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The determination of residual monomer in polymethylmethacrylate denture-base resins

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The residual monomer content of dental appliances has been implicated as a cause of burning mouths and, since several methods have been advocated for its estimation, a study to establish the best technique is described. It was established that the gas chromatographic technique gave the most reliable results and has been used on several types of methyl methacrylate resins cured under a variety of techniques.

1. Introduction

Over the years many different methods have been used for the determination of residual monomer in these resins primarily because of its effect as a plasticizer upon the mechanical properties.

The early work in this field consisted of using transverse and flexibility measurements [1] as a comparative assessment, whilst McLean and Kramer [2] used density determinations. Qualitative detection by chemical means has been advocated by Smith and Baines [3] and this method has been used by Walter and Glaisher [4] to study chemically activated (self-curing) resins.

Smith and Baines [3] compared the previous chemical methods for quantitative estimation, but state that a "more precise method for the physical estimation of residual monomer" is the infra-red absorption spectrophotometer. Good agreement was obtained using samples of known monomer content between the infra-red method and with a chemical technique which depended on the bromination of the double bond. Caul, Sweeney and Paffenbarger [5] also used an infra-red technique for measurement of the residual monomer content of "self-cure" resins.

The improvement in instrumentation in this field, therefore, reduced many of the problems of determining small amounts of organic materials and advantage of this has been taken by McCabe and Basker [6] who used a gas chromatographic technique for the determination of residual monomer. The continuing clinical interest in the residual monomer content of denture-base resins is due to the so called problems of "denture-base allergy" and burning mouths and McCabe and Basker [6] showed some correlation in two cases between the denture intolerance and the residual monomer content.

However, a high monomer content has also a more serious effect on the mechanical properties of a resin, since this reduces the glass transition temperature and a softer and more flexible denture base results which may adversely affect the clinical performance.

It is the object of the present paper to firstly establish which of the instrumental techniques is the most satisfactory and to use this to study various curing cycles for these resins and also the residual monomer in the various resin formulations.

2. Materials and methods

The pour resin materials were made by embedding a plastic pattern 70 × 25 × 3 mm in the duplicating material, which when set was opened and the pattern removed. The resin was then poured into the mould and cured in accordance with the manufacturers instructions for a complete denture. The heat-processed materials and the chemically activated materials were produced by investing

plastic pattern blocks in stone moulds in a dental flask, packing and processing in accordance with the manufacturers instructions. All analyses were carried out immediately after processing.

Each specimen was cut into small pieces approximately 6 mm square. The material was then milled to a powder for 20 seconds using a Glen Creston* hammer mill.

As a control, the same procedure was carried out on "Perspex"† material. Some of the material was taken to a powder and the remainder was left subdivided in approximately 6 mm squares. In this way, it was intended to monitor the affect of milling on the determination of residual monomer.

Each specimen was subjected to an extraction procedure involving 5 g of sample which was refluxed in methanol for 6 hours, except for the coarsely divided perspex which was allowed to reflux for 30 hours to ensure complete removal of monomer.

All results are means of five readings.

2.1. Infra-red spectrophotometry

A Perkin–Elmer* double-beam 177 spectrophotometer was used. The reference cell was a variable path length type with KBr windows and contained Analar methanol. The sample cell had a fixed path length 0.1 mm and contained an aliquot of extract. The variable path length cell could be adjusted to minimize the interference of solvent methanol. The spectrum was recorded and the characteristic peak carbonyl of 1727 cm^{-1} was examined by the base-line method. The instrument was calibrated by plotting concentration of methylmethacrylate in methanol against peak $\log P_0/P$ (Fig. 1).

2.2. Gas chromatography

A Pye–Unicam 104† was used with a glass column of 3 mm diameter and 150 mm long, containing Porpak Q. The oven temperature was 220° C. Nitrogen was used as a carrier at 40 ml min^{-1}. A small quantity of ethyl acetate (0.5% of the final volume) was added to the methanol extract as an internal standard. This eliminates the need for accurate sample determination. Approximately 1 μl of material was injected into the chromatograph and a typical tracing is shown in Fig. 2. A calibration graph was produced using known amounts of monomer in methanol and plotted against the ratio (the area for the sample)/(the area for the ethyl acetate) obtained from the chromatograph. This reduced variables in the technique and the concentration of residual monomer in the unknown samples can be easily obtained.

*Perkin–Elmer Ltd, Beaconsfield, Bucks.
†W. C. Pye and Co. Ltd, Cambridge.

