

Dynamic mechanical analysis of heat, microwave and visible light cure denture base resins

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The clinical durability and performance of a denture are limited by the properties of the denture base resins used in the fabrication of the prosthesis. Among the properties considered important for denture base resins are viscoelastic properties such as storage modulus, damping and glass transition. In this study, dynamic mechanical analysis using a flexural mode of deformation in the temperature range 25–180 °C has been used to characterize the viscoelastic properties of three denture base resins with different curing modes including conventional thermal cure, microwave cure and visible light cure. The resins studied were popular commercial systems. The results indicate that the microwave cure and conventional thermal cure resins are significantly different in their viscoelastic properties from the current visible light cure resin system. The latter resin is characterized by higher flexural modulus and loss modulus across the entire range of temperatures investigated and in addition shows higher glass transition temperature relative to the other resins studied. The results indicate that filler loading and crosslinking effects may be responsible for this behaviour of the visible light cure resin and may indicate a potential brittle behaviour not desirable in a permanent denture.

1. Introduction

Polymers used for restorative and other uses in dentistry cover a wide spectrum of materials from elastomeric types on the one hand (e.g. soft liners and maxillofacial materials) to rigid and hard materials on the other (e.g. filled resins and denture base resins). Because of the wide range of mechanical behaviour involved, and the close relationship of this mechanical behaviour with the viscoelastic properties centred around one or more glass transition phenomena (such as the α , β or other transitions), dynamic mechanical analysis (DMA) is a very valuable method to characterize dental polymeric systems. The sensitivity of DMA for the detection of glass transitions is well known and many investigators have used the technique to characterize viscoelastic properties of different dental polymers [1–13]. The information provided in DMA tests, such as storage modulus, loss modulus and tan delta, have been used to study heat cure denture resins in the past [10–13]. While the storage modulus (E') represents the stiffness or rigidity of a material by defining the stress to strain ratio during elastic deformation (i.e. the proportionality constant between stress and strain), the loss modulus is associated with the energy absorbed by the resin to increase its segmental molecular vibration or translation of chain positions during dynamic deformation. Such absorption of energy for molecular segmental vibration or chain translation rather than for elastic deformation, results in damping of the amplitude of specimen oscillation during dynamic deformation.

Tan delta, the ratio of loss modulus to storage modulus (i.e. E''/E') is also used to define damping in the system. Dentures are subject to flexural stress cycles during mastication. The denture base resin should be sufficiently stiff (i.e. possess adequate flexural modulus) without at the same time being too stiff, which may make the denture brittle and cause its premature failure during mastication or when it accidentally falls on a hard surface. There is also potential influence of transitions and damping effects on creep behaviour of dentures. For these reasons, flexural modulus and other dynamic mechanical properties of denture base resins are of importance to ensure durability of permanent dentures during their clinical service. DMA analysis provides valuable information not only on these properties, but also on the transitions and structural changes in denture base resin formulations, with differences in their compositions. There is a need to characterize these properties of typical denture base materials. The objectives of this investigation were:

1. To characterize the dynamic mechanical properties of currently available commercial denture resin systems, with special emphasis on the different formulations used for heat, visible light and microwave modes of curing.
2. To determine the glass transitions near and above the ambient temperatures in the oral environment and their relationships to the compositions of the formulations and the curing methods used.

3. To understand the changes in the viscoelastic properties as a function of temperature and correlate these changes with the structures and transitions in the materials.
4. To characterize the thermal expansion variations and softening across a wide range of temperatures including the glass transition in a thermomechanical analyser (TMA) and weight loss measurements in a thermogravimetric analyser (TGA) and correlate this information to the dynamic mechanical properties and their changes.

2. Materials and methods

2.1. Materials

Three denture base resin systems were evaluated in this investigation and are listed in Table I with information on their curing mode, manufacturer and primary composition in the formulation. The materials were selected from popular commercial brands to include three different curing modes from the conventional thermal to the visible light cure and the more recent microwave cure systems. From the three systems of Lucitone, Acron MC and Triad, it appears that the Triad is different in its use of urethane dimethacrylate, a bifunctional monomer with known tendencies for crosslinking and a microfine silica filler to act as a thickener and reinforcement of the resin. All resins contain polymethylmethacrylate (PMMA) or a copolymer of PMMA (e.g. Lucitone which is a copolymer of PMMA and polybutylmethacrylate) with small additives (e.g. 7% in Lucitone) of a crosslinker (e.g. glycol dimethacrylate). The denture base resins (e.g. Lucitone 199 and Triad) are generally reinforced with rubber to enhance toughness and impact resistance. Previous reports indicate that the amount of residual monomer content is less than about 5% in resin systems generally used in denture base [14, 15]. Initiators such as benzoyl peroxide, camphoroquinone, etc. are also added in addition to other proprietary modifications, if any. According to information supplied by the manufacturers, none of the three systems uses any plasticizer.

