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Viscoelastic properties of a room-temperature curing dimethacrylate resin

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The viscoelastic properties of a thermosetting resin prepared from bis-phenol A and diglycidal methacrylate were examined using three dynamic test methods. A strong dependence on frequency and temperature was observed, and the nature of this dependence, together with comparative data obtained for an epoxy resin, enabled some predictions on structural mechanisms to be made.

1. Introduction

In recent years, a thermosetting dimethacrylate resin prepared from bis-phenol A and glycidyl methacrylate has found specialist application in dentistry (as a filling material [1]) and in industry (for contact mouldings, filament windings and thick sheet fabrications [2]). Particularly useful characteristics of this resin are that it may be cured rapidly at room temperature and that it exhibits both low polymerization exotherm and low polymerization shrinkage.

The polymer is referred to as bis-GMA [1], its chemical name being 2,2-bis[*p*-(2′-hydroxy-3′-methacryloxypropyl)phenylene]-propane [3]. The structural formula is compared with methyl methacrylate and epoxy resin in Fig. 1. The bis-phenol A nucleus of the epoxy molecule is present, but the epoxy end groups are converted to methacrylate groups. Bis-GMA was originally prepared with the intention of retaining the desirable physical and mechanical properties of epoxy resin whilst the slow ring-opening curing reaction would be replaced by a quicker double-bond opening free-radical reaction.

The uncured resin has a high viscosity due to the molecular size and to hydrogen bonding, and is usually diluted with monomers such as tetraethylene glycol dimethacrylate and methyl methacrylate. Several chemical modifications have also been developed such as ethoxylated bis-phenol A dimethacrylate and terephthalic acid-based aromatic dimethacrylates.

There is little reported work on the properties of the bis-GMA polymer itself although work has been carried out on a range of highly-filled particulate composites in which bis-GMA forms the matrix [4, 5].

In this investigation, three dynamic mechanical test methods were used to determine the viscoelastic properties of a bis-GMA resin, and similar tests were carried out on an epoxy resin for comparative purposes.

2. Experimental

2.1. Experimental methods

The three experimental techniques were selected to provide information over different ranges of the frequency spectrum. A free-oscillation torsion pendulum was used for data at low frequencies (10^{-1} to 1 Hz), a vibrating reed forced resonance test at intermediate frequencies (10^2 to 10^3 Hz) and an ultrasonic wave propagation method at

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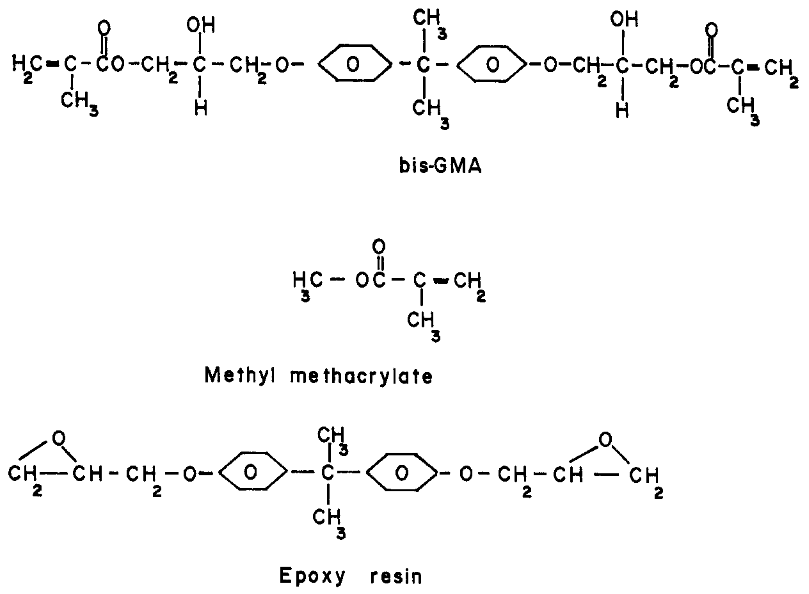

Figure 1 Structural formula of the bis-GMA monomer compared with methyl-methacrylate and epoxy resin.

high frequencies (10^6 to 10^7 Hz). The methods are described in detail elsewhere [6–8]; a brief summary is given below.

The torsion pendulum test induced oscillations in a long,rectangular, specimen and the elastic component (G') of the complex shear modulus together with the mechanical loss tangent or "damping" ($\tan\delta$) were derived from measurements of the period and rate of decay of the oscillations.

