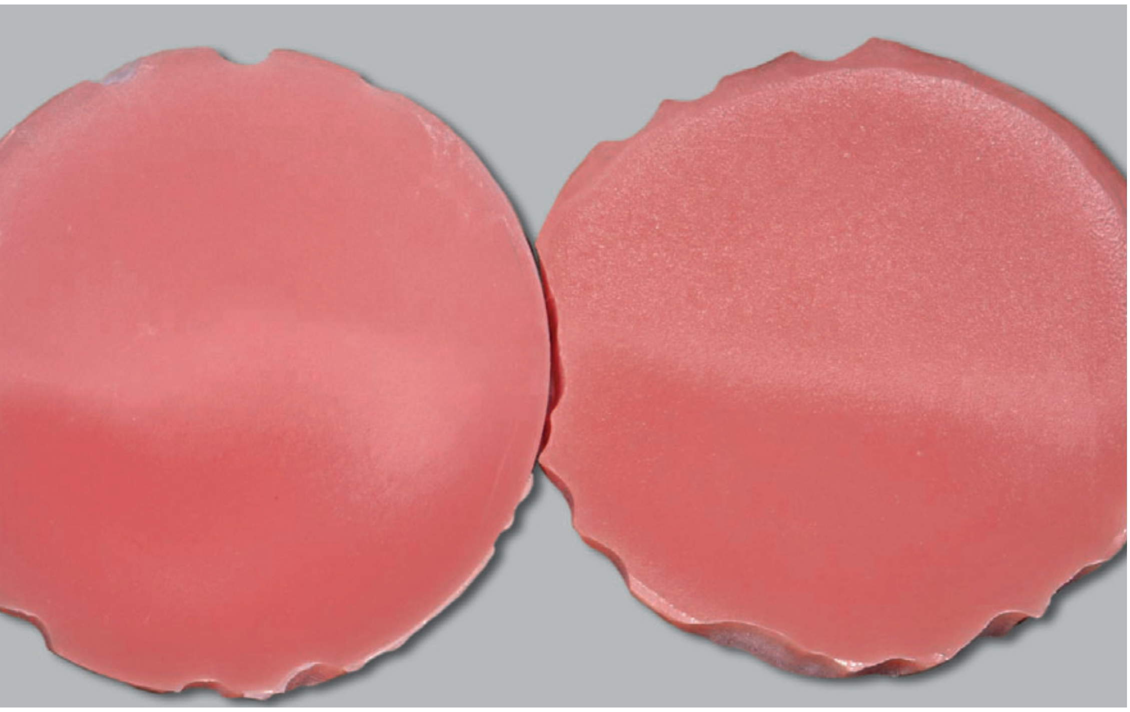


Summary

This article presents the results of advances made with the material polymethylmethacrylate that have led to improved chemical and physical properties. Acrylic resins with a defined mixing powder/liquid ratio of up to 10:3 (instead of the existing 10:5 to 10:7 by weight) have successfully been mixed to what is still a pourable consistency. The author highlights how much impact the change in the mixing ratio has on shrinkage or dimensional changes to the material and what advantages arise.

Key words

denture materials; chemical properties; physical properties; polymethylmethacrylate

Has PMMA Denture Material had its Day?

Karl-Heinz Körholz

Introduction

In an age when everything goes 'faster, higher and further', we almost take it for granted that there is always something new being developed, emerging from a new direction, and hence totally different and setting new standards. This is understandable in some areas of dental technology because of the rapid development in recent years – which has had varying degrees of success.

For example, new denture materials, specifically in the area of laboratory-made prosthetics, have almost always involved an entirely new range of materials. One might have thought that classic polymethylmethacrylate (PMMA) had slowly become obsolete and that all the promised improvements that actually made sense could, to a large extent, only be fully polymerised with UV light.

Residual Monomer Content

In fact, processing and handling of our familiar denture material is really not so complicated that we need to move away from the process or the processing method. However, it was the more or less unavoidable high residual monomer content that repeatedly caused justifiable concern. For instance, the fabrication of a partial and a complete denture as well as enlargement, relining and polishing were so low-maintenance and convenient that, from the point of view of industry, dental laboratories and dental practice, there was often a tendency not to ignore the well-known phenomenon of residual monomer, but instead to class it as unavoidable and perhaps even forget about it (just a little). This downside exists with every processed PMMA, irrespective of the working method, whether pressing, injection or casting. So should we be asking whether salvation is to be found in the light of polymerisation?