2.2. Methods

Rectangular bars 25 mm × 10 mm × 3 mm were fabricated from the different denture base resins studied. All the specimens were prepared in a stone mould. The fabrication procedures followed the manufacturer's

recommendations with proper flasking techniques, including the special flasks used for microwave cure. For the visible light cure and the microwave cure resins the specimens were cured from one side, then turned over and cured from the other side to ensure adequate curing.

The dynamic mechanical properties of the different denture base resins studied were determined in a TA Instruments DMA model 983. The instrument was interfaced to a computer control station Thermal Analyst 2000. Instrument control was carried out by the analyst system software. Dynamic mechanical analysis was carried out in fixed frequency flexural mode (1 Hz) with a pre-optimized oscillation amplitude of 0.6 mm. Temperature range studied varied from -50 to 180 °C using a liquid nitrogen reservoir. A sample size of $N = 7$ was used. TA Instruments software DMA version 4.2 was used for analysis, where appropriate.

TMA analysis of disc specimens (6 mm diameter × 3 mm thick) was also carried out in the temperature range 25–150 °C in TA Instruments TMA model to study thermomechanical behaviour in selected cases to better understand the DMA curves. Analysis was done with an expansion probe with no load to follow thermal expansion changes and a penetration probe under a weight of 5 g to follow softening associated with glass transition. In addition, TGA analysis in the temperature range 25–800 °C was used to characterize weight change dependence on temperature. TMA and TGA analysis were also conducted using Thermal Analyst 2000. TA Instruments TMA software version 4.0 and the general analysis utility version 4.0 were used for the TMA and TGA analysis, respectively, where appropriate.

3. Results

Fig. 1 shows typical plots of the storage modulus of the three resins as a function of temperature. The storage modulus changes show a similar trend with temperature in all three resins, but the Triad system shows a higher value across the entire range of temperatures. Fig. 2 shows plots of loss modulus values as a function of temperature and all three resins are characterized by two different loss modulus peaks. The peaks were observed in the temperature range 10–16 °C for Lucitone, 19–32 °C for Acron MC and 30–44 °C for Triad at the lower temperature range. Peaks were also observed at 107–115 °C for Lucitone

TABLE I Materials studied

Sample number	Material	Manufacturer	Type of cure	Primary composition
1	Triad	Dentsply International, York, PA, USA	Visible light	PMMA, urethane dimethacrylate, initiator, microfine silica, rubber toughener, etc.
2	Lucitone 199	Dentsply International, York, PA, USA	Heat	Copolymer (with PMMA and polybutyl methacrylate), rubber toughener, crosslinking additive, initiator, etc.
3	Acron MC	GC International, Scottsdale, AZ, USA	Microwave	PMMA, crosslinking additive, proprietary additives, initiator, etc.

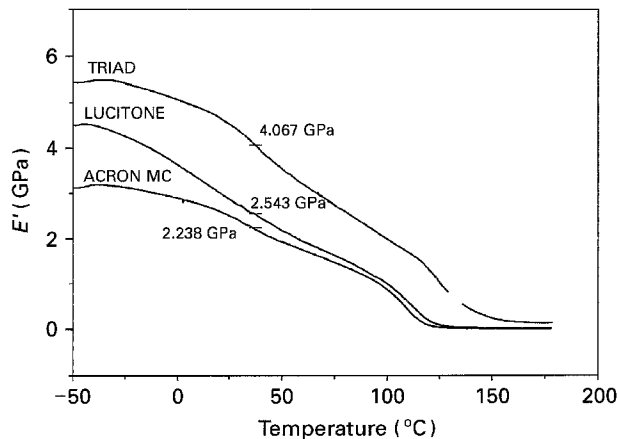


Figure 1 Flexural storage modulus change of different denture base resins as a function of temperature. The storage modulus value at 37°C is identified for each resin.