For the relevant theory, see, for example, Ward [9]. The equations used to calculate G' and $\tan\delta$ were:

$$G' = \frac{L}{\beta b^3 w}\left[\frac{4\pi^2 I}{T^2} - C_\mathrm{w}\right] \qquad (1)$$

$$\tan\delta = \frac{4\pi I\Delta}{4\pi^2 I - T^2 C_\mathrm{w}} \qquad (2)$$

where L is the specimen length, b the specimen thickness, w the specimen width, β a shape factor depending on the ratio of width to thickness of the specimen [10], I the moment of inertia of the inertial bar, C_w the torsional stiffness of the wire supporting the bar, T the period of oscillation and Δ the logarithmic damping decrement.

In the vibrating reed test, a rectangular specimen was mounted as a cantilever beam and forcing oscillations were applied to the fixed end. At resonance, the displacement of the free end of the beam is a maximum. The elastic modulus and loss tangent were calculated from the resonant frequency (f_r) and the half-width of the resonant peak using the relations:

$$E' = \frac{42.21\,\rho f_\mathrm{r}^2 L^4}{b^2} \qquad (3)$$

$$\tan\delta = \frac{f_2 - f_1}{3^{1/2} f_\mathrm{r}} \qquad (4)$$

where ρ is the specimen density, and f_1 and f_2 are the frequencies either side of resonance at which the amplitude of vibration is half the maximum amplitude.

The ultrasonic test incorporated pulse transit-time measurements from which longitudinal and transverse wave velocities (V_L and V_T) were determined. The elastic Young's modulus (E'), elastic shear modulus (G') and Poisson's ratio (ν), are related to the wave velocities by:

$$E' = \rho V_\mathrm{T}^2\left(3 - \frac{1}{K^2 - 1}\right) \qquad (5)$$

$$G' = \rho V_\mathrm{T}^2 \qquad (6)$$

$$\nu = \frac{K^2 - 2}{2(K^2 - 1)} \qquad (7)$$

where $K = V_\mathrm{L}/V_\mathrm{T}$.

2.2. Specimen preparation

The bis-GMA formulation* is a viscous, clear, light coloured, resin prepared from bis-phenol A and a compound of glycidyl methacrylate and glycidyl

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*Nupol 1629 Batch No. 646005 Freeman Chemicals Ltd, Ellesmere Port, England.

TABLE I Dynamic mechanical properties of the bis-GMA and epoxy resins

	bis-GMA				Epoxy			
	E ($\mathrm{GN\,m^{-2}}$)	G ($\mathrm{GN\,m^{-2}}$)	ν	tan δ	E ($\mathrm{GN\,m^{-2}}$)	G ($\mathrm{GN\,m^{-2}}$)	ν	tan δ
Torsion pendulum	3.32* ± 0.04	1.22 ± 0.01	–	0.035 ± 0.004	2.61* ± 0.06	0.944 ± 0.019	–	0.023 ± 0.001
Vibrating reed	3.78 ± 0.12	1.39* ± 0.05	–	0.020 ± 0.001	3.43 ± 0.07	1.24* ± 0.04	–	0.020 ± 0.001
Ultrasound	5.58 ± 0.10	2.06 ± 0.03	0.360 ± 0.005	–	4.64 ± 0.05	1.67 ± 0.04	0.384 ± 0.005	–

*Calculated values – see text.

acrylate [11]. This was cured at room temperature using the peroxide–amine free radical system with lauroyl peroxide as the catalyst and *NN*-dimethyl-*p*-toluidine as the co-catalyst. Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) monomers were used to dilute the resin and facilitate mixing. For each batch, 10 g of resin were combined with 1.0 g MMA, 1.0 g EGDM, 0.03 g peroxide and 0.01 g toluidine giving a working time of 3 to 4 min.

The epoxy resin† is an unmodified "bis-phenol A" epoxy of low viscosity. It was combined with hardener and accelerator in the ratio 50 : 25 : 1 and cured according to the manufacturer's instructions.

Specimens of both materials were conditioned in a desiccator at 60° C for 48 h.

3. Results

The dynamic properties of the bis-GMA and epoxy resins determined using the three techniques are shown in Table I. Values given are the mean and the standard deviations for batches of eight samples. The temperature of testing was 23° C and the frequencies (low, intermediate and high) were 0.8 Hz, 750 Hz and 5.3 MHz. Values for the real part of the complex Young's modulus at low frequencies and shear modulus at intermediate frequencies were calculated using the formula:

$$E' = 2G'(1+\nu) \qquad (8)$$

with the high frequency value of Poisson's ratio. This ratio is very nearly independent of frequency for the common polymers [12].

