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Misinterpretation of ISO 4049 standard recommendations: Impact on Young's modulus and conversion degree of dental composites

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Abstract

Objectives: The purpose of this study was to study the effects on Young's modulus and conversion degree of variations in polymerization conditions during the 3-point bending test of composite samples in accordance with the ISO 4049 standard.

Methods: Three nanocomposites were used in the 3-point bending test based on the conditions described in the ISO 4049 standard. Samples of 2 mm x 2 mm x 25 mm were fabricated and tested with a different number of irradiation points and irradiation time. Conversion degree of the samples were also measured by micro-Raman spectroscopy and correlated with the Young's modulus values obtained for each one.

Results: The variations in curing protocol during specimen's realization influenced the Young's modulus and degree of conversion of all composites. These two properties correlated well. The ISO 4049 standard defines the conditions for performing the properties tests of composites to allow reproducibility and comparison of different studies. Concerning the 3-point bending test, even a minimal change in the state causes differences in the results obtained. The standard should thus clarify the tools that can be used when producing samples in order to minimize discrepancies.

Significance: The influence of the parameters surrounding the design of the samples should be controlled and defined so as not to include bias in the studies carried out. This will allow literature studies to be compared with more accuracy.

Keywords: Dental composite, ISO 4049, Degree of conversion, Young's modulus, Micro-Raman spectroscopy, Three-point bending test.

1. Introduction

The study of composite materials is already very advanced for about several decades. The field of dental composite has also gained momentum with the decrease or total drop-out of the use of amalgams. Continuous improvements in composition and nano-technology integration have made it possible to expand their indications and facilitate their use. Studies exploring the properties of these materials are regularly emerging but the comparison sometimes seems difficult because different methods are used to study the same properties (Beolchi et al., 2015; Dewaele et al., 2009; Grohmann et al., 2017; Halvorson et al., 2003; Magalhaes Filho et al., 2016). The Young's modulus and the degree of conversion are important parameters that manufacturers and researchers analyse first.

The degree of conversion is a parameter that allows to know the level of polymerization of the monomer present in the resin matrix of the composites. This parameter can be measured with several methods like Fourier transform infrared spectroscopy or Raman spectroscopy (Al-Zain et al., 2019; Daugherty et al., 2018; Imazato et al., 2001; Moraes et al., 2008; Pianelli et al., 1999; Yokesh et al., 2017). These methods use the intensity ratio of carbon double bond (C=C) and carbon single bond (C-C), respectively at 1610 and 1640 cm^{-1}, in uncured and cured composite resin matrices. Raman and ATR-FTIR have the advantages of being non-destructive tests and require no sample preparation. (Bayındır et al., 2016; Dewaele et al., 2006; Lucey et al., 2015; Pianelli et al., 1999; Tarle and Par, 2018; Truffier-Boutry et al., 2003; Velo et al., 2019; Wang and Wang, 2019) The degree of conversion correlates with the Young's modulus (Daugherty et al., 2018; Li et al., 2009) that determines the threshold of resistance to deformation and thus allows to know the limits of use of these materials. For direct dental restoration composites, this property takes a particular importance because the material must acquire its final characteristics in around twenty seconds and should keep them as long as possible. In the literature, there are many studies concerning the resistance of these materials against various stresses (Ferracane et al., 2017; Ilie et al., 2017; Pick et al., 2010; Tavassoli Hojati et al., 2013; Thomaidis et al., 2013). Various tests are proposed to calculate Young's modulus conditioned by the different standards (Calabrese et al., 2015; Wang et al., 2003). These tests are sometimes difficult to

implement because they require specific machines and tools. For this reason, investigators prefer to use the Young's modulus values given by the manufacturers without questioning the validity of these values. The simplest and the most prevalent test that can be used is the 3-point bending test in accordance with the ISO 4049 standard. However, when making a sample for the 3-point bending test, the shape and the dimension of the specimens generate construction complications. Studies have reported some degree of heterogeneity concerning the light source used or the method of polymerization applied for the manufacture of these specimens (Rodrigues Junior et al., 2007; Scribante et al., 2019; Sideridou et al., 2011). Reports concerning these parameters show variations in test configuration despite the standards used, generating differences in the interpretation (Adabo et al., 2003; Palin et al., 2003; Sideridou et al., 2011; Zakir et al., 2013).

