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Theoretical prediction of dental composites yield stress and flexural modulus based on filler volume ratio

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Abstract

Objective: A costly advantageous approach in composites development process is to limit experimental tests by predicting mechanical properties with respect to their filler ratio. Models exist for other fields than dentistry. They have been compared to 3-point bending test experimental results for yield stress, flexural modulus and flexural strength.

Methods: Five formulations of the same experimental material were made. They were composed of an organic matrix and different ratios of silanated barium glass particles. The samples were stored in distilled water for 24h at 37°C prior to the 3-point bending test. The Turcsányi model for yield stress was notably investigated, and SEM was used to complete data analysis.

Results: The yield stress showed reproducible results and a good fit with Turcsányi model with respect to filler ratio. The flexural modulus data are not scattered but did not fit with the existing models. No trend could emerge for flexural strength and strain because of scattering; these properties are more unpredictable. The SEM observations of fracture areas confirm a good matrix-filler interface quality.

Significance: SEM pictures validated the numerical parameter obtained from Turcsányi model. The latter therefore seems to be applicable to dental composites. Firstly, it enables to predict the evolution of the material yield stress without testing all filler ratios. Secondly, this model provides a good way to get micro-information on the matrix-filler interface from macroscopic tests. The discrepancy between flexural modulus results and theory highlighted the necessity to include an “interface quality” parameter in accurate predictive models.

Theoretical prediction of dental composites yield stress and flexural modulus based on filler volume ratio.

1) Introduction

Defining the ideal filler fraction of a composite resin is an important step in the development of a dental material. The proportion of fillers into the matrix has indeed an impact on many mechanical properties, but few of them give data that are both trustable and relevant to study. Flexural strength and elastic modulus are part of them. Indeed, they describe well the mainly elastic behaviour of dental composites. These properties are very frequently studied as they are easy to identify with the common 3-point bending test. The elastic modulus predicts the material response to reasonable external load, through a linear stress-strain relationship. A high modulus means that the material is rigid enough to maintain its shape when loaded. It characterizes the first part of a stress-strain curve. However, according to Ferracane and Heintze [1, 2], this property is not well correlated to the clinical performance of composites. On the other hand, flexural strength corresponds to the maximum stress that a material can withstand before failure. This property is well correlated to clinical wear but does not provide information on the behaviour of the composite before failure. The two properties are thus complementary.

On the contrary, the yield stress is rarely studied whereas it completes the description of the behaviour between its elastic part and its failure. The yield stress corresponds to the stress beyond which plastic deformation occurs. For organic dental composites, molecular chains of the matrix are extended to an irreversible state and the material undergoes permanent plastic deformation. Small cracks can also appear at the interfaces between the matrix and the fillers. While only low impacts (like normal chewing) put a strain on a dental restoration, its shape and properties remain the same over time (wear and aging considerations being neglected). But if the yield point is exceeded once, residual deformation and internal stresses remain when the external stresses disappear. They modify the behaviour of the composite and are likely to shorten the life expectancy of the restoration. Thus, the yield stress is intuitively an important property to study, as a high yield stress is advantageous to enhance the stability of material's behaviour over time.

In order to speed up the composite development process, theoretical models would allow decreasing the number of experimental tests by predicting the mechanical properties of interest. It is therefore important to understand the evolution of these three main mechanical properties with respect to the filler fraction. For dental composites, several studies [3-8] report that the flexural modulus increases exponentially with the filler fraction, whereas flexural strength shows a maximum around 60 % of fillers in the total volume of a material. No study was found to evaluate the yield stress. No theoretical model to estimate any of these properties either. In any case, the results depend on many parameters, such as the nature and the characteristics of the fillers (shape, size, surface treatment), the nature of the matrix and the quality of their interface. The complexity of their respective influences makes the development of a predictive model a tough issue.

Outside of the dental field, Turcsányi introduced a simple equation providing the tensile yield stress of various composites. His model is interesting as it only takes into account the filler volume ratio, the yield stress of the matrix and the quality of the interface between the matrix and the fillers [9]. As far as we know and despite its apparent universality, this model has very rarely been applied to dental composites. It was misused when mentions were found [10, 11]. In both cases, test conditions were different from those used by Turcsányi and the transposability of the model had not been demonstrated. Otherwise no mention of the model was found for dental materials.

Still outside of the dental field, different models have been proposed to evaluate the flexural modulus. But they are complex and all have limitations, especially for high-filled composites [12]. For flexural strength and flexural strain, models are very rare. Indeed, experimental tests on dental composites are quite specific. On the one hand, they reach high filler ratio such as 60 vol% (60% by volume) and 80 wt% (80% by weight). On the other hand, the 3-point bending test has become the gold standard test for measuring the mechanical properties of dental composites, whereas theoretical models have been mostly developed for tensile test. In this study, we will thus focus on the 3-point bending test, which is easier to perform and less sensitive to the quality of both the device and the sample (compared to compressive or fracture toughness test, for instance) [13]. The aim of this study is therefore to challenge the accuracy of theoretical models when they are applied to dental composites and 3-point bending test.

For this purpose, even if dental composites hold a high proportion of fillers, the validation of predictive models requires a wide range of filler ratios for the same composite. Even unfilled samples are important for determining the properties of the matrix, although they do not have direct clinical application. Ideally, if models fit, testing low-filled samples during the development process would be sufficient to properly estimate the properties of real dental composites, without producing expensive high-filled samples. Otherwise, still with the objective of limiting experimental tests, the applicability range of theoretical models is important in order to develop numerical models. Simulations based on relatively simple models would be of great help in the development of dental composites. The long-term objective of this study is to play a part in the development of such numerical processes.

Flexural modulus, flexural strength and yield stress will be measured on an experimental dental composite for different filler ratios, with the 3-point bending test. Comparisons between experimental results and pre-selected theoretical models will lead to discussions on their potential, their range of applicability and the link between macroscopic and microscopic behaviour.

2) Materials and Methods

2.1) Materials

The composite resin, unfilled resin and fillers were supplied by DMG Chemisch-Pharmazeutische Fabrik (*Hamburg, Germany*). It is an experimental material. The matrix is composed of 2,2-bis(4-(2-hydroxy-3-methacryloxypropoxy)phenyl)propane (bis-GMA, 40.3wt% of the matrix), triethylene glycol dimethacrylate (TEGDMA, 19.9wt%), urethane dimethacrylate (UDMA, 19.9 wt%) and ethoxylated bisphenol A dimethacrylate (EBPADMA, 19.9 wt%). Starters (campherchinon, 2,4,6-Trimethylbenzodiphenylphosphine oxide) and stabilizers are embedded in the matrix. The fillers are mostly random-shape silanated barium glass particles (98.6 wt% of the fillers) with an average particle size of 7 μm . Pyrogenic silica particles are also used (1.4 wt%) with an average particle size of 0.04 μm .