High frequency values of tan δ were not determined as pulse distortion (due to frequency-dependent absorption effects inside the polymer) was marked. Such distortion complicates considerably the measurement of absorption [12].

Fig. 2 shows the variation in low frequency properties with temperature. The logarithmic decrement is also included as it provides a more sensitive indicator of transitions in the materials. The temperature dependence of the intermediate

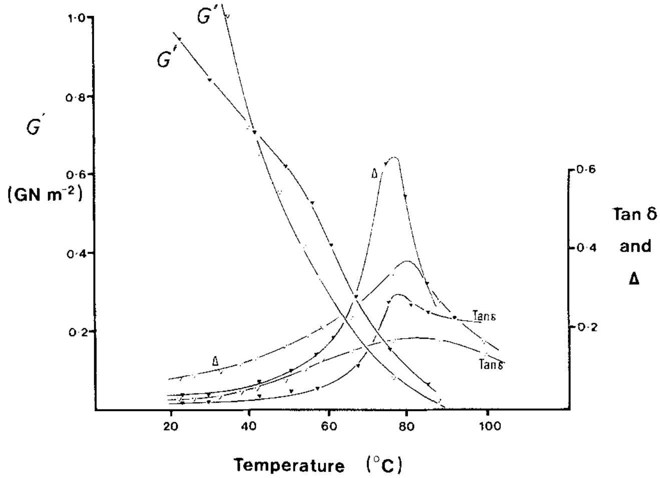

Figure 2 Torsion pendulum method: variation in properties of the resins with temperature. ▿ bis-GMA, ▾ epoxy.

†Araldite CY219 Batch No. 435143 Ciba-Geigy Ltd, Cambridge, England.

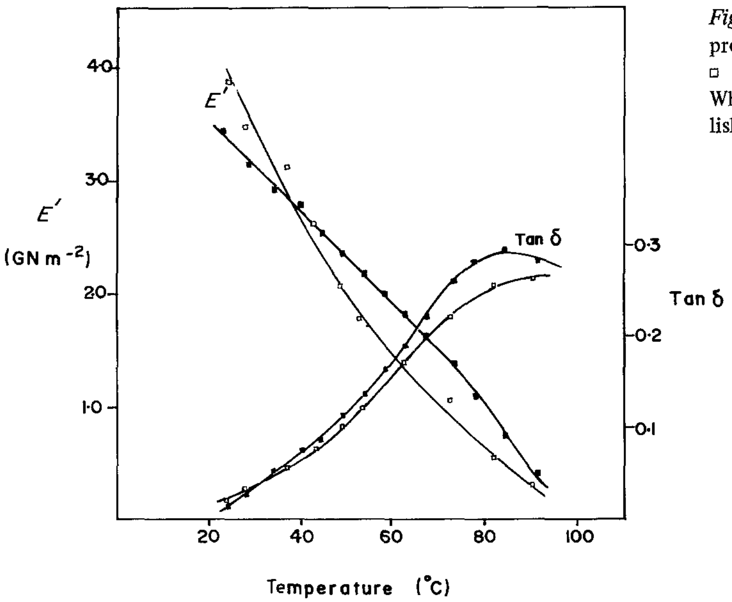

Figure 3 Vibrating reed method: variation in properties of the resins with temperature. □ bis-GMA, ■ epoxy. (Reproduced from Whiting and Jacobsen [18], with the publisher's permission.)

and high frequency properties is shown in Figs. 3 and 4. The restricted temperature range for the ultrasonic method is due to the need for liquid immersion and does not reflect any limitation in performance of the material.