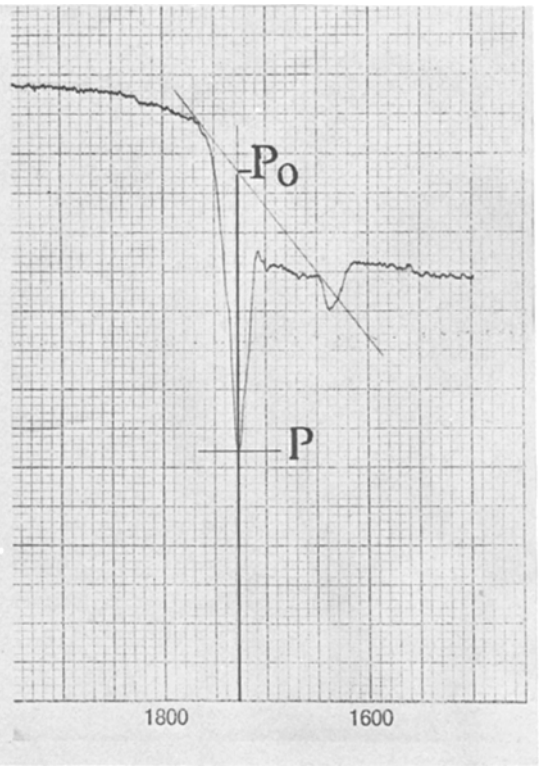

Figure 1 Infra-red spectrum of the characteristic carbonyl group of residual monomer of methylmethacrylate.

3. Results and discussion

Table I shows the effect of milling the sample on the residual monomer determined by gas chromatography. Since there is close agreement between both values and further refluxing of the milled sample did not change the concentration, it may be concluded that milling the sample does not adversely affect the residual monomer content.

TABLE I The effect of milling on residual monomer content determined by the gas chromatographic technique

Material	Reflux time (h)	Residual monomer content (wt %)
Milled sample	6	0.78
Perspex pieces	30	0.79

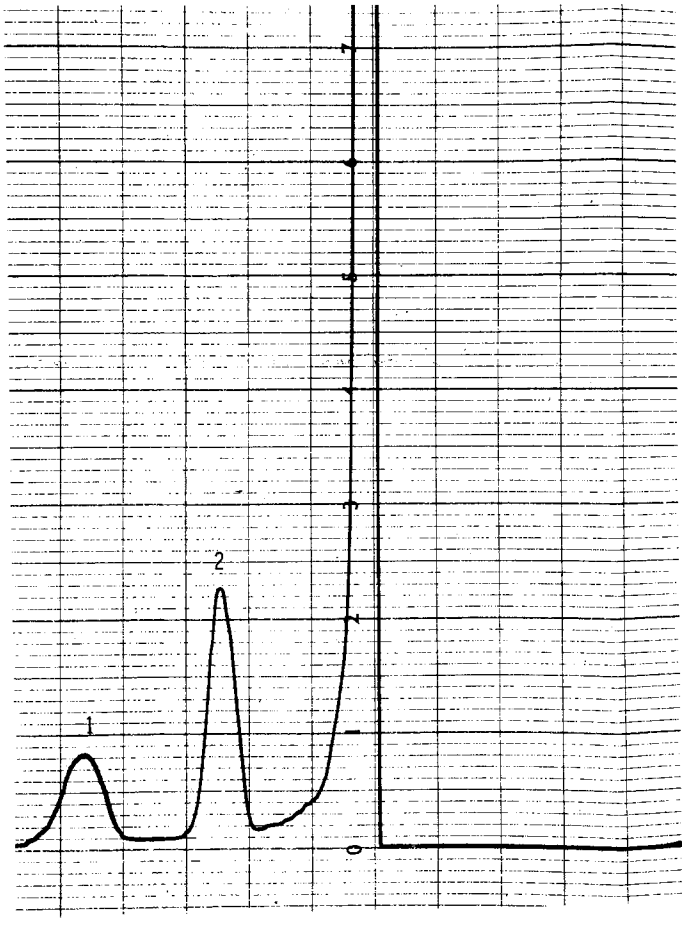

Figure 2 Characteristic trace from the gas chromatograph. Peak 1; Methylmethacrylate. Peak 2; Ethyl acetate.

The residual monomer contents for the pourable resins by the two instrumental techniques are shown in Table II. The agreement of the two methods is very good and may be taken as a corroboration of the values quoted. However, at low residual monomer values the agreement between the methods breaks down, as shown by the value for heat-cured Kallodent. From what we know of the low values expected for heat-cured materials [3], the gas chromatographic result of 0.48% must be regarded as the better value. It should be noted that in Smith and Baines' results,

TABLE II Percentage of residual monomer present (w/w) in different resin formulations

Manufacturer	Resin	Infra-red	Gas chromatography
Pour resins			
Chemical activation			
Coe Labs. Inc., USA.	Pour-n-Cure	4.69	4.44
Vernon-Benshoff Co. Inc., USA	Pronto II XL	3.67	3.52
Svedia, Sweden	Swe Flow	3.65	3.41
Kulzer Co., W. Germany	Palacast	2.40	2.39
Myerson's (Product Research Lab. Inc.), USA	Duraflow, Porit	3.90	3.69
Dentsply Int. Inc., USA	Trupour	4.67	4.60
Dreve, W. Germany	Castdon	2.32	2.16
Major Dent. Ind., Italy	Major F. R.	5.01	4.99
Heat activated			
Dental Manuf. Co., London (Kallodent 60 : cured for 14 h at 70° C.)	Kallodent 60	1.44	0.48

there was a difference of only 2% between the chemical technique and the infra-red technique at a concentration of 5.0% residual monomer, but 21% at a concentration of 0.64% monomer. It appears that at a monomer content below 1% the infra-red technique based on the carbonyl peak is inaccurate. By using more complex equipment, access could be gained to the carbon–carbon double bond peak which would probably improve the method.