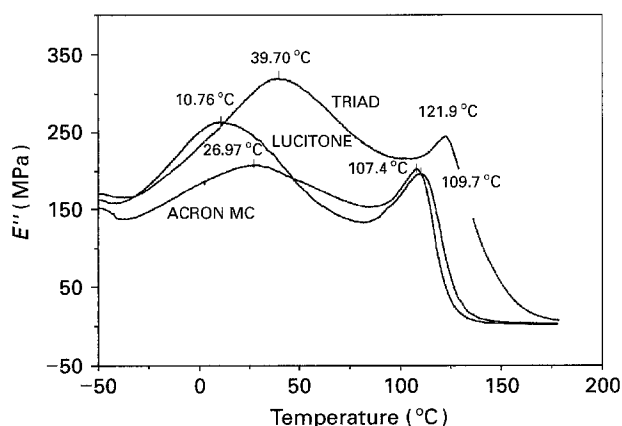


Figure 2 Loss modulus change of different denture base resins as a function of temperature. The loss modulus peak temperatures for α - and β -transitions are shown.

and Acron MC and 115–123°C for Triad at the higher temperature range. The lower temperature peak is conveniently designated as the β -transition and the higher temperature peak the α -transition. Fig. 3 shows plots of tan delta values, again as a function of temperature. Although minor peaks are observed for the β -transition, all resins are clearly characterized by a distinct tan delta peak corresponding to α -transition. Moreover, the tan delta peaks occur at higher temperatures than the loss modulus peaks, as is invariably the case in DMA analysis of all resins. An interesting feature of the tan delta peaks in the glass transition range is that the tan delta values of Lucitone and Acron MC are significantly higher than that of Triad. The mean values and (SD) of the storage modulus, loss modulus and tan delta at 37°C are shown in Table II. One-way ANOVA revealed significant differences of means of storage modulus, as a function of brands ($p < 0.001$). Duncan multiple range tests showed that while Lucitone and Acron MC were in the same homogenous subset, Triad had significantly higher mean storage modulus value. Table II shows these results with connecting lines between means in homogenous subsets and separating vertical lines to indicate differences between homo-

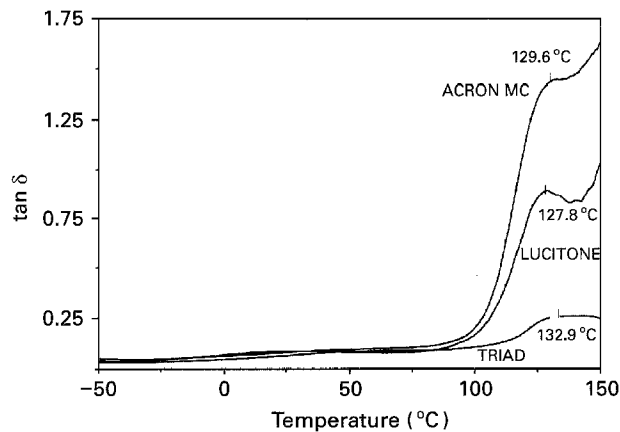


Figure 3 Tan delta change of different denture base resins as a function of temperature. Note the differences in the tan delta values at the region of α -transition. The lower value of tan delta for Triad appears to arise from the finite storage modulus past the α glass transition.

TABLE II Duncan contrast

Resin	Storage modulus mean (GPa) (SD)	Loss modulus mean (MPa) (SD)
Triad VLC	3.4121 (0.592)	289.67 (49.489)
Lucitone	2.4147 (0.212)	220.04 (35.10)
Acron MC	2.3194 (0.273)	192.17 (23.27)

genous subsets. Similar results were also observed for loss modulus means shown in Table II. ANOVA also showed that tan delta means (at 37°C) of the different resin systems were not significantly different from each other ($p > 0.05$).

TMA dimensional change curves under the expansion probe (with no load) for the different resin systems are shown in Fig. 4. Interestingly, Lucitone and Acron MC TMA curves generated by the expansion probe are characterized by a significant increase of dimensional change and an order of magnitude increase in thermal expansion coefficient across the α -transition temperature range, but no such remarkable changes were observed for Triad. The thermal expansion coefficient values calculated and illustrated in Fig. 5 indicate these changes very clearly. Additionally, the total dimensional changes of Triad ($< 0.8\%$) were significantly lower than those of both Lucitone and Acron MC ($> 2.0\%$) over the entire temperature range investigated. When TMA curves were generated with a penetration probe under a weight of 5 g, the penetration effect due to softening associated with glass transition was observed for Lucitone and Acron MC, but not for Triad (see Fig. 5).

