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The analysis of dental acrylic polymers by pyrolysis–gas chromatography

S. C. BROOKS, J. F. BATES
Department of Restorative Dentistry, Welsh National School of Medicine, Heath, Cardiff, UK

The vast majority of polymers used in modern prosthetic dentistry are acrylic. They may be homopolymers or copolymers. A technique is described which involves the pyrolysis (thermal degradation) and subsequent analysis by gas chromatography of these polymers. Sample introduction is by means of a ferromagnetic wire which supports a film of the polymer obtained from a solution of the polymer in chloroform. Quantitative determinations can be achieved with the use of relevant standard copolymer compositions.

1. Introduction

There is an extensive use of polymers in modern prosthetic dentistry, of which the vast majority are acrylics. These polymers may be hard and rigid, e.g. poly(methyl methacrylate) or, as in the case of higher methacrylates such as poly(butyl methacrylate), softer and more flexible. This difference in properties is attributed to the presence of longer side chains in the ester group of higher methacrylates which increases chain separation allowing more mobility within the structure and hence the more flexible product with a reduced glass transition temperature.

The selection of a suitable polymer or copolymer for a particular application involves choosing one which, when used in conjunction with the selected monomer component, will form a dough which when processed will produce a material with the desired physical and mechanical properties. When forming the dough it must produce good working properties.

In order to achieve this, the polymer chemist has at his disposal other modifications such as particle size, surface preparation and molecular weight of the polymer powder, amount of cross-linking agent, initiator and plasticizer in the liquid plus the curing system employed as well as polymer type.

For a characterization of any category of polymeric material it is of prime importance to be able to determine the chemical composition.

Common methods of polymer analyses include infrared absorption spectroscopy, X-ray diffraction, nuclear magnetic resonance, mass spectrometry, elemental analysis and calorimetric measurements [1]. However, inherent disadvantages of the various techniques include limited information, difficult interpretation, time consuming preparation or expensive equipment.

The application of a pyrolysis–gas chromatography (PGC) technique to the problem of polymer characterization, i.e. the degradation of polymers by thermal means to constituent monomers followed by chromatographic analysis, has been reviewed by Stevens [2]. Since methacrylate polymers have always been shown to degrade solely to constituent monomers [3], which eliminates difficulties concerning interpretation of results, this technique is of particular value for analysis of dental acrylic polymers. PGC systems of varying types have been reported in the dental literature [4–7]. Those whereby the pyrolysis products are swept directly on to the column, thereby eliminating the inaccuracy due to the loss of volatile components, are superior and offer the advantage of constant experimental conditions throughout. Also, easy sample preparation and the selection of columns which allow reasonable retention times for the elution of the monomer types likely to be encountered are desirable. These conditions are satisfied in the system described.

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2. Experimental details

2.1. Pyrolysis–gas chromatography (PGC) analysis

A Curie Point Pryolyser Unit was fitted to conventional gas chromatography equipment – the Pye Unicam 104 (Pye Unicam Ltd, York Street, Cambridge, UK). An "E-30" type, 10% silicone stationary phase column was used, operated at an oven temperature of 150° C with nitrogen carrier gas at a flow rate of 45 ml min^{-1}. The pryolyser functions in the following way.

A ferromagnetic wire, supporting the sample, is inserted into the top of the column to a depth of 7 cm, the packing material being removed to this level and held in position with a plug of silanized glass wool. A work coil of a radio frequency oscillator surrounds this region and absorbs energy rapidly from the radio frequency field until the temperature of the wire rises to the Curie point. At this temperature, which is dependent upon the alloy composition of the wire, the magnetic permeability falls suddenly and further heating of the wire ceases; thus the final temperature of the wire is maintained at the Curie point until the radio frequency field is removed. This is controlled by a time switch.

