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Frequency dependency of Young's modulus of dental composites

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The Young's modulus of 15 commercial dental particulate filled composites was measured with three different methods. The materials were tested with static, low-frequency, and high-frequency elastic deformations. The analysis of the results shows that the frequency dependence of the Young's modulus of elasticity follows the same empirical law for all frequencies. Furthermore, knowledge of the Young's modulus for the resin component at all frequencies suffices to predict the Young's modulus of any particulate-filled composite.

1. Introduction

In recent publications [1–3], the present authors reported on an investigation of the Young's modulus of commercial and experimental dental particulate filled composites. Besides these materials, the unfilled matrix phase and amorphous silica were also tested. The composites showed a wide variety in the composition of the matrix phase as well as in the origin, shape, size, and particle-size distribution of the filler phase. Young's modulus was determined by a non-destructive dynamic method using the fundamental frequency, which ranged between 2 and 4 kHz for the composites. A statistical analysis of the Young's moduli as a function of the volumetric filler fraction resulted in an exponential rule of mixtures between the matrix and the filler phase [1, 2].

There are other dynamic and static tests that can be used to determine Young's modulus. Ultrasonic tests are conducted from 5 MHz [4] to 30 MHz [5]; the torsion pendulum acts at rather low frequencies [6]; the dynamic mechanical thermal analysis measures elastic and loss components of a forced vibration at variable frequencies [7]; and the three-point bending test acts at 0 Hz. The literature gives substantial differences in the reported values for the Young's modulus of dental composites, depending on the test method used.

Therefore, the aim of the present paper is to investigate the influence of the test frequency on the Young's modulus of dental particulate filled composites.

2. Experimental methods

2.1. Materials and sample preparation

For a detailed description of the materials and sample preparation, see Braem [1]. Fifteen composites were selected for the present investigation: eight self-cured composites, which polymerize by mixing a base and catalyst paste, and seven light-cured composites, which polymerize after irradiation with 400–500 nm visible light (Table I). Rectangular samples (length, $l = 35$ mm; width, $w = 5$ mm and height, $Th = 1.5$ mm) were prepared according to the manufacturers instructions. The light-cured samples were illuminated for 60 sec on the top surface and for an additional 60 sec on the bottom surface (Luxor Activating Unit, ICI, Macclesfield, UK). All samples were finished with dry 600 grit abrasive paper, and stored for 24 h at room temperature before testing at ambient temperature conditions.

2.2. The fundamental period test (FPT)

The complete description of this dynamic technique and the method for determining Young's modulus from the fundamental period for the first harmonic of the freely oscillating sample are given by Braem [1] and Braem *et al.* [2]. (See also Fig. 1.) The results cited here are taken from these publications. Ten samples of each composite were tested in these investigations.

2.3. The dynamic mechanical thermal analysis test

The equipment used is the dynamic mechanical thermal analyser (DMTA) of Polymer Laboratories Ltd, Loughborough, UK (Fig. 2). A harmonic stress at constant frequency is applied to a clamped sample. The analyser unit compares the applied stress and the corresponding strain signals. The visco-elastic properties of the materials cause a time lag between input and output signals giving rise to storage and loss components of the strain, which are resolved by the counting circuits. A single cantilever set-up was chosen (Fig. 2, inset) with some minor modifications in the clamping device to compensate for the imperfect parallellity of the sample surface planes. The samples were tested at 0.1, 1 and 10 Hz. Three samples of each

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TABLE I Products, initiation type, batch numbers, and manufacturers. S = self-cured; L = light-cured

Product	S/L	Batch number	Manufacturer
P-10	S	112983	3M Co, St. Paul, MN, USA
P-30	L	Exp. Lot 5	
Silar	S	8601A + 8601B	
Silux	L	041183 5502 U 4Y3	
Adaptic	S	053183 3A001	Johnson & Johnson, East Windsor, NJ, USA
Miradapt	S	3D906 24051904	
Answer	S	201804 21300	
Occlusin	L	Lot SP06 Mar 84	ICI Plc, Macclesfield, UK
Estilux posterior Y	L	061984 182	Kulzer & Co GmbH, Bad Homburg, West Germany
Durafill	L	061984 139	
Biogloss	S	840522	De Trey AG, Zürich, Switzerland
Brilliant	S	150584-36	Coltène AG, Altstätten, Switzerland
Brilliant Lux	L	D3 120684-20	
Isomolar	S	B551183 + C701183	Vivadent, Schaan, Liechtenstein
Heliomolar	L	050384	

product were prepared with the same finishing and storage conditions as described above, and were tested under the above conditions.