The present study aims at investigating the influence of the polymerization protocol and the irradiation time on the degree of conversion and Young's modulus of three nanocomposites using micro-Raman spectroscopy as non-destructive approach. The hypothesis of this work stems from inconsistences of results obtained on Young's modulus as a consequence of misinterpreting the ISO 4049 standard recommendations.

2. Materials and method

2.1. Materials

The three nanocomposites used in this study were Ceram.x® Universal (Dentsply De Trey GmbH, Konstanz, Germany), Filtek™ Supreme XTE Universal (3M ESPE, St. Paul, MN, USA) and Tetric® EvoCeram Universal (Ivoclar Vivadent, Schaan, Liechtenstein). Table 1 describes the composition, recommended exposure time and Young's modulus given by the manufacturer for each composite.

The curing light D-Light® Pro (GC Corporation, Tokyo, Japan), with 1170 mW/cm² intensity in high power mode (measured with a radiometer Bluephase® Meter II (Ivoclar-Vivadent, Schaan, Liechtenstein) was used for irradiation of all specimens. Exit windows of this curing light had an external diameter of 8 mm and an internal diameter of 7.5 mm. This lamp produced a wavelength between 400-480 nm with a maximum at 400-405 nm and 460-465 nm during high power polymerization mode. The beam homogeneity was around 66% with 39° divergence.

2.2. Preparation of the composite resin specimens

Six specimens (2 mm x 2 mm x 25 mm) of each composite were produced with a steel split mold for each group of tests (Fig. 1a and 1b). The composite was inserted in the mold with one increment and covered with a microscope slide on both sides. The whole was pressed with mini clamps. The recommendations of ISO 4049 standard are to perform the samples as described above and to polymerize with overlapping points on both sides of the sample following the time recommended by the manufacturer of the composite. For the tests in the present study, 3 groups of samples were realized with a different method of polymerization. In group 1, polymerisation was realised with 3 points of irradiation without overlapping on one side of sample (Fig. 2a). In the group 2, for each irradiation time, polymerisation was performed with 5 overlapping points on one side of the sample (Fig. 2b). Finally, for group 3, the same protocol was used as for the group 2 but on both sides of the specimens (Fig. 2c). The polymerization protocol was realized with high power mode with different irradiation time (5 s, 10 s, 20 s or 40 s) that resulted in 4 subgroups. Specimens were removed from the mold, polished with extra fine grit silica carbide paper and stored in distilled water at 37 °C for 24 hours. The test conditions are summarized in Table 2.

For groups of overlapping irradiations, the tip of the curing light was placed at the centre of the specimen in contact with the glass and this section was irradiated. The tip of the curing light was moved to the section next to the centre overlapping the previous section by half the diameter of the exit window and irradiate with appropriate time in accordance to the test group. Then, the section on the other side of the centre was irradiated in the same way. The procedure was continued through the whole length of specimen and was repeated on its other side.

Before each experiment, the surface of the samples was checked and cleaned with a lint-free wipe. The sample handling was carried out with a contact on the surfaces not used for the measurements.

2.3. Micro-Raman Spectroscopy: Conversion Degree

All micro-Raman spectral acquisitions were performed with a Labram microspectrometer (Horiba Jobin Yvon, Villeneuve d'Ascq, France) coupled to an Olympus BH40 microscope (100x objective, NA = 0.9). The system was equipped with a 785 nm laser excitation was operating at titanium

sapphire laser. The laser power at the sample was 50 mW, which was non-destructive to the samples. The nominal laser spot size at the sample was assessed to be around 1 µm in diameter. Light scattered by the sample was collected through the same objective. A confocal pinhole of 150 µm rejects signals from out-of-focus regions of the sample. A multichannel charge-coupled device (C.C.D.) detector (1024 x 256 pixels) detects the Raman Stokes signal dispersed with a 4 cm^{-1} spectral resolution by a holographic grating (950 lines/mm). The spectral range of the analysis was from 600 to 1750 cm^{-1} and the acquisition time for each spectrum was 2 times 20 s. Eleven acquisitions were recorded every 2 mm along the length on the polymerized and their opposite sides for three composite samples of each group. All experiments were performed in an air-conditioned room with a constant temperature of 21°C. Spectral pre-processing was performed using Labspec 6 software (Horiba Jobin Yvon, Villeneuve d'Ascq, France). A normal variate correction and polynomial smoothing with size 9 and degree 6 was used. A polynomial type baseline correction with 8 degree and maximum point of 33 was realised on all spectrum. In methacrylate based composites, the aliphatic C=C stretching mode (1640 cm^{-1}) peak allowed evaluation of the polymerization degree and it was correlated with the aromatic C=C stretching mode (1610 cm^{-1}) peak, which was taken as an internal reference (Acquaviva et al., 2009; Khan et al., 2017; Lempel et al., 2014; Marovic et al., 2013; Silva Soares et al., 2003; Stansbury and Dickens, 2001).