New Approaches, Same Old Direction

As if a stealthy renaissance were happening in the polymer sector, current thinking has been moving forwards – not towards a totally different, new class of material but simply towards refinement of the familiar and convenient material PMMA. But what else about PMMA can be improved – and what actually works – if not its chemical and physical properties? Ideally, of course, improvements are required to both.

Denture Fabrication, Bite Planes and Drilling Templates for the Casting Method

Residual monomer content and shrinkage are a thorn in the side of all those involved in the production of dentures, including the denture-wearers. If anywhere, it is here that improvements could be made.

In the author's opinion, a well-known dental company has already achieved this with the injection technique[1]. However, in relation to the casting technique where a denture, a bite plane or an implant drilling template is made by the duplicating gel method, it is rather problematic at first sight. This is because the acrylic for pouring into the flask is not plastic, as it is in the injection technique, but must be thin and liquid so that it will flow cleanly into the gel mould and can be fully polymerised there in the pressure vessel. In the case of self-curing materials, this usually means using a higher proportion of liquid, which causes a high degree of shrinkage.

Residual monomer and dimensional change

Currently available high-quality pouring resins may be able to gain widespread acceptance and achieve respectable chemical and physical values because of their special composition. However, there always remains the problem that, like other self-curing polymers, they may still have a high residual monomer content immediately after curing, which can have an adverse effect on dimensional stability[2,3]. The DIN EN ISO 1567:2000 coming into force stipulates a maximum residual monomer content of 2.2% for heat-curing and 4.5% for self-curing resins, the content being measured after 48 hours' dry storage at room temperature. It is also worth remembering that the quantity of self-curing polymers processed is very large, particularly for complete dentures. In fact, the dental technician is required to use suitable water storage to reduce the residual monomer content, which is eluted out of the work piece after curing, or is re-polymerised, so that the patient is exposed to virtually no health risks. However, this still leaves the associated dimensional change in which water absorption additionally influences of the dimensions of the acrylic resin.

Acrylic resin shrinkage

One of the key reasons for poor denture stability, apart from a defective static occlusion, is the failure to pay attention to correct shaping of the denture base beforehand. The best base contouring, however, is not negated if a deterioration in the denture fit is due to increased resin shrinkage. One of the main causes of poor stability of a mandibular compared with a maxillary denture is also resin shrinkage. Even if the occlusion and base contouring were correct in advance of careful work, the shrinkage factor would still remain and could ruin the final outcome.

Secondary damage

If, as in this example, large-scale work, such as complete dentures, bite planes and implant drilling templates, is prepared entirely from self-curing materials, distortion, stress and hence the lack of fit between prepared work and casts will become ever greater and more visible. When the work is worn in the mouth, its intended position, the gingiva and the periodontium are stressed and damaged as a result, and drilling templates become inaccurate.

Where can shrinkage be seen and where does it have most impact?

Maxilla versus mandible

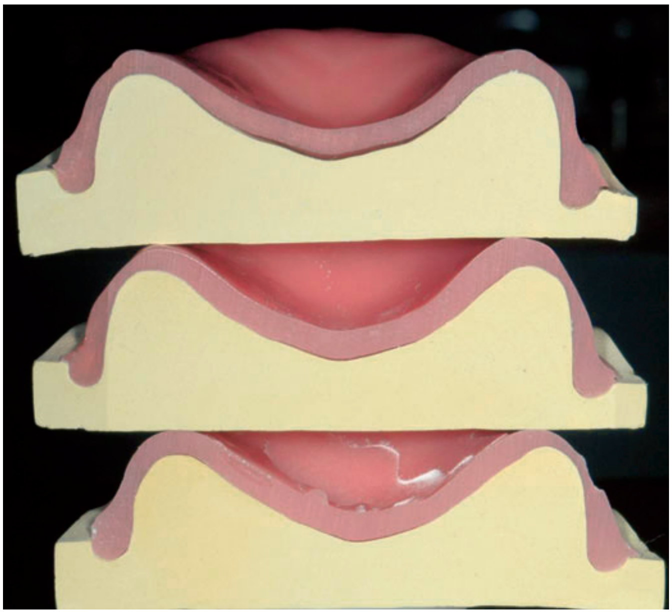


Fig 1 At the dorsal edge of a maxillary denture, the gap is very clear to see after sectioning of the models. Working without a gap is impossible because of the materials processed: plaster, acrylic and separator.