Five materials were made from the matrix and fillers described above, with different filler weight fractions: 0 wt% (no filler), 20 wt%, 40 wt%, 60 wt% and 80 wt%. They correspond respectively to 0 vol%, 9 vol%, 21 vol%, 37 vol% and 61 vol% filler volume fractions. The 80 wt%-batch was directly produced by DMG whereas the 20 wt%-, 40 wt%- and 60 wt%- batches were mixed from the pure matrix and the fillers by the Laboratory of Multimaterials and Interfaces (*Lyon, France*). The mixture is made using a double centrifuge during 4 minutes at 35 000 rpm. The resins have been since stored between 4 °C and 6 °C, without exposure to any light. Two series of samples were made, which differ in their storage time in the state of uncured resin: 3 or 4 months. They are named batches T3 and T4, respectively. In the first batch, the 20 wt% ratio was not considered.

2.2) Sample preparation

The samples were prepared in a 25x2x2 mm³ Teflon mould, in a darkroom. A glass slide was put on top for the light-curing. Two thin Mylar sheets were placed beforehand at the top and bottom of the mould to facilitate the handling and the unmoulding. Mylar sheet is well known to improve surface quality [14]. It also modifies the mechanical properties of the surface, probably by limiting the Oxygen Inhibited Layer (OIL). The curing was activated by blue-light with a polymerizing lamp (*DeepCureParadigm^{MC}*, 3M ESPE, Saint-Paul, USA). The wavelength of the light was between 430 and 480 nm, with a peak between 444 nm and 452 nm where the light intensity was 1470 mW/cm². The samples were exposed to the light through five 1cm-diameter holes whose device is pictured in *Figure 1*. The holes overlap by 5 mm. The resin was exposed for 20 s from each hole, starting by the centre of the sample. The sample was then unmoulded and the same protocol was used to expose the sample from the bottom. At the end of the process, each part of the sample was thus exposed to the same quantity of light (40 s on each side). With this methodology, the sample is slightly overcured compared to the manufacturer's recommendations. The aim is to minimise the curing gradient along the sample's depth to ensure the most homogeneous material possible. To complete the polymerization, the samples were stored for 24 h in distilled water at 37 °C. The water was then cooled down to room temperature during a few minutes. Then the samples were removed from the bath just before the bending tests. Between three and seven samples of each batch were tested. No polishing was performed before the tests.

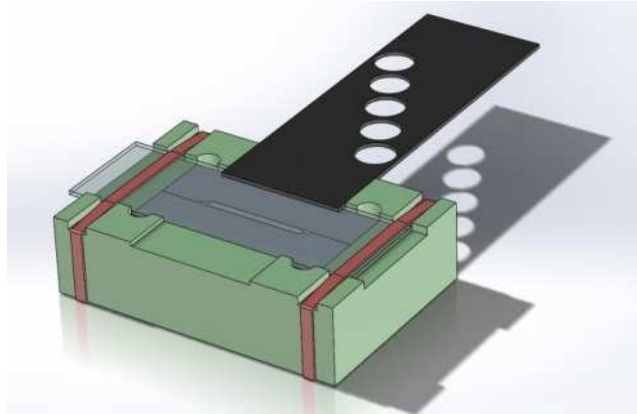


Figure 1: CAD image of the mould used to prepare the samples. Teflon is in green and grey, with transparent glass on top. The exposure mask is in black and elastic bands in red.

2.3) Bending test

The 3-point bending tests were performed with a ZwickRoellProLinestatic machine (*BZ 2,5/THIS, Ulm, Germany*) according to the recommendations of ISO 4049 [15] (*Figure 2*). The two cylindrical supports are spaced 20 mm apart. The cross-head speed is 0.75mm/min. The side of the sample which was exposed first to the polymerizing lamp was always placed on top of the device. The experiments were carried out in a room whose temperature was maintained at 23.5±0.5 °C. Relative humidity was not controlled.

Strain and stress vary along the sample and are maximal under the loading rod, at the centre of the sample on the tensile-stressed surface. According to the beam theory and for rectangular cross-section, the maximal stress σ is calculated as follows:

$$\sigma = \frac{3FL}{2bh^2} \quad (1)$$

Where F is the applied load, L the distance between the supports, b the width of the sample and h its thickness. The beam theory also allows calculating the strain at any point of the sample:

$$\varepsilon(x, z) = z \frac{d\theta}{dx} \quad (2)$$

Where θ is the angle between the vertical axis and an axis perpendicular to the lower surface of the sample. The maximum strain is:

$$\varepsilon = \frac{6Dh}{L^2} \quad (3)$$

Where D is the maximum deflection of the centre of the beam. Flexural modulus corresponds to the slope of the linear part of the stress-strain curve, which corresponds to the purely elastic behaviour. It is calculated in this area as follows:

$$E = \frac{L^3}{4bh^3} \left(\frac{dF}{dD} \right)_{(el)} \quad (4)$$

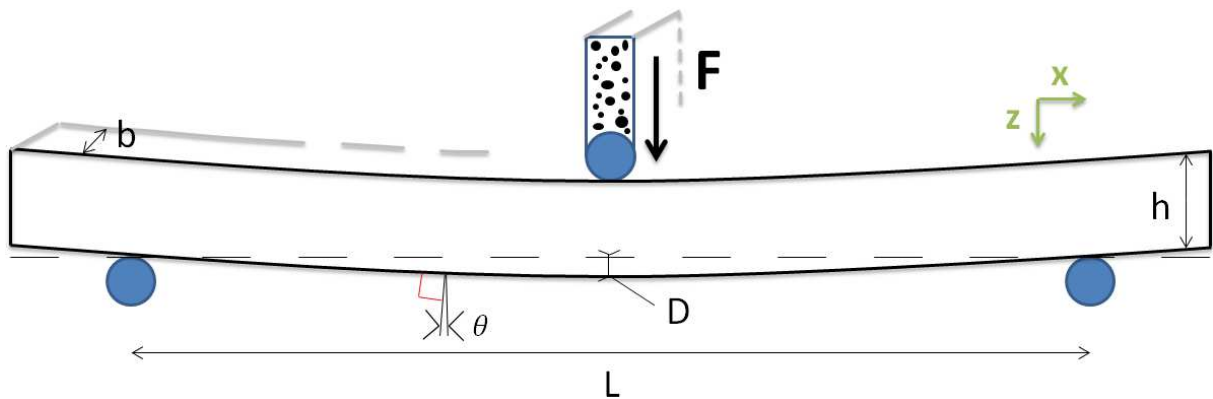


Figure 2 : Drawing of the configuration of the 3-point bending test. Speckles are spray-painted on the loading rod.

Since it is difficult to precisely point out the yield stress of the composite (σ_{yc}), this parameter is calculated by the classic 0.2 %-strain criterion, as shown in Figure 3. The 80 wt% samples need to be distinguished. They indeed break before reaching the yield stress. Therefore, for this ratio, the yield stress was taken equal to the flexural strength, as indicated in the conventional definition of the yield stress.