Wires of various alloy composition are available and cover the range 280 to 980° C. The wires selected for use in this analysis had a Curie point temperature of 480° C. This ensured that the pyrolysis temperature was higher than the degradation temperature of ~300° C for PMMA, but not excessively high which may encourage the formation of side products.

There are various methods of loading samples on to the wire, such as forming small loops to deal with insoluble polymers such as cross-linked cured products, but this work is primarily concerned with polymer powder components, all of which, when tested, were found to be soluble in chloroform (since insoluble cross-linked polymers are not used in dental technology as they would not produce a dough with monomer). The best results are normally obtained using polymer solutions.

A polymer/solvent ratio of ~1% was found empirically to be suitable. It is important not to "overload" the wire with polymer due to the danger of excessive polymer not pyrolysing and depositing on the packing material which could influence future analyses leading to erroneous results. The pyrolysis wire, fitted through the injection cap and septum, was first thoroughly "cleaned" in a bunsen flame for about 30 sec. This was also done between all samples. Strict attention must always be paid to cleanliness. The wire was then dipped into the polymer solution to a few millimetres depth. After allowing the chloroform solvent to evaporate, by waving the wire in the atmosphere, the injection cap was replaced (with the wire inside the column in the pyrolysis region). Residual solvent was allowed to pass through the column and when the carrier gas flow rate had stabilized, with the recorder base line constant, the pyrolysis mechanism was activated. A pyrolysis time of 2 sec was found to be sufficient since further pyrolyses of the same sample yielded minimal products.

Periodically the wire was dipped in pure solvent and brought to the Curie point temperature in exactly the same way. The lack of any pyrolysis products verified the effectiveness of the cleaning procedure.

2.2. Synthesis of copolymer standards

PGC analysis of the prosthetic acrylic polymers chosen indicated the presence of the following monomer units: methyl methacrylate (MM), ethyl methacrylate (EM), *n*-butyl methacrylate (BM), styrene (S) and 2-ethyl, hexyl acrylate (EHA). (See Table III.)

For the purpose of quantitative analysis of copolymers, a calibration system is required. For this a range of standards consisting of copolymers of methyl methacrylate with all the other monomers mentioned above were made in the following way: solutions of 0.1% benzoyl peroxide in all the monomers were prepared. These were mixed in the required proportions to form a range of comonomer solutions. Each container was sealed and placed in an oven which was gradually brought to 75° C to onset polymerization. This temperature was maintained for 48 h before raising to 100° C for maximum conversion.

The bulk polymerized copolymers were allowed to cool, removed and ground to powders ready for PGC analysis.

Comonomer solutions of the required proportions, similar to those mentioned above, were also prepared in isopentane solvent (which has a very short retention time and thus does not interfere with monomer elution in GC analysis) for a comparative analysis.

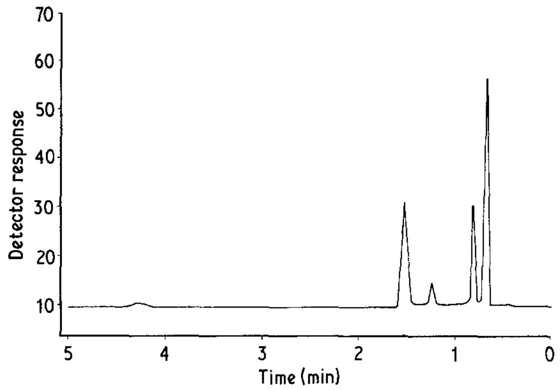


Figure 1 A pyrolysis–gas chromatograph of a mixture of copolymers. Elution order MM, EM, S, BM, EHA.

2.3. Proton-nuclear magnetic resonance analysis

This technique provides a means of checking the composition of the copolymers. The spectra were undertaken at the University College, Cardiff at 60 MHz using deuterated chloroform solvent and tetramethyl silane as internal reference.