The fact that denture resins shrink and consequently alter their shape has been illustrated, measured and compared for more than two decades with the aid of cutaway models on maxillary dentures[4]. The maxillary denture is usually smaller than the mandibular owing to lower levels of atrophy. This means that 10 to 15% less material is used in the maxilla. On the other hand, if a maxillary denture still has transverse stabilisation, when the distortion becomes visible our attention is usually drawn and confined to a single, small area: the base and the dorsal border (Fig 1).

The Eureka moment and occlusal interferences

This base and dorsal border area is of rather secondary importance because the adhesion surface for the eventual fit is otherwise far larger (again compared with the mandibular denture). A maxillary denture can be rendered stable again far more easily with a post-dam (suction) than a mandibular denture, even if the maxillary base does not lie against the gingiva in other areas, or at least it does so inadequately.

Maxillary and mandibular dentures, however, will shrink not only on the side adjacent to the gingiva, but logically also in volume. As previously mentioned, this can be seen particularly – or unfortunately only – on the maxillary denture in the dorsal area when compared with the model. As stated, however, this is only the visible part. What happens in the area of occlusion and the transverse dimension is not very visible or usually not visible at all: in other words, the individual tooth displacements are especially in the transverse direction. The resulting occlusal interferences can usually be re-ground as a misinterpreted occlusal increase, but only to a certain reasonable extent and in a way that will enhance function.

Loss of adhesion and positional changes of teeth

The dimensional change in the transverse direction greatly influences the adhesion of a denture. A mandibular denture base that is reduced transversally in distance because of shrinkage, is more likely to fit in the anterior area but will only fit in places in the molar region. The adhesion to the gingiva in such a case is interrupted a great deal because of the unsatisfactory congruence between denture base and the shape and path of the alveolar ridge. Thus any probability of fit, adhesion and positional stability of a denture with higher shrinkage is reduced because of a higher residual monomer content. Pressure points (and eliminating them), as well as remodelling processes of the gingiva are inevitable consequences, and are mainly accepted as 'natural or unavoidable'[5].

In the same way, this discrepancy also has a disastrous effect on a bite guard made from PMMA or a carefully prepared implant drilling template. A bite plane made from PMMA that shrinks in the transverse and sagittal direction because of properties of the material, will have a negative effect on the areas of the dentition on which it is supported, while a drilling template will not provide the practitioner with accurate preset points for placing implants.

Improvement is in sight!

For nearly 25 years, the company Retec Kunststofftechnik, Rosbach, Germany, has been a leading manufacturer of PMMA-based acrylics, especially in the field of dental prosthetic materials for all applications. These range from orthodontics to pink-coloured heat- and self-curing acrylics for fabricating partial and complete dentures through to highly transparent (clear) resins for bite planes, etc. Pouring resins for dentures is also a key market sector.

Many years of refining these materials have now made it possible to mix acrylics with a defined powder/liquid mixing ratio of up to 10:3 (instead of the previous 10:5 to 10:7 by weight) and still produce a pourable consistency. The following measurements are intended to show what impact this change in the mixing ratio has on shrinkage or dimensional change.

First study design

Maxillary denture bases of the same dimensions and thickness were first prepared on identical models. These were to be realised in acrylic resin by the conventional denture casting technique. The flasks from the PremEco® Line system were used for the test and four different materials from reputable manufacturers, specially intended as pouring resins for dentures, were worked according to the manufacturers' instructions, but with two different mixing ratios. The ratios were 10:6.25 and 10:5.5 powder/liquid by weight at a room temperature of 21°C.

The newly developed acrylics were used in parallel tests. They were mixed and worked under the same conditions but with a mixing ratio of 10:4.5 to 10:4 powder/liquid. The curing time was 30 min for all the products at 45 to 47°C water temperature and 2.5 bar pressure.