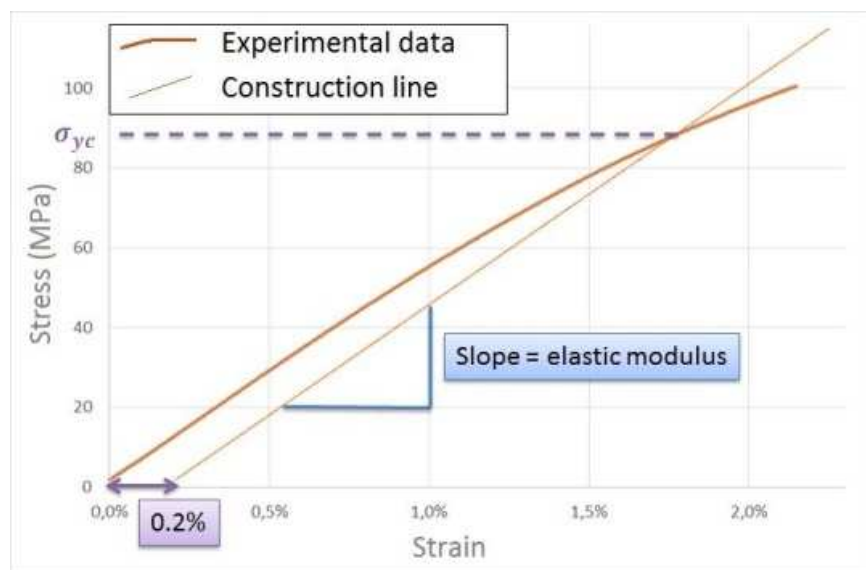


Figure 3: Yield stress determination on a classic bending stress-strain curve for a 60 wt% composite

2.4) Deflection measurements

A Digital Image Correlation (DIC) device was used. Two cameras filmed both the sample and the loading rod over the tests. The correlation was made thanks to spray-painted speckles on the loading rod. The speckles were not painted on the samples because their dimensions were too small, but the displacement of the rod is equal to the beam deflection as they are in direct contact. The movements which were measured by the cameras were calibrated with pictures of a standard speckles grid. In order to control the validity of the method, the displacements measured with DIC were also compared to those of the ZwickRoell machine. For every sample and stiffness, data appeared to be the same and all the more trustable.

2.5) Failure of the sample

During a bending test, the sample undergoes compressive stress upward its neutral axis and tensile stress below. In addition, dental composites can withstand higher loads in compression than in tension. Therefore the crack that ruins the sample starts from the centre of the tensile-stressed surface, where the stress is the highest [10]. The tests were performed until the samples broke.

Before the crack initiation, this area reaches plasticity first. So, locally, it can be considered that the area of the sample which determines the change in the behaviour of the material is subjected to a tensile test. Therefore, the Turcsányi model used for tensile test should be suitable for bending test too.

Samples were then observed with a Philips XL30 (*Semtech Solutions, Billerica, Massachusetts, USA*) environmental Scanning Electron Microscope (SEM) Philips XL30. They were not metallized before the observations.

2.6) The Turcsányi Model for yield stress

An interesting approach was used by Turcsányi [9] to predict the yield stress of composite materials with respect to their filler ratios. His model is worthy of interest because its equation only depends on the filler ratio, the yield stress of the matrix and the quality of the interface between the matrix and the fillers. It is notably independent from the nature and morphology of the fillers [9, 16]. This model was assessed for 25 different composites, but its accuracy has never been proven for dental composite materials that are much more filled.

This model was developed for tensile tests. For a composite, it is necessary to distinguish the apparent stress in the sample and the real stress withstood by the matrix: σ_m . In the worst-case scenario, where there is no adhesion between the fillers and the matrix, the matrix supports all the load and σ_m is written, for a given section and at any time:

$$\sigma_m(F, section) = \frac{F}{S_m} \quad (5)$$

Where F is the applied load and S_m is the matrix area of the section. The yield stress of the composite (σ_{yc}) is reached when the yield stress of the matrix (σ_{ym}) is reached in one random section. This occurs for the section with the highest filler ratio:

$$\sigma_{yc} = \text{Min}(\sigma_{yc}(section))_{\{sections\}} = \sigma_{ym} * (1 - \psi_{max}) \quad (6)$$

Where ψ is the filler ratio of a section, and ψ_{max} is the maximum value among all the sections of a sample. ψ_{max} can be evaluated by a probabilistic approach with respect to the filler volume fraction φ . Turcsányi chose a hyperbolic model that does not present any inconsistency for extreme values of φ . The yield stress of the composite is obtained by:

$$\sigma_{yc} = \frac{1 - \varphi}{1 + 2.5\varphi} \sigma_{ym} \quad (7)$$

However, this formula is only valid when there is no bonding between the matrix and the fillers. But a part of the load is actually transferred to the fillers through their common interface. A cohesive zone exists around the fillers, whose yield stress differs from σ_{ym} . Therefore, this parameter cannot be used as it is in (7). To estimate the relation between the substitute of σ_{ym} and φ , Turcsányi used 25 studies, from both its experiments and literature, in which the yield stress of various composites was measured with respect to the filler volume fraction. A simple exponential law was proposed to link these two data to a parameter B and to the yield stress of a pure matrix sample σ_{y0} , with an accuracy of 98 %. According to Turcsányi, this parameter B does not depend on the shape of the fillers, nor their size, composition, or composition of the matrix. It only distinguishes the nature of the interface between the matrix and the fillers [8]. Low values of B (< 3) correspond to weak interfaces, whereas strong interfaces reach values from 3 to 6 [12, 14]. Finally, the yield stress of the composite can be estimated by:

$$\frac{\sigma_{yc}}{\sigma_{y0}} = \frac{1 - \varphi}{1 + 2.5\varphi} \exp(B\varphi) \quad (8)$$

Several limitations exist for this model, which need to be challenged. Firstly, this model was not developed with dental materials. Saen [10] used this empiric law without justifying its applicability, and no other mention was found for dental materials. Secondly, the filler ratios of Turcsányi's studies ranged from 0 to 40 vol%. The match with the model has to be checked for higher filler ratios that are more appropriate for dental materials. This is why this study is going to test a wide range of ratios for a dental composite, from a pure matrix to a common 80 wt% ratio used in commercial resins. Finally, this formula was established on the basis of tensile tests, whereas dental composites are usually characterized using 3-point bending tests, as mentioned in section 2.3.

2.7) Elastic modulus models

Over the past century, several authors proposed models to predict the elastic modulus of composites filled with particles [12, 17, 18]. The models are based either on the theory of elasticity, on derivatives from the homogenization theory or on experimental data. The formulae are detailed in the annex.

These models have not been checked either for dental composites. In particular, their application field is limited to filler ratios lower than 20 vol%. When more fillers are introduced, these models tend to deviate from experimental data [12]. They will be compared to our experimental data too.

3) Results

3.1) General behaviour

For batch T3, the stress-strain curves of the most deformed sample for each filler ratio are plotted on the same *Figure 4*. The influence of filler ratio on the behaviour is well depicted. Adding fillers stiffens the material, whereas a less-filled sample can deform more. It is noteworthy that when the maximal strain exceeds a certain point, the sample is too deformed to ensure that all the assumptions of the beam theory are met. The exact threshold value is difficult to estimate but it could be around 5 % visually. Therefore, the data are more approximate at the end of the curves for low-filled composites. It can modify the flexural strength and the maximal strain of the test. However, the yield stress and flexural modulus values are not affected as they are calculated at low strain.

Figure 4 shows that the stress-strain curves are not linear until the sample breaks. Viscous and/or plastic components are added to the early purely elastic behaviour. This effect is more visible when the filler ratio is low.