2.3. The static test (STAT)

In the three-point bending apparatus (Dynstatgerät 5106, Zwick and Co., Einsingen, West Germany), a small metal rod bends the sample between two knife-shaped edge supports (Fig. 3). A digital gauge records the bending of the sample in micrometers. For each bending interval (ΔU), a corresponding force interval (ΔF) is recorded. Young's modulus is then calculated using Equation 1:

$$E = \frac{l^3 \Delta F}{4wh^3 \Delta U} \quad (1)$$

where l is the length of the sample segment between the supports, w the width of the sample, and h the height. Three samples of each product were also tested under the same finishing and storage conditions as described above.

3. Results

Table II gives the results of the measurements for the three different methods. These measurements yield values of Young's modulus at five different frequencies: at 0 Hz for the STAT, 0.1, 1 and 10 Hz for the DMTA and at the fundamental frequency for the FPT, which ranges from 2 to 4 kHz for the composites and 7 kHz for the silica. An additional investigation with the FPT procedure showed that changing the thickness of the sample enabled us to obtain a constant resonance frequency of 4 kHz for each tested composite (Table II). The resulting Young's moduli did not differ significantly from the FPT results with constant dimensions but variable fundamental frequencies, which implies that Young's modulus is constant within that frequency range. Therefore, the frequency range between 2 and 4 kHz will henceforth be considered as one resonance frequency.

For each of the five different frequencies, a regression analysis was performed in order to determine the dependency of Young's modulus on the volumetric filler fraction. In a previous paper [2], it was shown that the regression curve is of the form

$$\hat{E} = \hat{E}_r \exp(bx) \quad (2)$$

where $\hat{E}$ is the calculated Young's modulus of the composite, $\hat{E}_r$ is the calculated Young's modulus of the unfilled resin, x is the volumetric filler fraction,

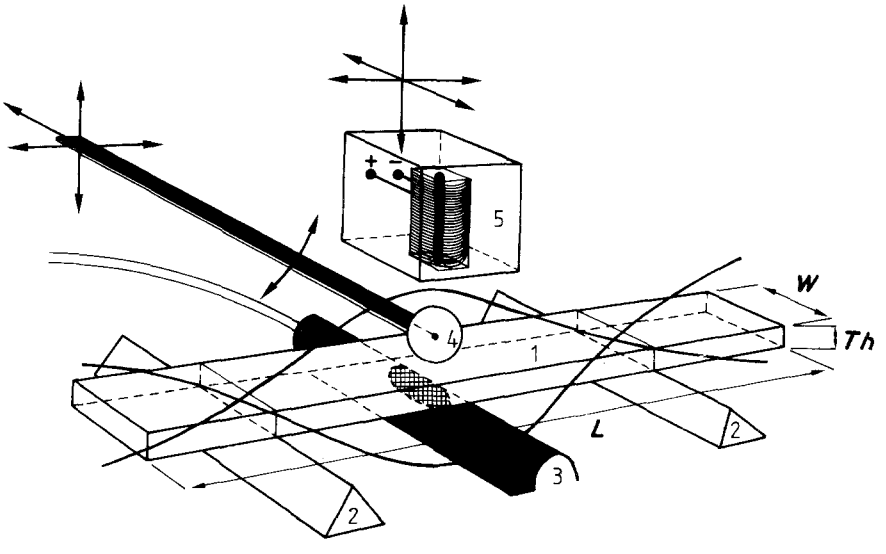

Figure 1 Schematic presentation of the rectangular sample (1) resting on two triangular supports (2). The microphone (3) is under the sample; the metal hammer (4) with the electromagnet (5) is above the sample. l is length, w is width, and Th is height (thickness) of the sample.