4. Discussion

In general, thermosetting polymers have a highly crosslinked network structure which is relatively insensitive to changes in the temperature or frequency of deformation. However, the results indicate that bis-GMA is not typical of this type, the mechanical properties being strongly dependent on temperature and probably also on frequency. Table I indicates that there is a large variation in response according to the method of measurement. Two important differences which may account for this are the strain rate and the strain amplitude induced during testing. These quantities were calculated for each method, and are shown in Table II.‡

In general, the moduli and damping of

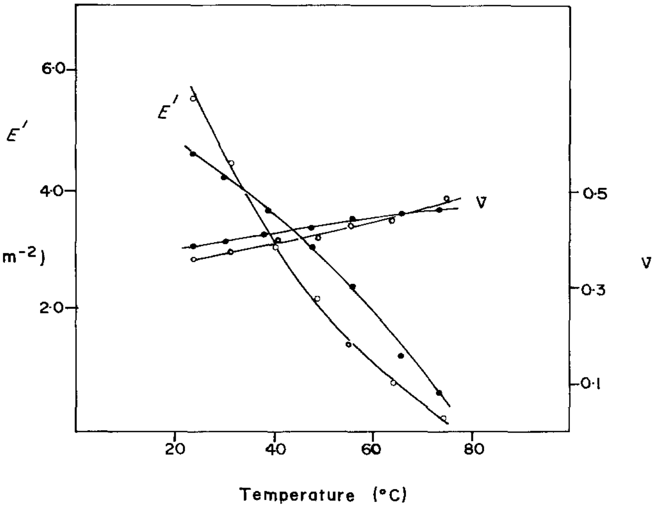

Figure 4 Ultrasonic method: variation in the properties of the resins with temperature. ○ bis-GMA, ● epoxy.

‡The strain amplitudes are maximum values calculated using standard formulae for rods and bars subjected to flexure and torsion. The strain amplitude for the ultrasonic method was calculated using the characteristic performance data for the particular piezoelectric ceramic. The maximum rate of straining for the dynamic tests was taken as the maximum strain multiplied by $2\pi f$, where f is the frequency of oscillation. It was assumed that the maximum strain in the specimen was the same as that in the ceramic. In practice, the specimen strain would be lower due to impedance mismatching at the various interfaces and absorption by the water.

TABLE II Strain amplitude and strain rate imposed during testing

Method	Maximum strain amplitude (%)	Strain rate (% sec^{-1})
Torsion pendulum	1.4	4.4
Vibrating reed	3.2×10^{-2}	101
Ultrasound	3.7×10^{-5}	1.2×10^3

polymers are not affected by the amplitude of the imposed strain providing that the amplitude is small. For example, for small strains in rubbers, the components of the complex shear modulus have been shown to be largely independent of the strain amplitude. Ferry [13] states that the strains of 1% fall well within the range of linear viscoelasticity.

Therefore, it is unlikely that the important differences between the methods is the strain rate, and that the dynamic properties of the bis-GMA resin are highly strain-rate dependent.

Further confirmation of this viscoelastic nature is given by the data for the temperature dependence of the dynamic properties (Figs. 2 to 4). The decrease in stiffness and increase in damping are sufficiently rapid to suggest that quite small amounts of thermal energy are required to cause molecular rearrangements.

The modulus and damping curves, determined at low frequencies show that, for bis-GMA, a transition occurs at approximately 80° C. This is probably the glass transition.

At intermediate frequencies, there is evidence of a peak at the high temperature extremity of the damping curve. The peak temperature (T_g) in this case is in the region 95 to 100° C.

A change in T_g with frequency is observed with most glassy polymers, and is due to the time dependence of the molecular processes responsible for the transition. The amount by which T_g is shifted is strongly dependent upon the activation energy for the particular structural change, but a typical shift for many common polymers is 7° C per decade change in frequency [10]. The smaller the shift, the higher the activation energy. For bis-GMA the shift is between 8 and 9° C per decade, which suggests that the activation energy is slightly lower than normal.

It is interesting to compare the response of this polymer with those of epoxy resin and polymethylmethacrylate (PMMA).

Epoxy resins are also thermosetting polymers and, in general have a highly crosslinked network structure. It has been proposed that the main molecular motion is a rotation of the glycidal ether portion of the molecule, but that movements may occur which are governed by the substituents on the central carbon bridge of the bisphenol residue. The temperature at which the glass transition occurs has been shown to be dependent upon these substituents, and also upon the detailed structure of the curing agent [14, 15]. Thus, T_g's of between 47 and 190° C have been reported for different compositions [16].

The precise composition used in this study has not been analysed previously, but the general type usually has a T_g in the region 120 to 170° C.

The results for epoxy resin CY219 show that its dynamic properties are strongly dependent on frequency and temperature in the same manner as are those of bis-GMA. The glass transition occurs in the region 78 to 85° C and its position varies according to the frequency of measurement. These observations suggest that this epoxy resin has a less rigid structure than normal, due possibly to the accelerated cure.