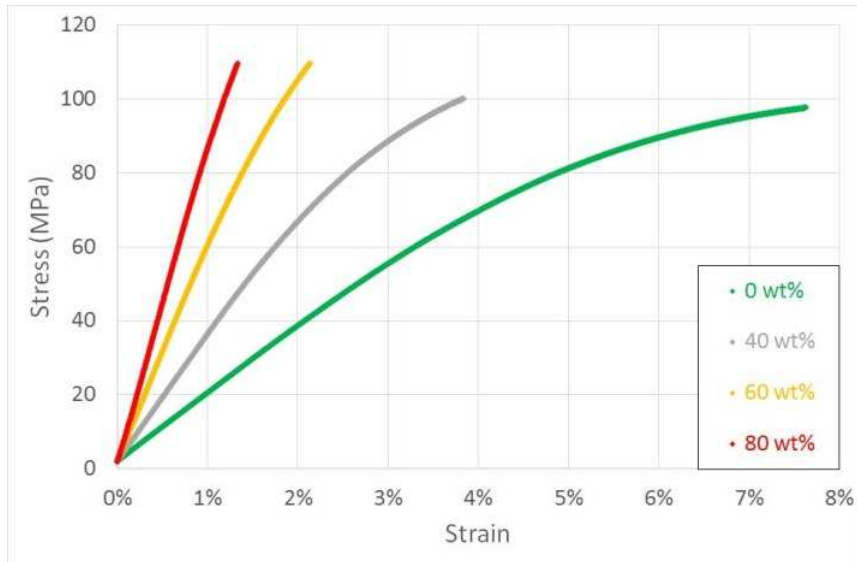


Figure 4: Stress-strain curves of the most strained samples of each ratio for batch C

3.2) Yield stress

The mechanical properties measured from the bending tests are summarized in *Table 1*. The yield stress of the batch T3 increased from 59.70 MPa for the unfilled resin to 100.48 MPa (+68%) for the 80 wt%-samples. For batch T4, it increased from 70.12 MPa for the unfilled resin to 107.20 MPa (+53%) for the 80 wt%-samples.

Duration of storage	Batch	Mass filler ratio	Volume filler ratio	Yield stress (Mpa)	Flexural modulus (Gpa)	Flexural strength (Mpa)	Maximal strain
3 months (batch C)	C ₀	0 %	0 %	59.70 ± 2.68	1.74 ± 0.11	80.22 ± 17.28	6.14 ± 2.30
	C ₄₀	40 %	21 %	66.61 ± 6.45	3.44 ± 0.10	95.80 ± 10.07	3.34 ± 0.40
	C ₆₀	60 %	37 %	96.12 ± 5.05	5.72 ± 0.31	81.70 ± 19.16	1.56 ± 0.46
	C ₈₀	80 %	61 %	100.48 ± 8.49	8.74 ± 0.23	100.48 ± 8.49	1.23 ± 0.11
4 months (batch D)	D ₀	0 %	0 %	70.12 ± 1.78	2.46 ± 0.11	78.78 ± 13.23	3.31 ± 0.62
	D ₂₀	20 %	9 %	78.99 ± 0.80	3.25 ± 0.11	98.50 ± 13.65	3.62 ± 0.87
	D ₄₀	40 %	21 %	85.22 ± 1.58	4.21 ± 0.20	103.53 ± 15.70	2.91 ± 0.45
	D ₆₀	60 %	37 %	99.16 ± 3.84	6.35 ± 0.14	116.18 ± 9.38	2.22 ± 0.20
	D ₈₀	80 %	61 %	107.20 ± 10.23	12.34 ± 0.28	107.20 ± 10.23	0.94 ± 0.13

Table 1 : Mechanical properties of resin composites measured by 3-point bending test

The Turcsányi model exhibited a good fit with the yield stress. In order to determine the B value of the Turcsányi model, the evolution of the yield stress for every filler volume ratio ($Re(X\%)$ on the figures) over the yield stress of the matrix ($Re(0\%)$) was plotted with respect to the filler volume ratio. The fit of the experimental data is shown in *Figure 5*. B was estimated at 3.98 ($R^2 = 0.88$) for batch T3 and 3.82 ($R^2 = 0.97$) for batch T4. Since the model of Turcsányi has never been validated for volume ratios higher than 40 vol%, a second evaluation of parameter B was carried out taking into account only the filler volume ratios lower than 40 %. For T3 and T4 batches, B is equal to 4.20 ($R^2 = 0.92$) and 3.98 ($R = 0.95$), respectively.

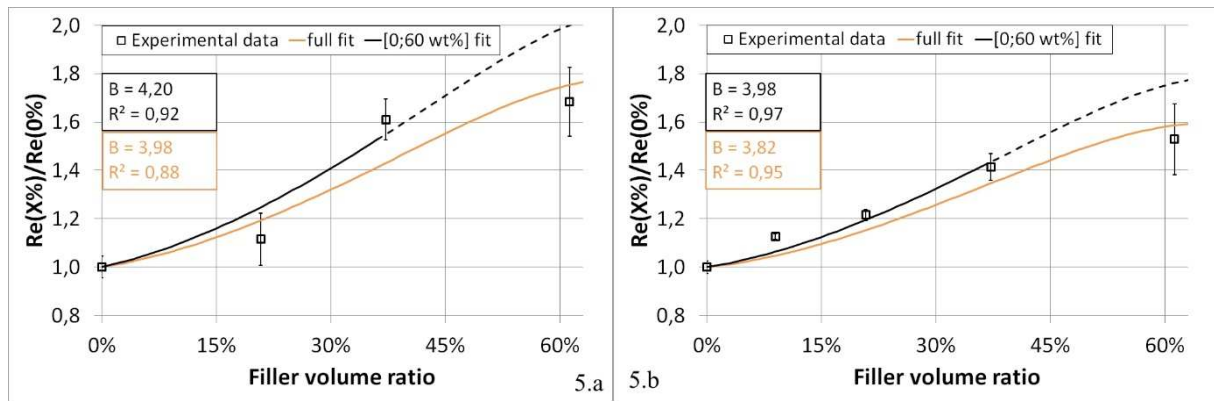


Figure 5 : Evolution of the yield stress of composite resins with respect to their filler volume fraction for batch T3 (5.a) and batch T4 (5.b)

3.3) Elastic modulus

The evolution of the flexural modulus with respect to the filler ratio is presented in *Figure 6*. It increased from 1.74 Gpa to 8.74 Gpa (+ 402%) for batch T3. For batch T4, it followed an increasing trend too, from 2.46 Gpa for the unfilled resin to 12.34 Gpa (+ 402% too) for the 80 wt%-samples. The two batches have the same ratio of about 5 between the 80 wt%-samples and the unfilled resin. It is also noteworthy that the increase between the 80 wt%-samples and the 60 wt%-samples was much higher than for the yield stress. Indeed the flexural modulus increased by nearly 100 % whereas the yield stress increased by only 8 % between the two highest ratios.