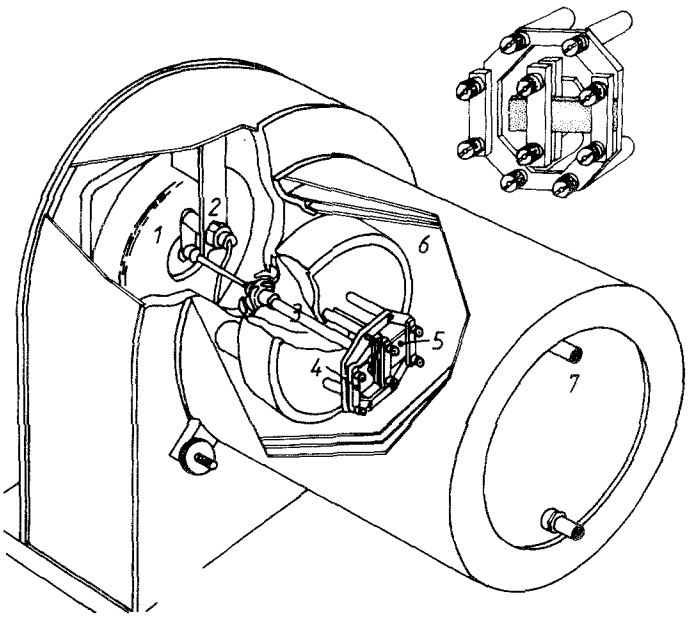

Figure 2 Mechanical head of the DMTA showing the sample mounting (inset) with (4) clamps, (5) sample; the vibrating system (1), displacement transducer (2) and drive shaft (3); (6) temperature enclosure; (7) liquid nitrogen gates.

and b the coefficient. The values of the parameters $\hat{E}_r$, $\ln \hat{E}_r$, and b for the five frequencies are given in Tables III and IV. They also give the 95% confidence intervals (*CI*) for these parameters using standard formulae. Fig. 4 shows the five plots of $\ln \hat{E}$ against x. The results mentioned in these tables for the FPT procedure are cited from [1].

4. Discussion

Although there is a slight increase of Young's modulus for the unfilled resin in the DMTA method from 0.1 to 10 Hz, the results of Table III show that the differences are not statistically significant. Furthermore, the difference between the STAT and DMTA results are also insignificant due to statistical fluctuations. But the *CI* of $\hat{E}_r$ for the FPT (2692–3578 MPa) does not overlap with the *CI*s of any of the four other frequencies, which indicates that Young's modulus of the resin component increases with higher frequencies, at least up to the resonance frequency.

From Fig. 4, it is clear that Young's moduli of the pure silica for all five frequencies do not differ significantly. The calculation of $\hat{E}$ for $x = 1$ (representing purely the filler phase) from Equation 2 for the FPT yields a value of 60 259 MPa with a 95% *CI* between 51 990 MPa and 69 843 MPa. An acceptable value (64 673 MPa) was obtained by the authors with the STAT test.

Fig. 4 seems to indicate that the curves at different frequencies approach the value of Young's modulus for silica, which is about 70 000 MPa [8], extrapolated to 100% filler concentration. But, for the unfilled resin, the methods used yield different results, for which the slope (b) decreases with increasing frequencies. However, this impression could not be demonstrated statistically, as can be seen from Table IV, since all the *CI*s of the coefficients b for the five frequencies clearly overlap. This is due, of course, to the large standard deviations s_b for the STAT and the DMTA methods, between 0.44 and 0.60, as compared

TABLE II Dynamic Young's moduli under flexure (in MPa) for the different methods and volume percentage of inorganic filler (VFC) of dental composites [1]