The basis of observation and the assessment criteria in the three groups were defined as follows:

- Impression of mixing behaviour, good pourability (in minutes), ease of pouring into the flask, from when and for how long the mixed resin is stable (in minutes).
- Visual check of the denture base after deflasking; first fitting after deflasking – visual check; second fitting after lifting off and repositioning again – visual check; third fitting after lifting off, dorsal trimming and repositioning – visual check; fourth fitting after lifting off, dorsal trimming, finishing and repositioning – visual check.
- Ease of grinding by cross-cut milling, finishing and smoothing with sand paper, polishing with pumice and high-glaze finishing.

Results of these observations

- The resins with a higher monomer content basically had a 14% longer pouring phase and a later standing phase.
- The pourability was partly reduced time-wise by 50%, but this sounds more dramatic than it is because the pouring phase of 3 to 4 minutes was reduced to about 1.5 to 2 minutes, which would give any dental technician enough time to fill a flask with acrylic resin.
- The stability of the resin was reduced by about 30% from 6.5 to 4.5 minutes.
- In comparison with the resins processed in a powder/liquid mixing ratio of 10:6.25, an improvement in fit of up to 33% was observed with a dosage of 10:4 immediately after deflasking.
- The fit after lifting off and repositioning was as much as 50% more accurate when comparing the different products in the 10:6.25 with the 10:4 mixture of the new resin (Figs 2 to 5).
- The visual results were far more satisfactory after grinding, finishing and the subsequent polishing because of the better shine with the 10:4 mixture (Figs 6 to 8b).

Second study design

In the second study design, any possible transverse change was measured. This involved preparing a test piece from class IV plaster in a U-shape, which approximated to a dental arch. Pins were inserted in the middle and at the ends of these test pieces. The distances on this U-shape were measured (Fig 9).

- Measurement 1: top outer external distance AB = from outer surface pin to pin
top outer external distance BC
top outer external distance AC
- Measurement 2: bottom inside external distance AB = from inner surface pin to pin
bottom inside external distance BC
bottom inside external distance AC

This shape was duplicated. Instead of teeth, as would normally be the case, identical pins were inserted into the hollow mould and the mould was then realised in acrylic resin. In each case the quantity of resin corresponded to the quantity required to create a complete denture.