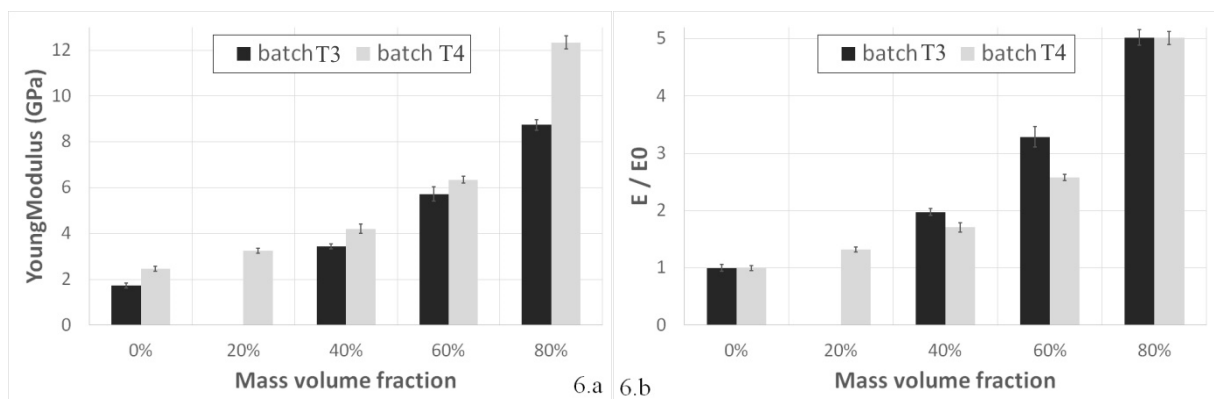


Figure 6 : Evolution of the flexural modulus (6.a) and the ratio E/E_0 (6.b) of DMG experimental composite with respect to the filler volume fraction

The consistency of the flexural modulus with the theoretical models presented in the annex was checked out in *Figure 7*. Except for Guth and Paul formulae, all the models underestimate the experimental value of flexural modulus. Paul's model seems to follow quite the same trend, but with an offset. The second model proposed by Bourkas fit relatively well even if the trend seems to increase more rapidly for high filler ratios. Other models are quite different with respect to experimental data. For all the models, the discrepancy between experimental and theoretical data is visible as soon as the filler fraction exceeds 20 vol%.

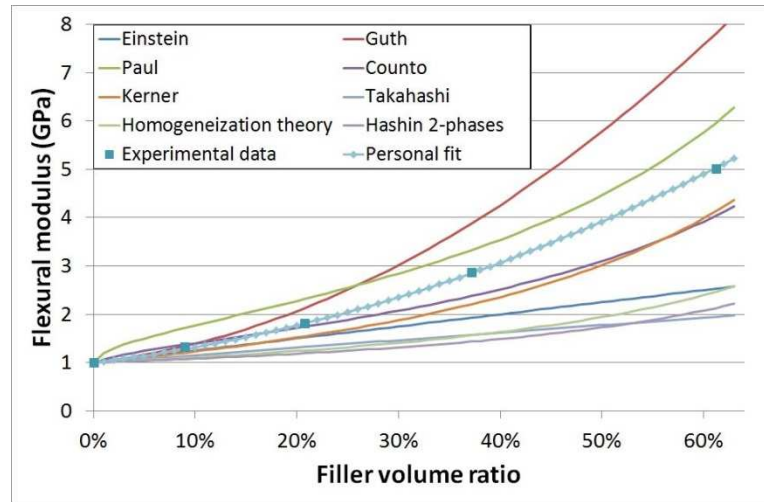


Figure 7: Comparison between the experimental data of flexural modulus and the common theoretical models for composites filled with particles

Considering these differences, another personal model was proposed on the basis of Einstein formula (Eq. 10) and Guth formula (Eq. 11). The only variable is the numerical term before φ^2 . It was optimised by the least squares method. Its value was estimated to 6.7. The personal fit was finally done with the following model, with good match:

$$E_c = E_m(1 + 2.5\varphi + 6.7\varphi^2) \quad (9)$$

3.4) Flexural strength and maximal strain

The evolutions of flexural strength and maximal strain with respect to the filler ratio are shown in Figure 8. The flexural strength did not follow an apparent and reproducible trend as the data were very scattered. For batch T4, it showed a maximum of 116.18 MPa for the 60 wt%-samples, starting from 78.78 MPa for the unfilled resin, and decreasing to 107.2 MPa for the 80 wt%-samples. The properties are worse and quite stable for batch T3. The data are also more scattered: the standard deviation is greater than 10 % whereas it is about 2 % for the yield stress (except for the most filled batch) and 4 % for the flexural modulus.

Data scattering is encountered again for maximal strain. A decreasing trend shows that samples containing less fillers can deform more than high-filled materials. However, the relative evolution is not reproducible from one batch to another.

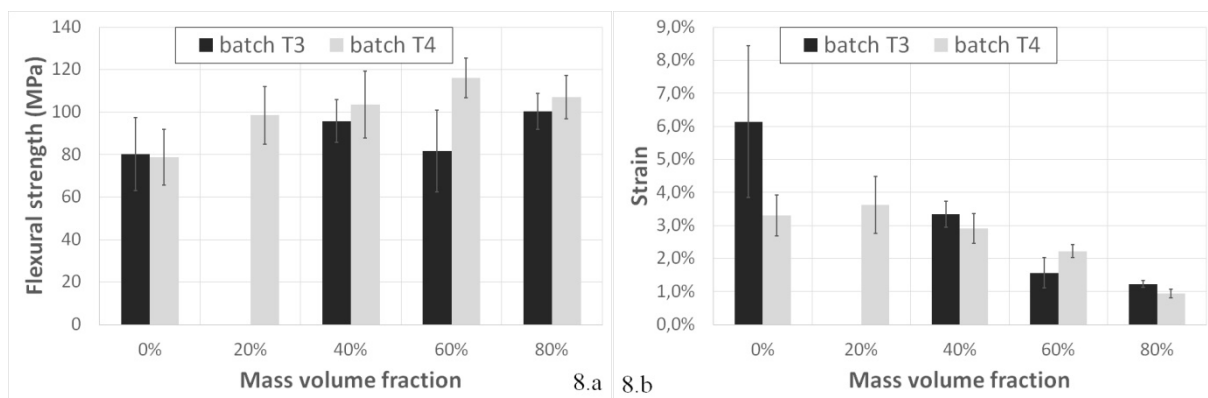


Figure 8: Evolution of the flexural strength (8.a) and the maximal strain (8.b) of DMG experimental composite with respect to the filler volume fraction

3.5) Samples failure and SEM observations

All the samples broke suddenly with an apparent brittle behaviour. This assumption was confirmed by the SEM observations of the fracture surfaces. Signs of fast fracture like crack planes and a rough surface [19] were noticed, especially for low-filled composites (Figure 9). A lot of uncovered particles are visible (Figures 9-12). The SEM pictures also validate that this material has a strong interface between the fillers and the matrix. Mirror configurations were indeed exhibited between the two parts of the broken samples: the same big particles were found on both sides of the fracture area (Figures 9-10). More rarely, negative prints corresponding to a debonding of the particle (Figure 9, Figure 11.b) are visible. These events were more difficult to observe for high-filled composites (60 wt% and especially 80 wt%) where few matrix was visible between the fillers (Figure 11, Figure 12.b). Finally, damaged barium glass particles are often visible and devoid of matrix (Figure 11.a, Figure 12).