TGA plots of different resins are also shown in Fig. 6. The onset temperature of the major phase of resin decomposition occurs at about 276°C for Acron MC and Lucitone and at 314°C for Triad, indicating that more thermal energy is needed for the breakdown

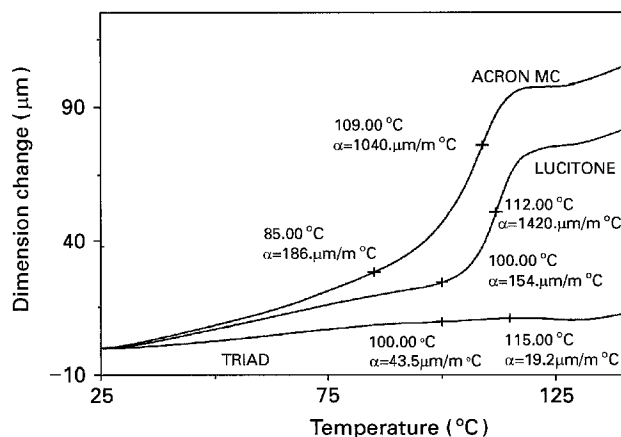


Figure 4 Thermal dimensional change (detected by an expansion probe using a thermomechanical analyser under no load) as a function of temperature for different resins. Note the dimensional and thermal expansion coefficient changes (indicated in the figure) with temperature at the α glass transition region for the Lucitone and Acron MC resins. Triad shows no such distinct effect.

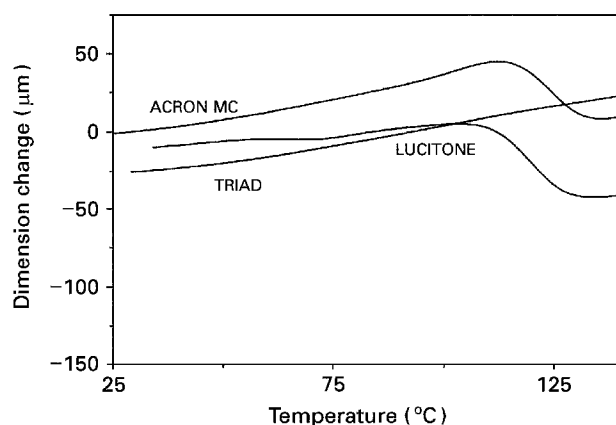


Figure 5 Dimensional change as a function of temperature under a penetration probe with a 5 g load. Note the penetration effects during softening at the α glass transition for the Lucitone and Acron MC resins. Triad shows no such distinct effect.

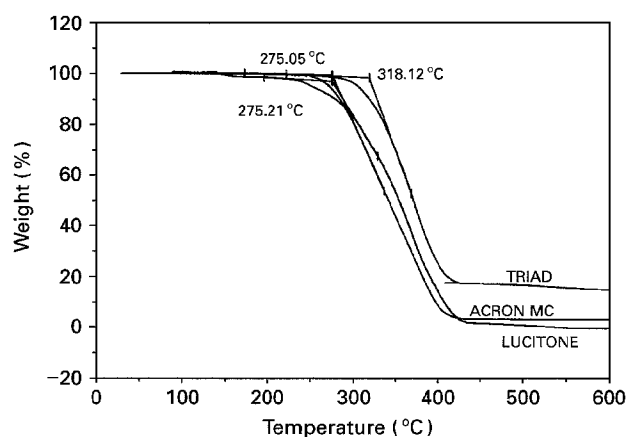


Figure 6 TGA profiles of the different resins. Note the onset temperature of decomposition indicated in the figure for each resin.

of the Triad formulation. In addition, approximately 14.25 wt % residual filler is left behind in the Triad system even after heating to 800°C. There was also approximately 2% residual filler in Acron MC.