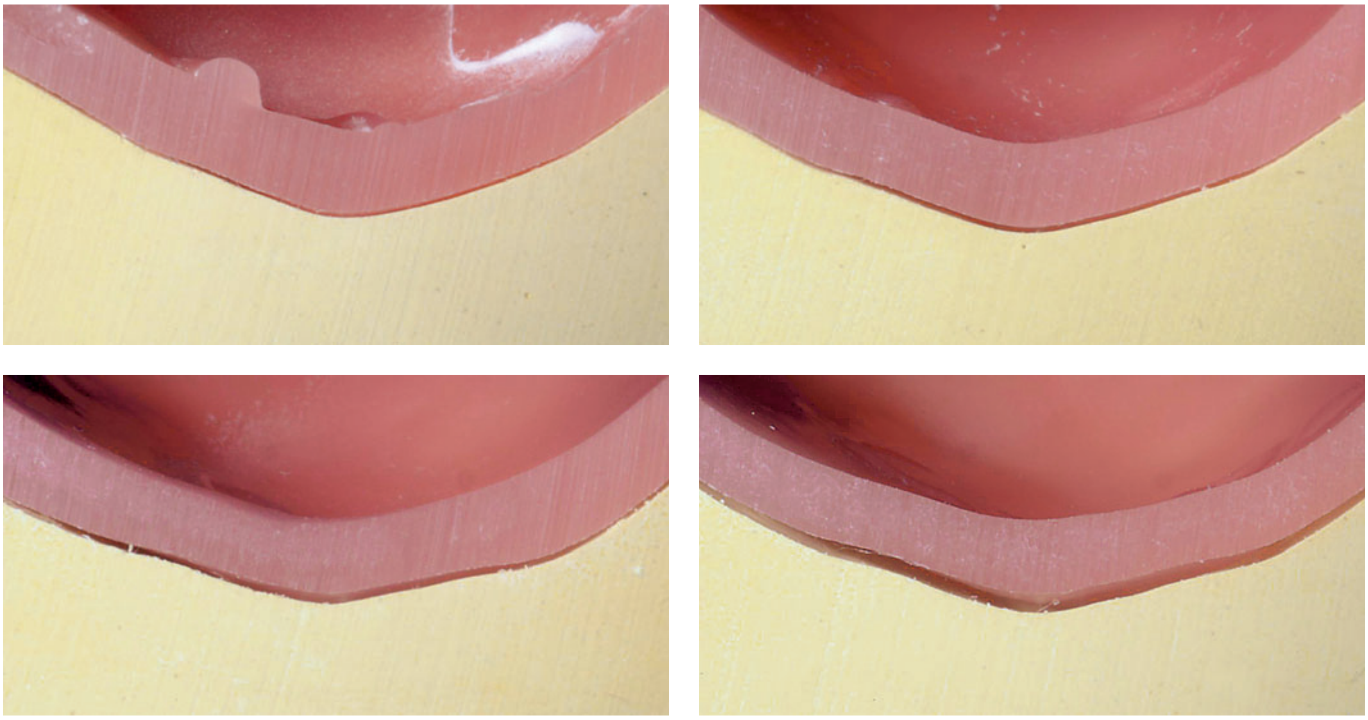


Fig 2 to Fig 5 After lifting off, dorsal trimming and repositioning, there was a visible gap between each cured denture base and the model. However, the differences in dimension, especially after 5 days and longer, are very pronounced. Comparing Figure 2 with Figures 3 to 5 clearly shows the success of the improved mixing ratio.

Fig 6 Grinding tests were performed on separately made acrylic plates and these can be seen at the edges.

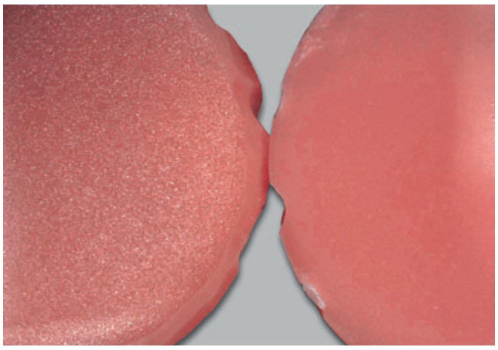
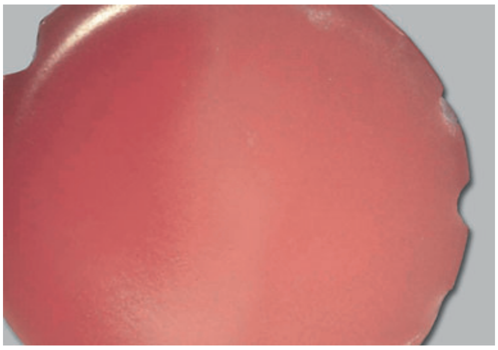
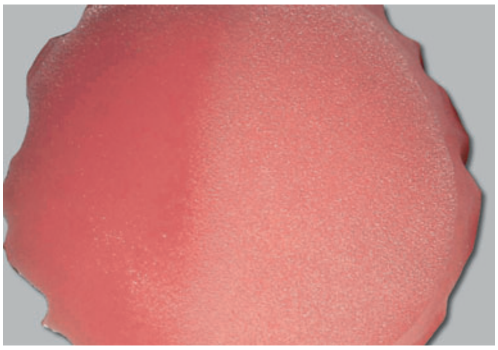


Fig 7 The homogeneity of the 10:4 mixed acrylics can already be seen on the unworked sides.





Figs 8a and 8b The surfaces were first left untreated. Only one side (the left here) was worked with high-shine buffers and polishing paste.

Measurements on the original test piece

The external and internal distances were then measured both at the tips (top) and directly at the point where the pins exited the resin (bottom) (Figs 10 and 11).

After curing, the duplicates were measured again. Three measurements were taken, their mean was calculated ± 0.02 mm and included in the analysis. All the subsequent measurements were performed in the same way (Table 1a).

The measurements were performed at intervals: after deflasking, after 3 hours, after approximately 15 and 25 hours, and finally after 5 days. The differences immediately after deflasking can be seen in Tables 1b and 1c. There was a reduction on average of 0.32 mm for the top measurements and 0.43 mm for the bottom measurements with the 10:6.25 mixtures, whereas the 10:4 acrylic mixtures were shortened by an average of 0.12 mm on the top measurements and by 0.22 mm in the bottom distances.