Product	VFC (%)	STAT (MPa)	DMTA (MPa)			FPT (MPa)	
		0 Hz	0.1 Hz	1 Hz	10 Hz	2 kHz–4 kHz	4 kHz
		Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	Mean ± S.D.	
P-10	69.1	13 997 ± 848	14 125 ± 326	14 791 ± 410	15 488 ± 418	25 117 ± 429	25 706
Occlusin	69.0	16 532 ± 503	12 886 ± 218	13 808 ± 211	14 458 ± 180	23 774 ± 225	23 605
P-30	69.6	16 396 ± 427	13 647 ± 112	14 458 ± 130	15 140 ± 112	23 385 ± 223	24 110
Adaptic	58.4	12 697 ± 336	12 883 ± 537	13 490 ± 676	14 125 ± 568	21 412 ± 230	20 170
Miradapt	63.2	12 666 ± 729	12 023 ± 168	12 589 ± 121	13 183 ± 120	20 320 ± 196	19 281
Estilux posterior	58.1	9 856 ± 492	9 705 ± 148	10 000 ± 132	11 482 ± 143	17 408 ± 476	18 057
Brilliant	53.9	9 951 ± 645	10 233 ± 403	10 715 ± 437	11 220 ± 461	16 586 ± 276	15 498
Biogloss	51.9	9 017 ± 604	9 205 ± 208	9 795 ± 187	10 233 ± 197	15 190 ± 385	14 483
Brilliant Lux	49.8	8 544 ± 244	6 824 ± 109	7 719 ± 56	8 541 ± 77	14 451 ± 176	14 322
Heliomolar	49.1	6 415 ± 284	5 445 ± 229	6 061 ± 276	6 631 ± 301	10 612 ± 240	10 641
Answer	39.7	5 718 ± 323	3 119 ± 182	4 436 ± 193	4 775 ± 208	9 932 ± 275	10 281
Isomolar	45.3	3 912 ± 339	4 677 ± 114	5 333 ± 129	5 984 ± 126	9 619 ± 307	10 120
Silux	36.3	5 912 ± 247	5 140 ± 177	5 534 ± 214	5 916 ± 242	9 382 ± 155	9 066
Silar	35.4	5 565 ± 228	5 848 ± 43	6 194 ± 40	6 501 ± 49	9 075 ± 167	8 447
Durafill	37.5	2 877 ± 196	2 825 ± 162	3 289 ± 119	3 837 ± 113	6 085 ± 88	6 664

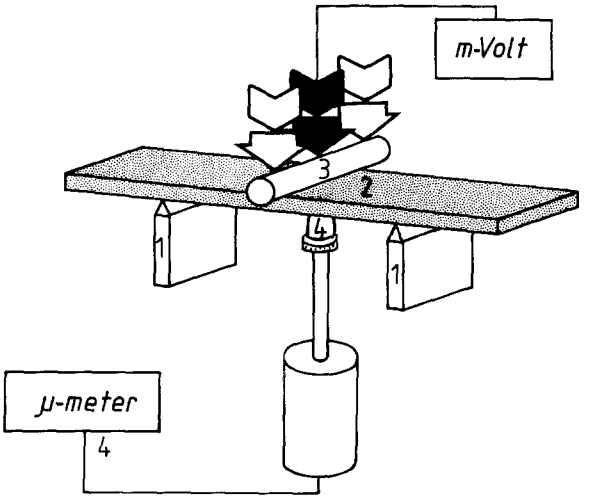

Figure 3 Schematic presentation of the static test (STAT) used: (1) supports; (2) rectangular sample; (3) metal rod transmitting the load; (4) digital gauge and micrometer recording the bending of the composite sample.

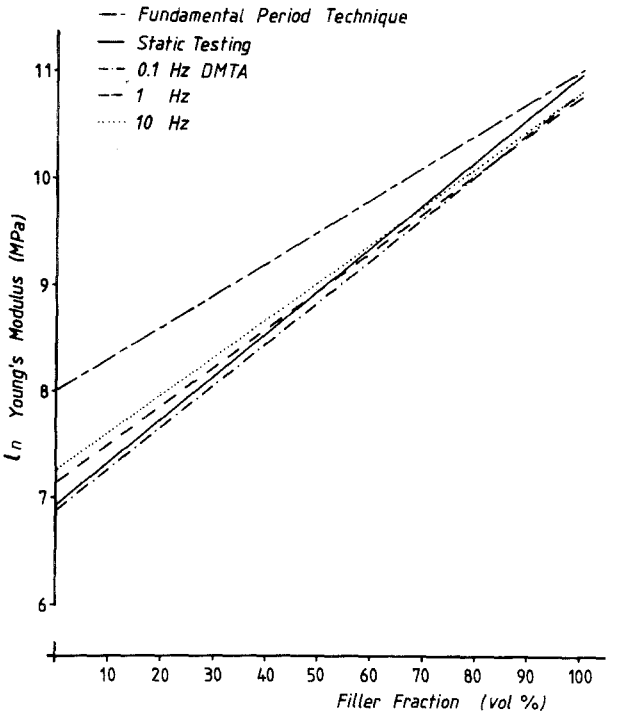

Figure 4 Regression analysis for the three methods for five frequency ranges. The volumetric filler fraction is given on the abscissa; the natural logarithm of the Young's modulus in MPa is given on the ordinate.