4. Discussion of results

The results of this study reveal interesting differences in the dynamic flexural behaviour, thermal dimensional changes including thermal expansion coefficient differences, softening and thermal breakdown characteristics between the different resin systems studied. The viscoelastic behaviour of the thermal cure system Lucitone and the microwave cure system Acron MC appear to parallel the previously reported modulus changes of PMMA denture resin systems [10–13]. Loss modulus peak (obtained at low frequencies) is often considered as a better indicator of glass transition temperature (T_g) than tan delta peak because it closely corresponds to the T_g value determined by other methods such as DTA, whereas tan delta peak occurs at 5–15°C higher [14]. Based on this premise, the start of α glass transition at approximately 90°C and a loss modulus peak in the range of 107–115°C in both Lucitone and Acron MC reflect the PMMA composition, which is dominant in these systems. On the other hand, the α glass transition of Triad occurs at a higher temperature range (start: 105–110°C; loss modulus peak 115–122°C). The end of α glass transition is indicated by a steady-state value of storage modulus for all resins in Fig. 1 and this occurs at the higher temperature of 150°C for Triad as opposed to 125°C for Acron MC and Lucitone. In addition, the steady-state value of storage modulus at the end of glass transition is negligible for Lucitone and Acron MC, but finite for Triad. After completion of α -transition, this finite value of storage modulus is also reflected in the lower tan δ peak value for Triad during the α -transition. Since tan δ is defined as E''/E' , the value of storage modulus E' at the glass transition will determine the tan δ even if the loss modulus E'' values may appear to be not significantly different for the different resins during this transition range. Differences were also observed for the β -transition, with Triad showing higher T_g . The higher temperature range of glass transitions and other observed differences may result from two possible causes: (1) the higher degree of crosslinking in Triad because of the addition of bifunctional urethane dimethacrylate to PMMA; and (2) the presence of about 14% filler in the resin. Both of these factors are known to cause a shift to higher temperature and broadening of the peaks in loss modulus or tan delta peaks, as well as the observed changes in the storage modulus [14, 15]. To separate the effects of these two factors will need more detailed research with similar experimental compositions involving variations in crosslinker concentrations with and without filler additions. Unfortunately, both these factors also influence the dimensional and thermal expansion coefficient variations observed in TMA analysis because both filler concentration and crosslinking would tend to lower the thermal expansion coefficient and overall dimensional changes. It has been previously reported from dilatometer measurements that a change of slope occurs at about 75–80°C in the dimensional change versus temperature curve of PMMA resin [15]. This is in agreement with our results for both Acron MC and Lucitone. On the other hand, the thermal expansion

coefficient of Triad fails to indicate such a detectable change. This, coupled with the observation of the higher breakdown temperature in the TGA curve and the consequent higher thermal energy indicated for the initiation of the resin decomposition for Triad, supports the possibility of a higher degree of crosslinking in this system, compared to the other resins studied.

The differences in the properties observed for the different denture base resins have significant clinical implications. The presence of a higher degree of crosslinking in Triad and the presence of 14% or more microfine silica in its formulation may result in brittle behaviour, and this is borne out by the DMA results of higher glass transition temperatures and significantly higher flexural modulus values. The use of the Triad system for permanent dentures may be contra-indicated by the results of this study. It is also clear that the microwave cure system shows comparable properties to that of the conventional heat-cure denture base resin. The advantages of the fabrication of a denture using microwave cure over conventional heat cure is that the curing time is significantly shortened from several hours to 3 min. This is a significant advantage, but other advantages such as improved mechanical properties claimed by the manufacturer are not supported by our study. In general, the mean storage modulus value for conventional heat-cured resins was nominally higher than that of microwave-cure resins over the entire range of temperatures, although the difference was not statistically significant. Thermal cure may be expected to provide a more uniform cure across the entire material because of homogenous heat distribution. Microwave heat distribution is uneven and heterogeneous and this may be a limitation of the microwave cure of bulk structures. Although the modulus values of thermally cured Lucitone and microwave-cured Acron MC showed no significant differences in modulus values, the lower values of flexural strength reported for Acron MC *vis-à-vis* Lucitone in flexural strength studies [16] may be the result of this limitation.

5. Conclusions

There are significant differences between the visible light cure resin (Triad) and the thermal and micro-

wave cure resin systems (Lucitone and Acron MC) in dynamic mechanical properties, dimensional/thermal expansion coefficient and softening characteristics over a wide temperature range. Triad shows a more brittle behaviour and may be contra-indicated for permanent denture application. This appears to be the result of the higher crosslinking and the presence of approximately 14% microfine silica as a filler.

There are no significant differences in the properties of heat-cured and microwave-cured systems.

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