It is noteworthy that the unfilled resin samples broke, in most cases, in three pieces instead of two for filled composites. In these conditions, the cracks propagated symmetrically with respect to the centre of the sample. They were located between 1 and 2 mm from the axis of the loading rod.

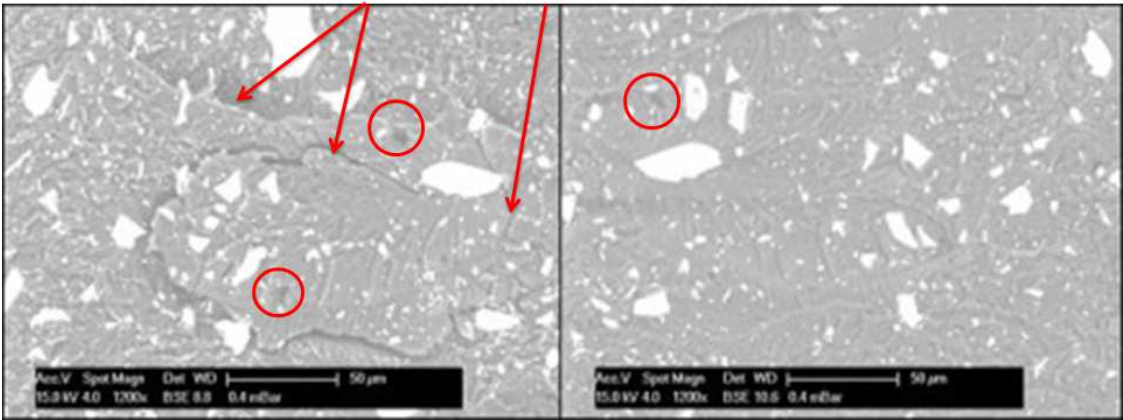


Figure 9: SEM pictures of a 20 wt% composite sample in a mirror configuration. A rough surface and few micrometers particles can be seen on both sides. Crack planes (arrows) and debondings (circles) are also visible

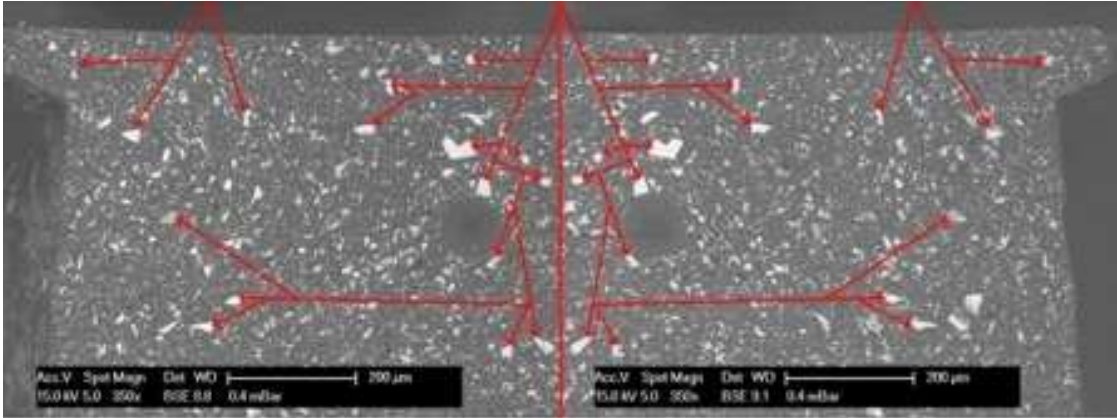


Figure 10: SEM pictures of 40 wt% composite on two opposite sides of the fracture area (mirror configuration) Some broken barium glass particles are highlighted by red arrows. A sample with an unusual big air bubble was chosen to facilitate the comparison

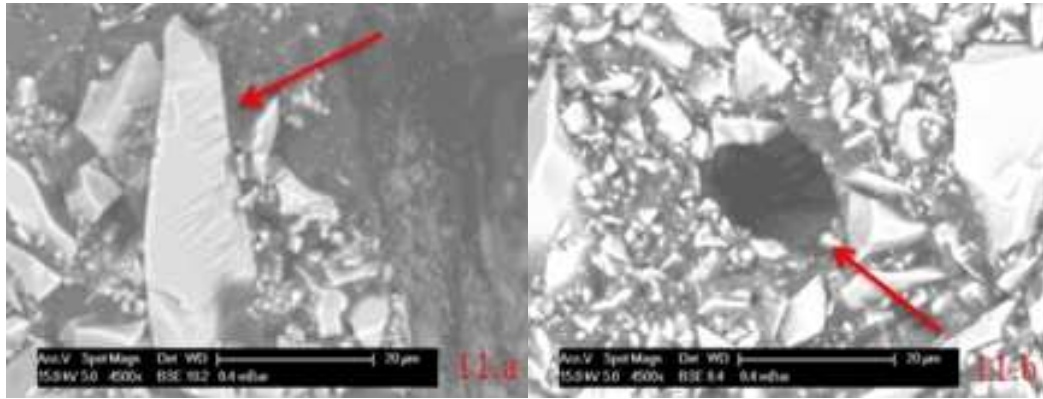


Figure 11: SEM observations of a (a) damaged barium glass particle and (b) a debonding print in a 80 wt% composite

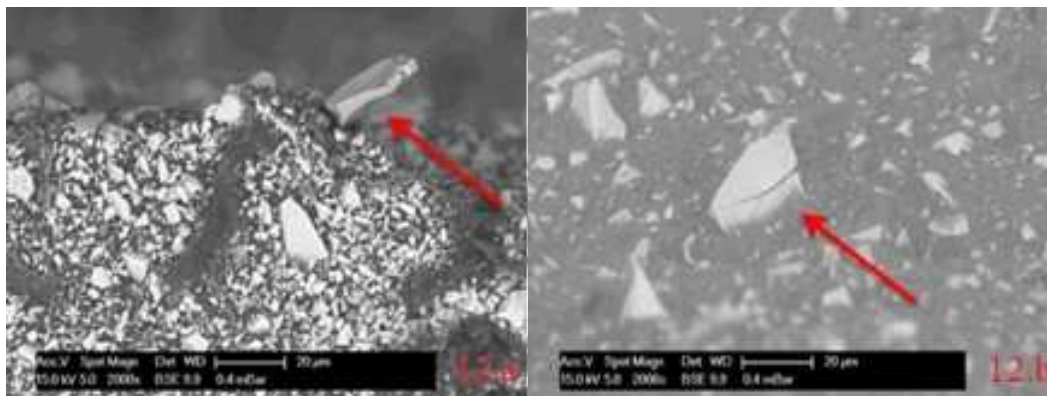


Figure 12: SEM observations of broken and uncovered barium glass particles for 80 wt% and 40 wt% composites, respectively

4) Discussion

The main output of this study is that both groups exhibited promising results with respect to the Turcsányi model. For each estimation, the parameter B corresponded to a good quality of interface. This was an expected result as the fillers were exposed to a classic silanisation treatment to enhance adhesion to the matrix. The fit with the model was good, considering the coefficients of determination between the experimental data and the model close or greater than 0.9. Therefore, the Turcsányi model seems to be applicable to the 3-point bending test on dental composite materials.