to the standard deviation s_b of 0.14 for the FPT method. This large difference is a direct consequence of the smaller numbers used in the present investigation. One may suppose that an increase in the number of samples in both the STAT and the DMTA could well lead to statistically significant differences. Strong support for such an hypothesis is given in Table V where the *CI*s of the coefficients b have been calculated with the same standard deviation s_b of 0.14 as obtained from the FPT method with 57 composites. The overlap between *CI*s then disappears except for a very small interval of 0.05 between FPT and DMTA at 10 Hz. This approximation does indeed indicate that the coefficients b decrease with increasing frequencies.

The results shown in Fig. 4 are in agreement with the interpretation of the physical processes involved. Pure silica behaves like an elastic amorphous material, so one would expect Young's modulus to be independent of frequency, at least in the investigated range. Resin, however, is a visco-elastic material that exhibits relaxation processes. With some simplification, relaxation phenomena are described by the product of the frequency f times the relaxation time τ, where τ is an exponential function of the inverse of the temperature. Therefore, at lower temperatures, i.e., at higher frequencies, relaxation effects are frozen out, so there is less strain for the same stress and hence a higher Young's modulus. At lower temperatures the material also becomes stiffer, which also augments Young's modulus. In between a pure resin and silica, the logarithm of the Young's modulus of a composite is a linear combination of the logarithm of the moduli of the phases [1, 2].

From Fig. 4 and the results in Tables III and IV, it is obvious that Equation 2 is, in fact, a function of frequency f as follows

$$\hat{E}(f, x) = \hat{E}_r(f) \exp [b(f)x] \quad (3)$$

where $b = \ln \hat{E}_s - \ln \hat{E}_r(f)$, and $\hat{E}_s$ the constant value of Young's modulus for pure silica. This means that the Young's moduli of the different composites for two different frequencies f_1 and f_2 are related by a simple power law:

$$\hat{E}_1 = C \hat{E}_2^d \quad (4)$$

where subscripts 1 and 2 refer to the two frequencies, and

$$C = \frac{\hat{E}_{r1}}{\hat{E}_{r2}^d} \quad (5)$$

with

$$d = \frac{b_1}{b_2} \quad (6)$$

However, in applying these formulae one must take into account the *CI*s for the different coefficients b and

TABLE III Values of $\hat{E}_r$ and $\ln \hat{E}_r$ with 95% *CI*s for the different frequencies. N stands for degrees of freedom

Method		N	$\ln \hat{E}_r$	$CI(\ln \hat{E}_r)$	$\hat{E}_r$ (MPa)	$CI(\hat{E}_r)$ (MPa)
STAT	0 Hz	13	6.93	(6.30, 7.57)	1027	(545, 1934)
DMTA	0.1 Hz	13	6.88	(6.19, 7.57)	975	(490, 1939)
	1.0 Hz	13	7.14	(6.58, 7.71)	1266	(722, 2221)
	10.0 Hz	13	7.29	(6.78, 7.79)	1459	(879, 2420)
FPT		55	8.04	(7.90, 8.14)	3103	(2692, 3572)

TABLE IV Values of coefficient b with corresponding standard deviations (s_b) and 95% *CI*s for the five different frequencies. N stands for the degrees of freedom

Method		N	b	s_b	CI(b)
STAT	0 Hz	13	4.03	0.55	(2.85, 5.22)
DMTA	0.1 Hz	13	3.93	0.60	(2.65, 5.22)
	1.0 Hz	13	3.61	0.49	(2.56, 4.66)
	10.0 Hz	13	3.48	0.44	(2.53, 4.43)
FPT		55	2.97	0.14	(2.69, 3.25)