After 5 days and storage in water, the pin measurements reveal an average decrease of 0.35 mm for the top and 0.42 mm for the bottom measurements with the 10:6.25 acrylic mixtures (see Table 1d). When the 10:4 mixtures were used, the top measurements from the pins shortened by an average of 0.15 mm and the bottom by 0.26 mm (Table 1e).

Measurements of weight or volume

Direct comparison (Table 2) shows the reduction for the top and bottom measurements for the 10:6.25 and 10:4 mixing ratios. It is important to note that these values are only

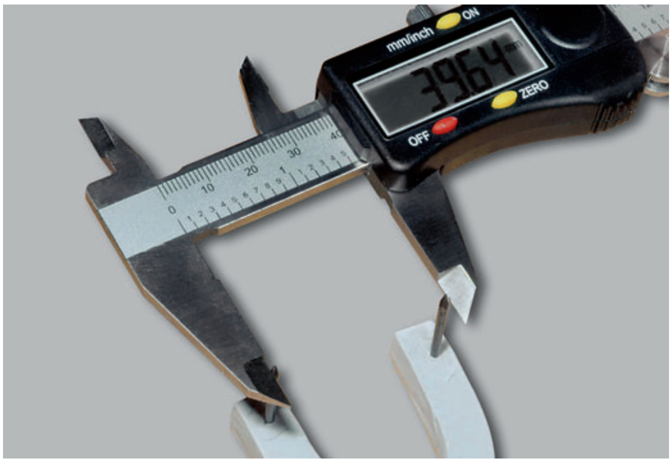
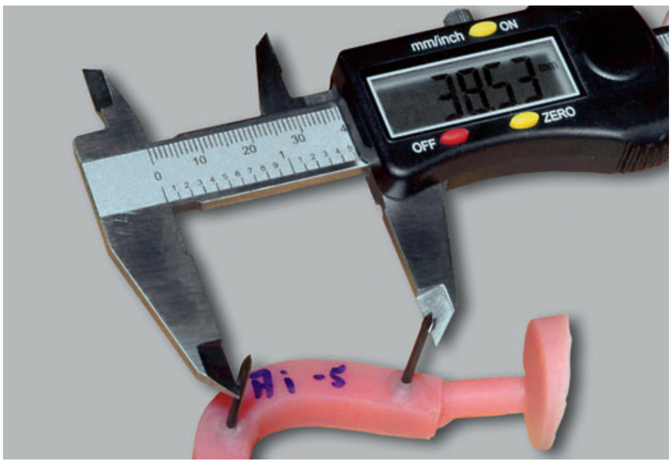


Fig 9 To determine the transverse and sagittal change, a test piece made of class IV plaster was produced in a U-shape which approximates to a dental arch. Pins were inserted in the middle and at the ends of the these test pieces. The distances on this U-shape were measured.



Figs 10 and 11 The same measurements are taken of the test pieces reproduced in acrylic as on the original, in other words the distances at the tips of the pins and at the point where the pins enter the acrylic. These values are then compared with those of the original.

Fig 12 Measuring cup and mixing, stirring and pouring beaker in one: if correctly used, these give the user a high degree of convenience when stirring and pouring denture materials.

representative and reproducible if the same mixing ratio is always chosen and adhered to. In practice, users may wonder whether the figures are given in volume or in weight proportions. Some manufacturers provide measuring vessels as standard and sensibly give mixing details in grams. This largely removes the trial and guesswork for dental technicians (Fig 12).

Successful campaigns and training activities have commendably been run by reputable plaster manufacturers for years, and have demonstrated the importance of accurate measurement, and ultimately made it 'socially acceptable'. Should accurate measurement not be equally important when using acrylic resins?

Trials have also shown with hindsight that weighing, however unfamiliar it may seem to some dental technologists at first, is still the most accurate method. Especially when resins are processed in a cooled state, the stirred mixtures for pouring are of variable viscosity. With powder, the question is whether to measure bulk weight or settled weight.