Despite the difficulty of associating the parameter B , representative of the interface quality, with a physical characteristic of the interface, the SEM pictures confirm that this material has a strong interface between the fillers and the matrix. Mirror configurations were exhibited between the two parts of the broken samples. The same big particles were found on both sides of the fracture area (Figures 6-7). This means that the crack propagated in a straight line. The high strength of particles-matrix silanized bonds makes it easier (less energy required) for the crack to pass through the barium glass particles rather than bypassing them. It is more difficult to find smaller particles broken on both sides of the fracture area. Indeed, the decrease in particle size also reduces the difference of energy between the two paths. At some point, the crack will preferentially propagate through the filler-matrix interface, or directly through the matrix. Few particles as small as $3\ \mu\text{m}$ could undoubtedly be observed as broken. Failure is more frequent for larger particles of about $10\ \mu\text{m}$ and above. This size limit is consistent with Belli's observations [19] who did not find cracked particles smaller than $10\ \mu\text{m}$ for commercial composites. Otherwise, the bigger the particles, the more likely they are to fail. Nevertheless, some big particles are also completely uncovered (Figure 11.a, Figure 12). For this debonding phenomenon, a weakness at some point of the interface might have enabled the bypassing path. In this case, the imprint of the particle could be observed on the opposite part of the sample.

Finally, it was rare to observe partially covered particles, which would have been the case if the matrix itself was weak. Therefore, the value of B is consistent with the fracture area observations.

However, the range of validity of this model is questionable. Indeed, Turcsányi limited its measurements to a maximum filler volume fraction of 40 %, whereas dental composites exceed this value. In the literature, few authors studied the influence of filler ratio over a large range. For a filler fraction ranging from 0 vol% to 50 vol%, Ikejima noticed that flexural strength varied non-linearly [3]. The way it varied is very similar to the Turcsányi model. In addition, three curves were plotted with respect to the quality of the filler-matrix interface, which shifted in accordance with the model's expectations. Still for flexural strength, Braen also found a shape similar to the Turcsányi model [6], whereas results were more random for Ferracane [7]. Nevertheless, no theoretical model was compared to their results, and therefore Turcsányi model's validity range could not be checked. Our results tend to touch this sore point: the estimations made on the [0 ; 60 wt%]-range resulted in a better coefficient of determination than the full-range fit (even if both are good). This is partly due to the way in which the yield stress of 80 wt% samples is calculated. As explained before, the yield stress was taken equal to the flexural strength. Therefore, samples which are broken too early due to initial defects decrease the mean value of the yield stress. For the other ratios, on the contrary; early failures have no consequence on the yield stress determination. The yield stress of the 80 wt%-ratio was therefore slightly underestimated. Otherwise, both the coefficient of determination and the parameter B would have increased, making the [0 ; 60 wt%]-fit and the [0 ; 80 wt%]-fit closer.

But the deviation from the model can also be explained by physical elements too. One hypothesis is a particular layout of high-filled composites. When the filler ratio becomes too high, the thickness of matrix between two fillers is thin enough to create a local stress concentration. Therefore, the proportional law used to calculate the stress response to the load cannot truly be used. If two particles are in contact, the load transfer is not the same either. To that end, the SEM pictures of the 80 wt% composite showed a very compact structure in which the matrix is barely visible. The distance between the fillers may be small enough, if not non-existent, to not behave like a viscoelastic material but like an elastic network [20]. In these conditions, the concepts used to calculate the matrix stress in Turcsányi model are not completely representative of the real test.

At the other extremity, the unfilled resin was also a source of uncertainty. Indeed, these samples were subject to high deformation and often broke into three pieces instead of two. The cracks did not propagate at the centre of the sample. This indicates that we most likely went beyond the domain of validity of the beam theory. In particular, the curvature radius must remain lower than ten times the thickness of the sample. Otherwise shear might appear and straight sections do not remain planar. The failure into three pieces is the proof that other phenomenon step in with respect to the theory. Therefore, the formula used to calculate the maximum stress may not be accurate for relatively high deformations. If the yield stress of full matrix samples is not reached soon enough, it can slightly modify the value used as common denominator. However, this remark surely affects the calculation of the flexural strength more than the yield stress.

Another point that could explain the deviation from the model is the value of 2.5 in the Turcsányi formula (Eq. 8). In fact, this parameter represents the packing of the fillers, which allows estimating the filler content of the most filled section of the sample. For crystalline structures with regular layout of homogeneous spherical particles, this value is generally between 2.3 and 2.5 [9]. But the particles of the DMG composite have random shapes. This decreases the compactness of the filler lattice. But at the same time, particles have different sizes. This enables small particles to fill interstitial sites and increase compactness [20]. In the absence of further information, 2.5 was considered a good approximation for this parameter. Nevertheless, the choice remains subjective.

Apart from these good considerations, it can be noticed that the properties from batches T3 and T4 were slightly different. Nevertheless, the results show the same trends. To explain the differences

between the two batches, it has been proven that the production history of the resin before curing has an influence on the mechanical properties after curing [21]. It includes the room relative humidity and temperature during the production of the matrix, the mixture with fillers, the storage before curing and the curing atmosphere. Both batches were stored in different pots. Nevertheless, the pots were produced on the same day under the same conditions. Therefore, the process history should be the same. Storage time was also presented as a factor that can have a significant impact on the mechanical properties of dental composites [22]. However, the trend on mechanical properties is expected to be more downward as water causes hydrolysis of the matrix and makes it swell, enhancing movement between polymer chains [7]. A contrary effect has never been demonstrated. More likely, the temperature history is the parameter that was not fully controlled. Even if the temperature of the test room was relatively stable, a small variation of a few degrees could exist across the room. In addition, Carreira found that, for bigger samples in water, nearly one minute was necessary to cool down a sample by 15 °C [23], and that the duration was highly temperature dependent. Therefore, the cooling process could not have been exactly the same between the two batches. The samples temperatures could be slightly different, resulting in differences in mechanical properties [24]. To sum up, the difference between the two batches must be noticed with caution and not over considered. The most important fact is that both batches fit with Turcsányi's model instead of giving conflicting results.

Apart from the yield stress, most of common models to estimate the flexural modulus are not adapted to our experimental results. As mentioned by Sideridis [12], these models indeed deviate for high filler ratios – in this study, immediately after 20 wt% samples –. But they do not consider, for example, the size and shape of the fillers which are likely to influence the elastic modulus [20]. The models also assume that there is perfect adhesion between the fillers and the matrix, resulting in strain continuity at their interface [12]. Sideridis observed that this assumption is false, for instance because of local plastic deformation around debonded particles [12]. Models also do not take into account any interaction between the fillers, which is the case when the filler ratio increases. The sum of these micro-effects changes the macroscopic behaviour of composites. These points reinforce the idea that including the interface quality in predictive models is a requirement for high filler ratios models. The model we proposed (Eq. 9), based on Einstein's, works well. However it must be considered again with different composite materials, in order to include an interface influence instead of fixed numerical parameters.