3. Results and discussion

3.1. Pyrolysis–gas chromatography

A PGC trace of a mixture of copolymers of MM, EM, S, BM and EHA is shown in Fig. 1. The retention times of these peaks were reproducible and coincided with those of the relevant monomers when injected directly on to the column as in conventional GC analysis. Thus, separation and identification of constituent monomers in copolymers was achieved.

Fig. 2 indicates the relationship of the peak height ratios of the pyrolysis products with composition of copolymer for the different copolymers studied. Linear regression analysis (Table I) indicates the overall fit to a straight line but as by definition the line must pass through both the 0 and 100% origins clearly only the MM–EM display this relationship. However, the most important regions are at the low ratio ends (high MM) and statistical evidence indicates a good straight line fit through the origin for all copolymers in this region.

The plots of peak height ratios against composition obtained by the injection of the relevant monomer solutions were broadly similar to those for the pyrolysis products. However, a statistical analysis by means of the students' *t*-test revealed differences in some cases. Comparisons were carried out for 1 and 20% composition for all copolymer types as these were regarded as of most practical value. The data are presented in Table II together with the standard error of the means at these compositions.

As mentioned previously methacrylates are expected to degrade solely to their constituent monomers. However, acrylates (where the methyl groups on the asymmetric carbon atoms along the polymer chain are replaced by hydrogen atoms) have been shown to degrade by a different mechanism resulting from the abstraction of the tertiary hydrogen atom mentioned [8]. This may yield other products and the effect is escalated where high proportions of acrylate units are present because of the increase in the likelihood of consecutive acrylate units being present along the polymer chains which are responsible for the alternative degradation mechanism. Therefore, only at low percentages of acrylate would a linear regression be reasonably expected.

The technique is also able to differentiate between random copolymers and polymer blends, the copolymers always breaking down to constituent monomers in almost identical proportions, whereas different samples of a

TABLE I Linear regression analysis of copolymer calibration plots

Copolymers	Overall fit			Best fit		
	r	*m*	*c*	*r*	*m*	*c*
MM–EM	0.999 97	1.002	−0.180	0.999 97	1.002	−0.180 (up to 100% EM)
MM–BM	0.995 7	1.125	+0.802	0.999 4	1.212	−0.028 (up to 25% BM)
MM–S	0.991 5	0.978	−4.182	0.998 3	0.702	−0.587 (up to 25% S)
MM–EHA	0.962	2.079	+2.807	0.999 6	2.747	+0.129 (up to 10% EHA)
				0.989 9	2.848	+0.099 (up to 2% EHA)

r = coefficient of linear regression.
m = gradient.
c = intercept.