Table 1

a Measurements on the original test piece

b Acrylics 10:6.25 ratio immediately after deflasking

c Acrylics 10:4.0 ratio immediately after deflasking

d Acrylics 10:6.25 ratio after 5 days and storage in water

e Acrylics 10:4.0 ratio after 5 days and storage in water

Distances (mm ± 0.02 mm)		Top outer	Bottom inner
a	AB	Ø 39.45 mm	Ø 35.86 mm
	BC	Ø 38.87 mm	Ø 34.76 mm
	AC	Ø 39.20 mm	Ø 35.23 mm
b	AB	(39.45) 39.14 (–0.31)	(35.86) 35.49 (–0.37)
	BC	(38.87) 38.43 (–0.44)	(34.76) 34.29 (–0.47)
	AC	(39.20) 38.84 (–0.33)	(35.23) 34.79 (–0.44)
c	AB	(39.45) 39.27 (–0.18)	(35.86) 35.64 (–0.22)
	BC	(38.87) 38.74 (–0.13)	(34.76) 43.58 (–0.18)
	AC	(39.20) 39.15 (–0.05)	(35.23) 35.98 (–0.25)
d	AB	(39.45) 39.15 (–0.35)	(35.86) 35.51 (–0.35)
	BC	(38.87) 38.45 (–0.42)	(34.76) 34.38 (–0.38)
	AC	(39.20) 38.86 (–0.34)	(35.23) 34.76 (–0.35)
e	AB	(39.45) 39.32 (–0.13)	(35.86) 35.60 (–0.26)
	BC	(38.87) 38.71 (–0.16)	(34.76) 34.45 (–0.22)
	AC	(39.20) 39.05 (–0.15)	(35.23) 35.92 (–0.31)

(original measurements in parentheses; blue text indicates difference)

Table 2 Comparison of differences (mm and %) after 5 days (blue text indicates difference)

Distances (mm ± 0.02 mm)	Top outer		Difference in mm (in %)	Bottom inner		Difference in mm (in %)
Mixture	**10:6.26**	**10:4**		**10:6.26**	**10:4**	
AB	–0.30	–0.13	–0.17 (–40%)	–0.35	–0.26	–0.09 (–25%)
BC	–0.42	–0.16	–0.26 (–56%)	–0.38	–0.22	–0.16 (–42%)
AC	–0.34	–0.15	–0.19 (–55%)	–0.53	–0.31	–0.22 (–41%)

It is better to talk about 'bulk density', which is defined as the quotient of mass and volume. Strictly speaking, this can only be ascertained by weighing[1]. Anyone wanting to set a mixing ratio accurately or even change it cannot simply rely on how it feels and measure out the materials freely. Measuring cups and/or scales are essential tools (Figs 13 and 14).

Fortunately, there are more and more suggestions as well as helpful and useful improvements from the dental industry. To this end, the company Megadental, Büdingen, Germany, the sales partner of Retec Kunststofftechnik, has developed a special measuring, dosing and mixing set (megaExact kit) for all PMMA materials (Fig 15). This is supplied with scales and is an excellent addition, which I am happy to recommend.

Conclusions

I think it has clearly been shown that it is not always a totally new or unknown material that is needed to improve our working processes.

It will probably never be possible to eliminate entirely a certain amount of residual monomer from the processing of PMMA. Any reduction in this amount by industry in the manufacturing process is not only a key point to be stressed when a dentist is giving his patients medical advice in his practice, but it also creates more certainty during further processing in the laboratory. One particular reason is that the necessary storage in water often cannot even take place since the schedule for fabrication and relining is usually too tight. This is precisely why reducing the residual monomer level is so important. Internal gas chromatography analyses of the new denture materials in the analytical laboratory of Retec Kunststofftechnik revealed that the residual monomer content decreased by 30 to 50% in comparison with standard Retec products, thereby substantiating the measurements discussed above (Figs 16 and 17). Reducing the residual monomer content also had a positive effect on the physical properties of the new PMMA materials.

Looking at the huge repercussions for acrylic processing brought about by an improved mixing ratio, in relation to reduced residual monomer content and shrinkage, it makes one reflect how little extra effort is needed for a dental technologist to improve his/her work. Simply measuring the powder and liquid components systematically will eliminate an enormous potential for error in the fabrication of dentures, which the patient will directly experience.

Fig 13 Scales that are easy to handle create less work than one might at first think, but provide added accuracy when measuring materials.