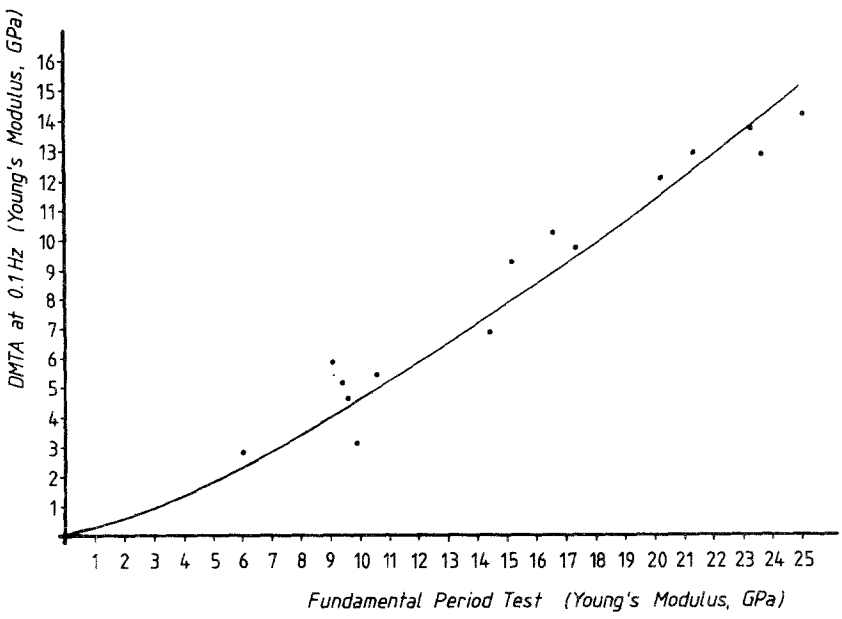

Figure 5 Results obtained with the DMTA at 0.1 Hz against those obtained with the FPT.

Young's moduli $\hat{E}_r$. For example, comparing the results of the STAT at 0 Hz (subscript 1) and DMTA at 10 Hz (subscript 2), one finds from Table IV that the *CI*s of the coefficients b overlap in the same way as the *CI*s of $\hat{E}_r$. This is even more pronounced in Table V. This means that d equals 1 and C equals 1 within statistical significance, so that $\hat{E}_1$ equals $\hat{E}_2$. Even a better case is made in comparing the results of the FPT at resonance frequencies with the DMTA at 0.1 Hz. From the results of Tables III and IV one finds that $C = 16.60$ and $d = 0.76$. Furthermore, a linear regression analysis of the logarithm of Equation 4, i.e.,

$$\ln \hat{E}_1 = \ln C + d \ln E_2 \quad (7)$$

where E_1 and E_2 are the Young's moduli, respectively, at resonance frequency and at 0.1 Hz (Table II), yields $C = 13.90$ and $d = 0.78$. Their 95% *CI*s are (3.81, 50.66) and (0.63, 0.92), which shows that the predicted values $C = 16.60$ and $d = 0.76$ are corroborated by the statistical analysis. Furthermore, the *CI* of d (0.63, 0.92) excludes ($p < 0.05$) the value 1 ($b_1 = b_2$), which would have yielded a linear dependence of the Young's moduli at the resonance frequency and at 0.1 Hz. This deviation from linearity is shown in Fig. 5.

4. Conclusions

The above discussion leads to the following important conclusions for the frequency range between 0 and about 7000 Hz, which is the resonance frequency for the silica:

The Young's modulus of elasticity at all frequencies follows the same exponential law as a function of the filler fraction (Equation 3).

Because the Young's modulus of pure silica remains constant between 0 and 7000 Hz, it suffices to know the frequency dependence of the resin component to predict the Young's modulus of any particulate filled isotropic composite.

TABLE V Values of coefficient b with corresponding standard deviations (s_b) and 95% *CI*s for the FPT results. N stands for the degrees of freedom

Method		N	b	s_b	*CI*(b)
STAT	0 Hz	55	4.03	0.14	(3.75, 4.31)
DMTA	0.1 Hz	55	3.93	0.14	(3.65, 4.21)
	1.0 Hz	55	3.61	0.14	(3.33, 3.89)
	10.0 Hz	55	3.48	0.14	(3.20, 3.76)
FPT		55	2.97	0.14	(2.69, 3.25)

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