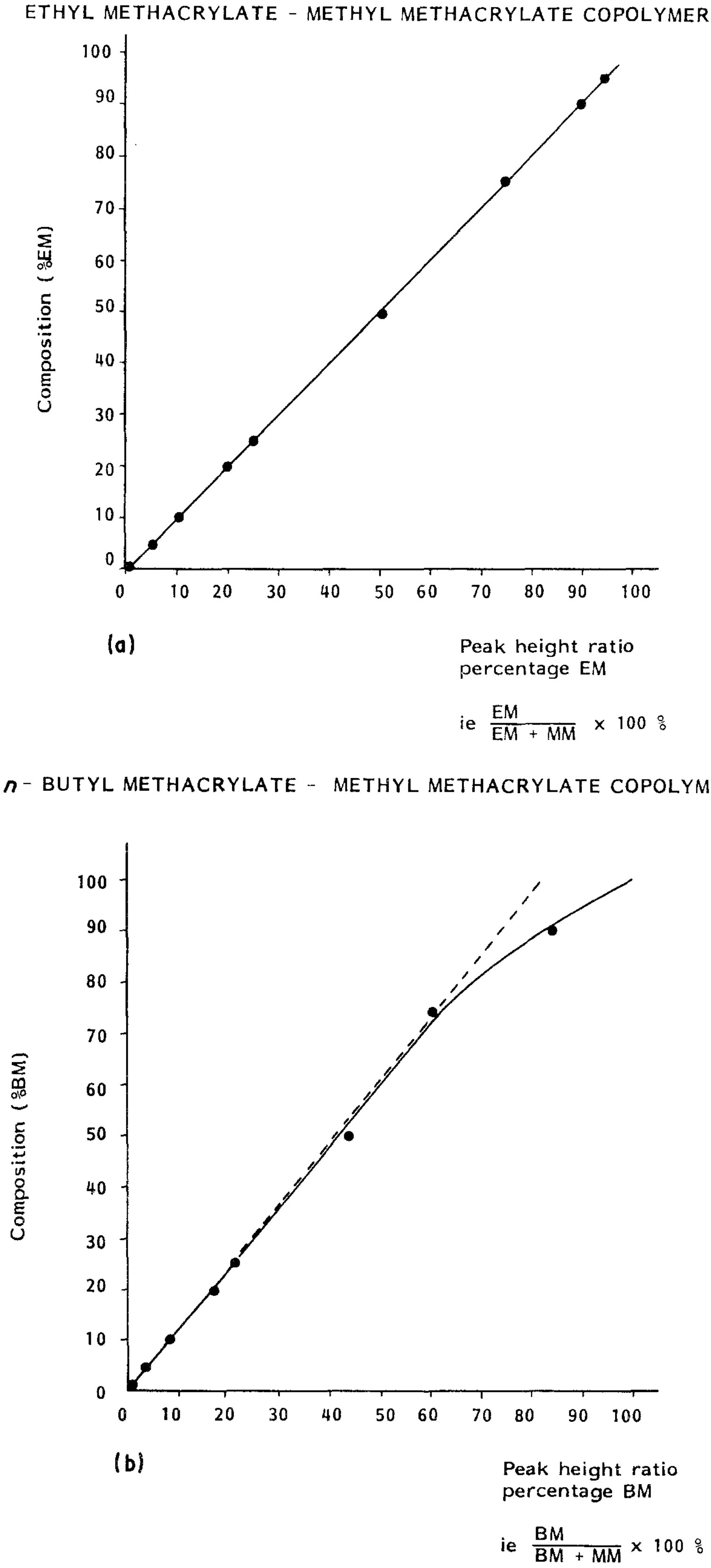
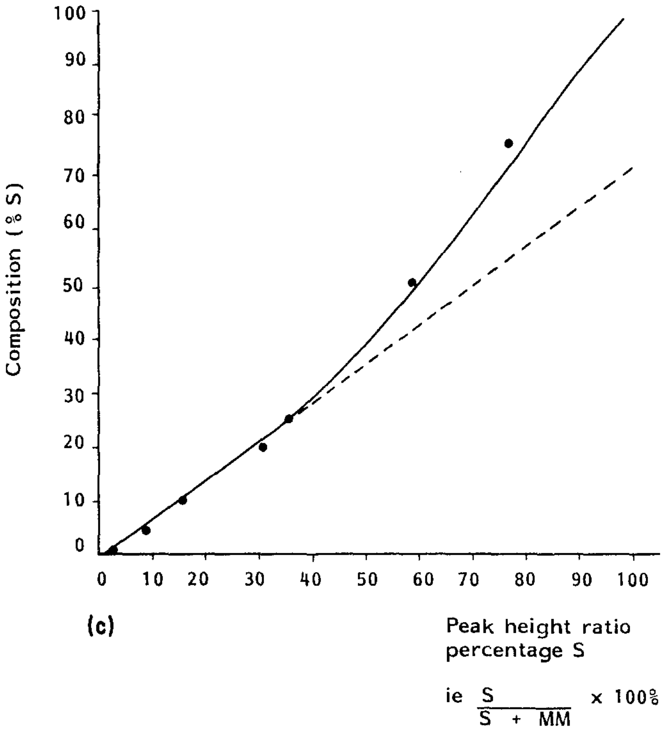


Figure 2 Calibration curves for the copolymer systems.