Fig 14 One of many combined weighing, measuring and pouring vessels.

Fig 15 The megaExact kit is an excellent and useful addition, which no laboratory should be without (Megadental, Büdingen, Germany).

Figs 16 and 17 Comparing the reduction in the residual monomer content of the standard Retec products with that of the newly developed Retec 'plus' products.

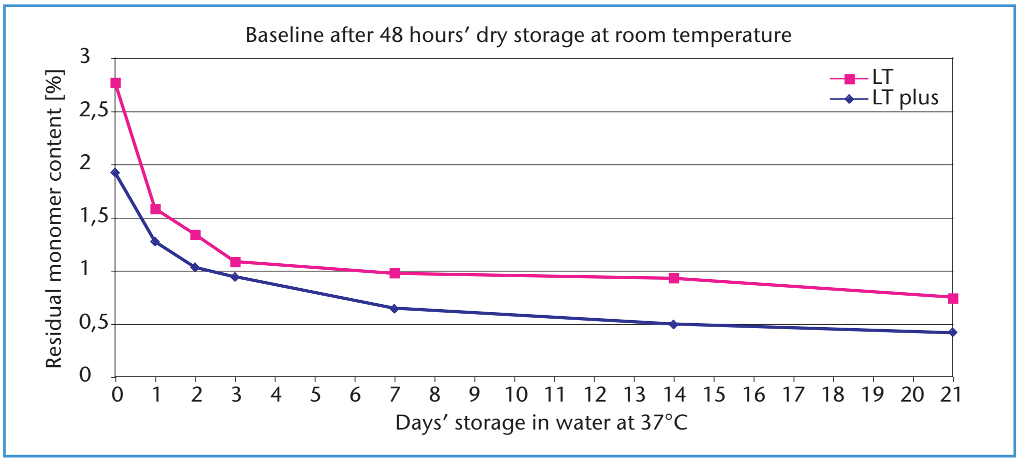


Fig 16 LT and LT plus (mixing ratio 10:7 and 10:5 respectively).

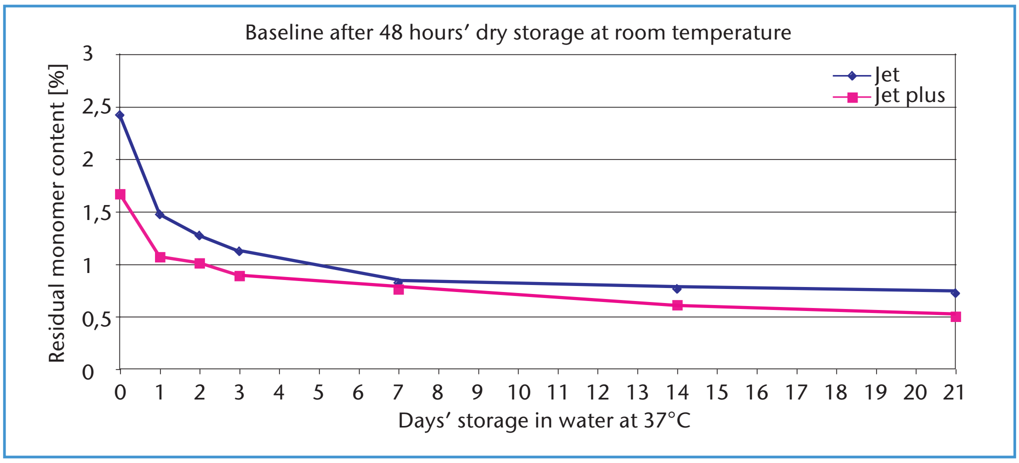


Fig 17 Jet and Jet plus (mixing ratio 10:5 and 10:4 respectively).

Improving denture adhesion, more consistent dimensional accuracy of the denture base and the associated tooth positions, and reducing the occlusal interferences that have to be ground back at the expense of tooth substance are considerable improvements that this acrylic resin provides, as well as a more homogeneous and easier-to-polish resin surface.

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Address for correspondence

Karl-Heinz Körholz, Trigodent – Prothetische Schulungen (prosthetic training courses)
Hervester Strasse 38, 46286 Dorsten-Wulfen, Germany
Email: K@rl-Heinz.de

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