In the gas chromatographic technique the constituents are separated before they are measured and this eliminates base-line interference, provided the peaks are sufficiently separated. Therefore, at low residual monomer values, the gas chromatographic technique is the method of choice.

The residual monomer content of the pourable resins is exceptionally high by the standards of the heat-cured materials. If there is a correlation between high residual monomer and acrylic intolerance, then this should be demonstrable most easily with this group of materials. However, the adverse affect of the monomer on the mechanical properties of the denture base may be a more important factor in limiting the clinical usefulness of pourable resins [7]. Braden [8] has shown that the glass transition temperature for a typical pourable resin can fall to 90° C. All this is almost certainly a sequel to the high residual monomer noted here (Table II), but possibly also to a lower overall molecular weight. The important clinical significance is that it can be expected to produce greater creep [9] and low-temperature distortion, which adversely affects the fit of the appliance [10].

The difference between the pour resins and the heat-cured materials must obviously be an expression of the polymerization kinetics produced by the differing processing cycles and the initial monomer/powder ratio used. Work is in progress on the polymerization kinetics which will include studies of residual monomer content of the processed resins.

The levels of residual monomer in chemically activated materials (self-cure, such as Croform) have also been examined at different time intervals. For these studies the experimental procedure was changed slightly because of the greater accuracy at low concentrations of the gas chromatograph, which was the only instrument used. Since ethyl acetate interfered with the infra-red technique, it was added after refluxing for the gas chromatograph technique data, but when the infra-red technique was not used a solution containing 0.5% of ethyl acetate in methanol was made up and powdered samples refluxed in this solution, thus eliminating the experimental error in measuring small quantities of ethyl acetate into the solution prior to using the gas chromatograph. The concentration of residual monomer in Croform immediately after curing was 1.79% by weight, which reduced to 1.4% after storing in water for 24 hours. The reduction in residual monomer was 21%. By comparison, the heat-cured material Stellon, when heated for 7 hours at 70° C and boiled for 3 hours, gave figures of 0.17% which was reduced to 0.14% when stored for 24 hours in water. This again gives a 21% loss in 24 hours. A high temperature cure is essential to produce near complete polymerization, or exceedingly long and impractical times at 70° C must be used. This is in agreement with Smith [11]. The advantages of this nearly complete cure at a high temperature must be compared with the disadvantage of an increase in the thermal contraction on cooling and a less accurately fitting base. In the low temperature cure, the base will be a better fit, but will have slightly more residual monomer present. Whether this is of clinical significance when the levels are as low as 1.79% is doubtful and much of this will be leached out in water rapidly.

This loss of residual monomer due to leaching out into the surrounding water and also due to the uptake of water by the resin will lead to a plasticization of the resin, which will make it more flexible and resilient. It could be anticipated, therefore, that the higher the residual monomer concentration initially, the greater the water uptake and the more flexible the material will be.

It would be anticipated, therefore, that the examination of worn complete dentures would show low levels of residual monomer and this proved so when dentures were taken at random from patients being supplied with new dentures. The dentures were five to ten years old and the results of these tests were 0.24, 0.55, 0.38, 0.32, percentages of residual monomer. They are considerably higher than those reported by McCabe and Basker [6] using similar instrumentation.

Similarly, these authors reported values for the various types of curing and for chemically-activated previously. In one case cited of a burning mouth, their estimate of residual monomer was 0.23%

which is similar to the levels reported here for normal dentures bases and is much higher than their figures of 0.053% and 0.045% for cures of 7 hours at 70° C, and 3 hours at 100° C. The values given for a self-cure resin were 0.185%.

The figures published in this paper, using two techniques, are in agreement with the chemical and infra-red method used by Smith and Baines [3] and with Caul, Sweeney and Paffenbarger [5] using an infra-red technique, where values between 1.7 and 5.7% residual monomer were obtained with varying concentration of promoter. Koppang [12] using the Smith and Baines technique, recorded values of 2 to 3%.

The difference between the reported work and McCabe and Basker's [6] may arise because of difference in the treatment of the sample prior to refluxing and also because of the added accuracy of using an internal standard of ethyl acetate. However, it would seem, judging from all the reported work, that the values and conclusions put forward by Smith [13] are substantially correct, but that the gas chromatographic technique is an improvement on the chemical methods utilizing bromination of the double bond, and on infra-red techniques.

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