STYRENE - METHYL METHACRYLATE COPOLYMERS



2-ETHYL, HEXYLACRYLATE-METHYL METHACRYLATE COPOLYMERS

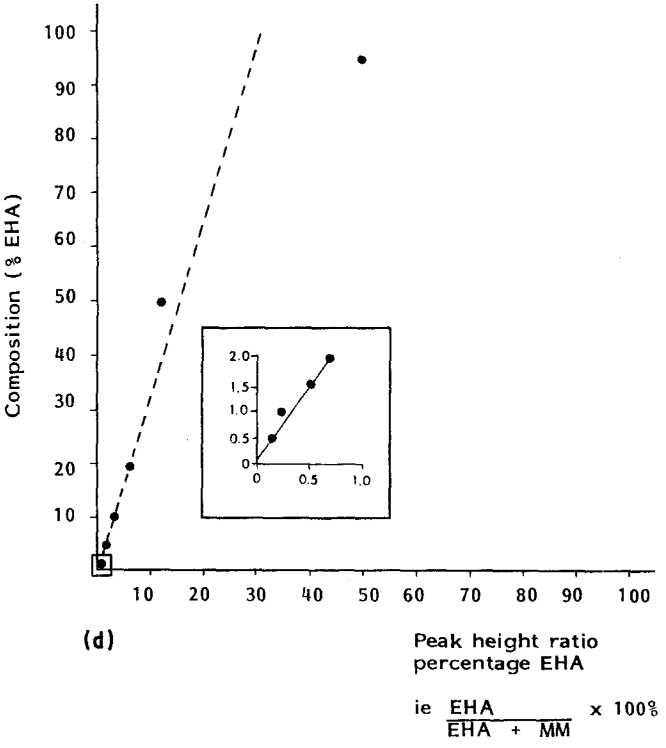


Figure 2 Continued.

TABLE II Statistical comparison of pyrolysis determinations and injected monomer determinations for calibration using students' t-test

Copolymers (with MM)	Standard error of mean	Determination from injected monomer calibration (%)	Significance	% error by using monomer calibration when significant
EM 1%	0.011	0.973	NS	–
EM 20%	0.098	19.976	NS	–
BM 1%	0.028	0.852	HS	14.8
BM 20%	0.114	17.56	HS	12.2
S 1%	0.063	0.524	HS	47.6
S 20%	0.378	15.80	HS	21.0
EHA 1%	0.128	0.91	NS	–
EHA 20%	0.101	19.60	S	2.0

$p > 0.05$ NS.
$p < 0.05$ PS.
$p < 0.01$ S.
$p < 0.001$ HS.

blend will tend to produce different ratios of constituent monomers.

Traces of monomer units may be detected when they are as low as ~0.1% but at these levels they may, in fact, be present only as a consequence of slight impurities in the original monomers before the suspension polymerization in their production.

An extensive analysis of polymer powder components of prosthetic acrylic products was undertaken. Heat-cured denture base polymer powders were found to consist almost entirely of PMMA, some being copolymers of MM with small amounts of one of the other monomers mentioned. These are present presumably to influence their working properties, i.e. the increased chain separation produced by the incorporation of higher methacrylate units will encourage the absorption of incoming monomer liquid and thus reduce the doughing time.

Rigid autopolymerizing resins (denture, orthodontic, repair materials) again usually have polymer powders consisting mainly of PMMA but often with larger proportions of higher methacrylates which serves to aid the more rapid intake of monomer liquid into the powder.

