POMA* | | None | | 0.71 | 4.53 | 4.1 | 100 |
| POMA* | 1 | 900 | 1 | 0.65 | 1.36 | 0.89 | 22 |
| POMA | 3 | 900 | 1 | 0.11 | 0.51 | 0.04 | 1 |
| Pellicle (p)* | | None | | 1.41 | 0.71 | (−0.05) | |
| p* | | None | | 0.78 | 0.81 | (+0.05) | |
| PBMA-p | | None | | 0.96 | 4.38 | 3.62 | 100 |
| PBMA-p | | None | | 0.81 | 3.6 | 2.84 | 78 |
| PBMA-p | 1 | 900 | 1 | 0.69 | 1.1 | 0.34 | 9 |
| PBMA-p | 1 | 900 | 1 | 0.74 | 1.06 | 0.3 | 8 |
| PBMA-p | 3 | 900 | 1 | 0.71 | 1.05 | 0.29 | 8 |
| PBMA-p | 3 | 900 | 1 | 0.69 | 0.88 | 0.12 | 3 |
| PBMA-p | 6 | 900 | 1 | 0.72 | 0.89 | 0.13 | 4 |
| PBMA-p | 6 | 900 | 1 | 0.71 | 0.92 | 0.16 | 4 |

\* Data corrected for moisture displaced over 25–105 °C

single vortex washing with water (900 μL, 60 s) removed 78 ± 5% of the coating, and after three washings, the residual proportion of polymer was insignificantly small. In contrast with the PBMA-coated samples, POMA was completely removed from HA by 2.7 mL of water. At the molecular level, this lack of compatibility may be due to unfavourable interactions between the inorganic HA substrate and the non-polar, long and bulky alkyl side-chain of the POMA molecule.

The TG has also been used to investigate the capacity of PBMA to adhere and remain bound to HA substrates modified by prior deposition of a salivary pellicle, Table 2—a tightly bound thin film formed from the mucins and proline-rich proteins present in saliva [20]. Pellicle-coated HA beads exhibited a higher average mass loss, 0.76% over 240–450 °C (*c.f.* 0.47% for pellicle-free HA); this proportion has been included in calculating net loss percentages. The proportion of PBMA found by TG on unwashed pellicle-modified HA was similar, though less reproducible, to that on unmodified HA, Table 2. However, ca. 90% of PBMA on pellicle-modified HA substrates was removed by a single wash (900 μL). Multiple washes, however, still left residual amounts of PBMA of 4–5%, about one-sixth of corresponding figure for pellicle-free HA. This indicates the presence of a partial but substantive film of PBMA on pellicle-coated HA, thereby identifying

this polymer as a candidate material for in-home dental treatments demanding the application of a non-permanent coating onto dental surfaces.

## Conclusions

Thermogravimetry has been used to assess the substantivity of poly(butyl methacrylate) and of poly(octadecyl methacrylate) coatings on HA, a dentally relevant substrate and commonly used mimic of human enamel. Poly(octadecyl methacrylate) coatings exhibited poor substantivity, but poly(butyl methacrylate) yielded substantive surface structures on both HA beads and on pellicle-coated HA beads.

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