In contrast, PMMA is a linear amorphous thermoplastic and is well recognized to have a strongly viscoelastic nature. At temperatures below the T_g, it is thought that a general co-operative movement of the main polymer chain takes place and that there may be additional mobility associated with the carbomethoxy groups pendant from the main chain [17]. The glass transition occurs at approximately 115° C and is caused by a general increase in flexibility of the main chains.

Some predictions may be made concerning the structure of the bis-GMA polymer. The difunctional components, the bis-GMA itself and the glycol dimethacrylate, probably lead to the formation of a pseudo-crosslinked structure, a close, regular spacing being prevented by the large size of the bis-GMA monomer. Entanglements, which have some of the characteristics of crosslinks, and some inter-molecular hydrogen bonding would be expected. In addition, the rapidity of cure would lead to a low degree of polymerization and contribute to the formation of an irregular and poorly crosslinked structure.

There are a large number of possible molecular motions in such an irregular and hybrid structure. The similarity in properties to the epoxy resin suggests that rotation about the ether bond, and movements governed by the substituents of the central bridge of the bisphenol component, make an important contribution to the total deformation. Some pendant carbomethoxy groups may be present due to the addition of the methacrylate monomer, and there is probably some mobility associated with these. Other sites for molecular motion are difficult to identify precisely without further experimental analysis.

There are some interesting additional features of the mechanical response of bis-GMA. The glass transition peak is broad in comparison to those of epoxy resin and PMMA. This may be due to the diluting monomers which were added to the original resin, or to two or more different relaxation mechanisms with similar activation energies.

There is no evidence of a secondary (or β) transition in the temperature spectra. Epoxy resin normally has a β-transition in the region -60 to $-30°$ C [16]. This is due to motion in the epoxy part of the molecule, and comprises a stress relaxation process which is thought to be responsible for the outstanding toughness of these resins. A transition has also been identified in PMMA. This occurs at 40° C and is due to the pendant carbomethoxy groups. The low activation energy for this motion makes it difficult to resolve by mechanical methods.

A β-transition may occur in bis-GMA. The absence of a second peak in the spectra may be due to insufficient resolution of the experimental methods, to a masking effect caused by the proximity of the glass transition, or to the relevant secondary processes occurring at a temperature below the experimental range.

References

1. R. L. BOWEN, *J. Amer. Dental Ass.* **66** (1963) 57.
2. R. J. LEWANDOWSKI, E. C. FORD, D. M. LONGENECKER, A. J. RESTAINA and J. P. BURNS, in Proceedings of 30th Annual Conference, Society of Plastics Industry, Delaware, USA (1975).
3. R. L. BOWEN, *J. Dental Res.* **58** (5) (1979) 1493.
4. C. Mc D. HANNAH and E. C. COMBE, *Brit. Dental J.* **140** (1976) 167.
5. P. H. JACOBSEN, *ibid.* **150** (1981) 15.
6. R. WHITING and P. H. JACOBSEN, *J. Dental Res.* **59** (1980) 55.
7. *Idem, J. Biomed. Eng.* **5** (1983) 31.
8. *Idem, J. Dental Res.* **59** (1980) 1978.
9. I. M. WARD, "Mechanical Properties of Solid Polymers" (John Wiley Ltd, Chichester, England, 1971).
10. L. E. NIELSEN, "Mechanical Properties of Polymers" (Reinhold, New York, 1967).
11. R. L. BOWEN, U.S. Patent 3 0066-112 (1962).
12. B. E. READ and G. D. DEAN, "The Determination of Dynamic Properties of Polymers and Composites" (Adam Hilger Ltd, Bristol, England, 1978).
13. J. D. FERRY, "Viscoelastic Properties of Polymers" (John Wiley and Sons, London, 1961).
14. H. LEE and K. NEVILLE, "Handbook of Epoxy Resins" (McGraw-Hill, London, 1967).
15. C. A. MAY and F. E. WEIR, *SPE Trans.* **2** (1962) 207.
16. C. A. MAY and Y. TANAKA, "Epoxy Resins – Chemistry and Technology" (Marcel Dekker Inc., New York, 1973).
17. K. DEUTSCH, E. A. W. HOFF and W. REDDISH, *J. Polymer Sci.* **X111** (1954) 565.
18. R. WHITING and P. H. JACOBSEN, *J. Biomed. Eng.* 5 (1983) 31.

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