Resins which are intended to be softer, more

TABLE III Polymer powder composition for a selection of materials

Material	Manufacturer	Category	Polymer powder composition				
			MM	EM	BM	S	EHA
Acron Rapid	Howmedica Int, Ltd, Dental Fillings Division, London, UK	Denture base	100	–	–	–	–
Trevalon	AD Int, Ltd, De Trey Division, Weybridge, UK	Denture base	98.7	–	1.33 (±0.03)	–	–
Croform	Davis Schlottlander & Davies, London, UK	Repair material	96.2	–	–	–	3.82 (±0.08)
Kindercryl	Metrodent Ltd, Chancery Lane, Huddersfield, UK	Orthodontic resin	99.0	–	–	0.98 (±0.04)	trace
Orthocryl	Dentaurum Pforzheim, Germany	Orthodontic resin	80.8	19.20 (±0.10)	–	–	–
Forestacryl strong	Forestadent, Bernhard, Forsher, Pforzheim, Germany	Orthodontic resin	87.1	–	12.90 (±0.57)	–	– (Blend)
Peripheral seal	AD Int, Ltd, De Trey Division, Weybridge, UK	Reline material	–	100	–	–	
Coe super soft	Coe Laboratories Ltd, Chicago, Illinois, USA	Soft lining material	–	100	–	–	

± figures are standard errors of the mean.
NB Although standard errors are low the determinations can only be as accurate as the calibration plots.

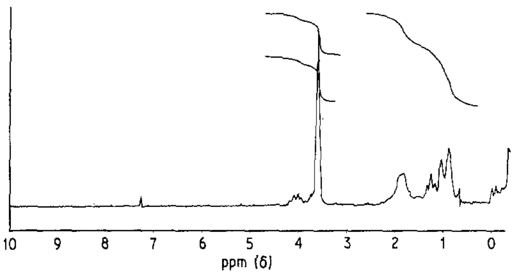


Figure 3 Nuclear magnetic resonance spectrum of a copolymer of 80% MM, 20% EM.

flexible materials, e.g. soft liners, have polymer powder components which are, generally, poly(ethyl methacrylate). These are used in conjunction with butyl methacrylate monomer liquid which may contain other additives, e.g. plasticizers, depending on the specific requirements of the material.

Table III lists a selection of materials, manufacturers, intended applications and polymer powder compositions.

3.2. Proton-nuclear magnetic resonance analysis

Fig. 3 shows the spectrum obtained from a copolymer of 80% MM, 20% EM (as determined by PGC analysis). The peaks appearing between 3.3 and 3.85 δ and between 3.85 and 4.3 δ are signals due to the $-OCH_3$ and $-OCH_2-$ protons, respectively, in the methacrylate ester groups. The ratio of the two reflects the relative amounts of MM and EM units present in the sample.

This particular determination produced a result of 24% EM, 76% MM which is in reasonable agreement with the PGC determination. This result was typical for copolymers which contain comparable amounts of constituents. However, when much smaller amounts of one comonomer are present (as is very often the case in commercial polymers) this method becomes inaccurate due to the slight overlap of peak ranges and interference with base-line noise. Also, the relative abundance of $-O-CH_2-$ protons determines only the relative amount of higher methacrylate present and not the particular type. Other regions of the spectrum have to be carefully examined for this to be established and interpretation can be difficult, becoming virtually impossible if more than one type of higher methacrylate is present. Therefore, this technique has limited use but provides a useful check on pyrolysis–gas chromatography determinations where significant proportions of the main constituents are present.

4. Conclusions

1. Separation and identification of constituent monomers in dental acrylic copolymers was achieved.

2. Provided conditions ensure that methacrylates do, in fact, degrade solely to constituent monomers a quantitative assessment is possible. The relevant standard copolymer compositions must be used for calibration purposes.

3. Nuclear magnetic resonance determination provided a useful check and yielded confirmation of PGC analysis where significant proportions of the main constituents were present.

4. Prosthetic acrylic polymer powders were found to be mainly poly(methyl methacrylate) (PMMA) but resins which are intended to form much softer materials were usually poly(ethyl methacrylate) (PEMA).

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