Flexural strength is more unpredictable as it depends on many parameters such as the size and shape of the fillers, along with the filler ratio. Nevertheless not every influence is well-known [25, 26]. They are also significantly related to surface quality: defects such as initial micro-cracks can easily break the sample under low stresses [19]. Therefore, no trend or predictive model was found and results were more scattered. Even if flexural strength is the preferred way to estimate the survival of a clinical restoration, numerous samples are necessary to estimate the value of this property.

5) Conclusion

In the present study, the accuracy of a theoretical model to predict the yield stress of dental composites was evaluated. Based on the experimental data we obtained, we showed that the Turcsányi model initially proposed for tensile yield stress could be adapted to the conventional 3-point bending test. Correlation between the theoretical flexural yield stress and the experimental points is good. But some bias can make the model differ, especially for high-filled composites. These results are promising in order to have an easy and less expensive method to predict the yield stress of dental composites. It would be interesting to check whether the parameter B varies in accordance with the theory when the interface strength decreases, for instance because of an accelerated aging protocol. On the contrary, flexural strength is more unpredictable because it depends on many parameters. Finally, common models for flexural modulus deviate from the experimental data for ratios greater than 20 vol%,

making them inapplicable to dental composites. This highlights the importance of including the strength of the filler-matrix interface in predictive models for mechanical properties.

Annex

Flexural modulus determination

The very beginning of a bending test always starts with a small bias: the stress-strain curve is convex instead of linear. For dental composites, the extreme surface is an Oxygen Inhibited Layer (OIL) where curing is less important. Its properties are worse than those of the bulk. When the applied loads are small, the importance of the OIL on the global behaviour cannot be neglected. Thus the flexural modulus cannot be truly estimated on this part. For all the samples of this study, the part of the curve between 15 MPa and 30 MPa was always considered as linear. Therefore, this range was used as a reference to calculate the flexural modulus of every sample of each ratio.

Yield stress extrapolation

It is noteworthy that, if some samples broke after their yield stress point, some others broke before reaching the yield stress, especially for 40 wt%- and moreover 60 wt%-samples. These early failures are likely due to random initial defects [13] in the samples. They do not represent the behaviour of a good-handled restoration that should operate beyond its yield stress point. Nevertheless, the bulk properties of the material remain the same as those of the other samples of the batch. In order to better estimate the true yield stress and to base the study on a large enough amount of data, the theoretical yield stress was extrapolated (*Figure 13*).

Simple polynomial models were tested, from second to fifth degree. Extrapolations were made on data beyond 15 Mpa, removing the very initial biased part of the curve. The average of the second-degree and the third-degree extrapolations was also calculated. Empirically, this “mean” model had the best fit with the experimental data with an accuracy of 1 MPa in the estimation of the targeted value (for samples which did not fail before their yield stress). Therefore, the average of second and third degree polynomials was used to extrapolate the theoretical yield-stress of the samples which broke too early.

The 80 wt% composite is an exception. Because of the more linear elastic behaviour of this composite, the polynomial estimations were less accurate and resulted in very high values for the yield stress. These high values are anyway not reachable by the material before failing. Therefore, for the 80 wt% samples, the common definition of the yield stress was used: the yield stress was considered equal to the flexural strength.

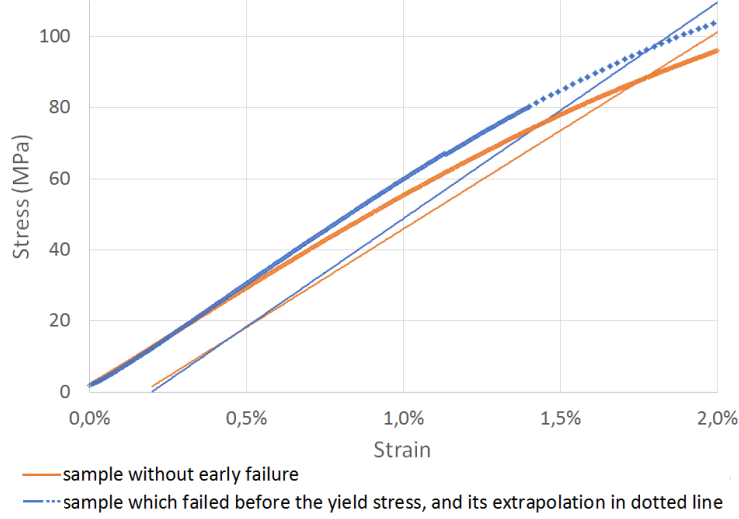


Figure 13: Example of a 60 wt% - sample that failed before its yield stress (in blue), compared to a good sample (in orange)

Elastic modulus models

The theoretical models faced to elastic modulus experimental data are detailed hereafter:

Einstein:
$$E_c = E_m(1 + 2.5\varphi) \quad (10)$$

Guth:
$$E_c = E_m(1 + 2.5\varphi + 14.1\varphi^2) \quad (11)$$

Paul:
$$E_c = E_m \left(\frac{1 + (m-1)\varphi^{2/3}}{1 + (m-1)(\varphi^{2/3} - \varphi)} \right) \quad (12)$$

Counto:
$$\frac{1}{E_c} = \frac{1 - \sqrt{\varphi}}{E_m} + \frac{1}{E_m(1 - \sqrt{\varphi})\sqrt{\varphi} + E_f} \quad (13)$$

Kerner:
$$E_c = E_m \left(\frac{\frac{\varphi G_f}{(7-5\nu_m)G_m + (8-10\nu_m)G_f} + \frac{1-\varphi}{15(1-\nu_m)}}{\frac{\varphi G_m}{(7-5\nu_m)G_m + (8-10\nu_m)G_f} + \frac{1-\varphi}{15(1-\nu_m)}} \right) \quad (14)$$

Takahashi:
$$\frac{E_c}{E_m} = 1 + \varphi(1 - \nu_m) * \frac{E_f(11 + 18\nu_m + \nu_m^2) + E_m(\nu_f - \nu_m - 2)}{E_f(9 - \nu_m - 10\nu_m^2) + E_m(9 + 3\nu_f - 5\nu_m - 5\nu_m\nu_f)} \quad (15)$$

Hashin-Shtrikman lower bound:
$$E_c = E_m + \frac{\varphi}{(E_f - E_m)^{-1} + (1 - \varphi) * (E_m + \frac{4}{3}G_m)^{-1}} \quad (16)$$

Euler & Van Dyck:
$$E_c = E_m \left(1 + \frac{1.25\varphi}{1 - 1.2\varphi} \right) \quad (17)$$

Narkis:
$$E_c = E_m * \frac{1}{1.5 * (1 - \varphi^{1/3})} \quad (18)$$

Bourkas (I)
$$\frac{E_c}{E_m} = 1 + \frac{\varphi}{\frac{m}{m-1} - \varphi^{1/3}} \quad (19)$$

$$\frac{E_c}{E_m} = 1 + \frac{\varphi}{\frac{1}{m-1} + \varphi^{1/3} - \varphi^{2/3}} \quad (20)$$

Where E_c , E_m and E_f are the elastic modulus of the composite, the matrix and the fillers, respectively. ν_m and ν_f are the Poisson ratios of the matrix and the fillers, respectively. G_m and G_f are the shear modulus of the matrix and the fillers, respectively. m is the ratio of E_f over E_m .

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