The degree of conversion (DC) was calculated as the ratio of the aliphatic C=C stretching mode (1640 cm^{-1}) and aromatic C=C stretching mode (1610 cm^{-1}) peaks in cured and uncured materials using Eq. (1), where R is the ratio of intensities of the 1640 cm^{-1} and 1610 cm^{-1} peaks in the spectra of the cured or uncured specimens.

$$DC\ (\%) = \left[1 - \frac{R_{cured}}{R_{uncured}}\right] \times 100 \qquad (1)$$

2.4. Three-point bending test: Young's Modulus

The three-point bending test was done in accordance with the ISO 4049 standard procedure. Specimens were placed on two parallel rods (2 mm diameter) with 20 mm between their centres in a universal test machine (Zwick/Roell Gmbh, Germany). Another rod (2 mm diameter) applied a load on the specimen at its centre (Fig. 1c). The device was calibrated to provide a constant crosshead

speed of 0.75 mm/min. The load exerted on the specimen at the point of rupture or the elastic limit was noted and Young's modulus (E, in MPa) was calculated from the strain–stress curve, carried out with force-displacement data, according to Eq. (2), where σ is the stress and ε is the strain.

$$E = \frac{\sigma}{\varepsilon} = \frac{d\sigma_2 - d\sigma_1}{d\varepsilon_2 - d\varepsilon_1} \qquad (2)$$

2.5. Statistical analyses

All statistical analyses were performed with RStudio software (version 1.2.5001). Results were exploited using a mixed linear model because our test protocol included multilevel data. Micro-Raman spectral data, the influence of irradiation time, method of polymerization, irradiated side and composite, were considered as fixed effect covariables and their involvement were verified by a sequential introduction into the model. The measurements made on each point and the sample parameters were considered random effect variables to account for the correlation inter-specimen and inter-measuring points data. Variations of these terms in intercepts and slopes within the model were characterised. The restricted maximum likelihood method was used to calculate the model coefficients. The normality of the random variables and their independence were verified by Shapiro–Wilk. Wilcoxon test allowed a comparison in results and 0.05 significance level was used.

For 3-point bending test, irradiation time, polymerization method and composite has been considered fixed effect covariables. Young's modulus measures and sample number were considered random effect variables in the mixed linear model used in the same conditions. The normality of the random variables and their independence were verified by Shapiro–Wilk and Wilcoxon test were performed to compare results with a significance level 0.05.

3. Results

3.1. Degree of conversion by micro-Raman spectroscopy

The Fig. 3a compares micro-Raman spectra for Filtek™ Supreme XTE composite uncured and cured according to the condition described for group 3. The degree of conversion was calculated using the intensity ratio of two Raman peaks at 1610 and 1640 cm^{-1} corresponding to aromatic and aliphatic C=C vibrational modes, respectively (Fig. 3b). This ratio was calculated for all 3 groups of composites

and the conversion ratio (DC) evaluated using Eq. (1). All data are represented in Fig. 4 which shows that the degree of conversion of all composites did not exceed 60%. With group 3 (Fig. 4c) specimens produced in accordance with ISO 4049 standard, the maximum degree of conversion obtained was (59.14 ± 2.29)%, (55.09 ± 0.39)% and (55.93 ± 1.56)% for Filtek™ Supreme XTE, Ceram.x® and Tetric® EvoCeram, respectively. The lowest degree of conversion was found in group 1 (Fig. 4a) with the lowest irradiation time. The calculated values were (35.79 ± 9,92)%, (38.42 ± 10.35)% and (34.63 ± 7.35)% for Filtek™ Supreme XTE, Ceram.x® and Tetric® EvoCeram, respectively.

The increase in polymerization time induced a significant increase in the degree of conversion for these three composites in all groups. With the polymerization method used for group 3, the degree of conversion was significantly higher than for group 2, which is itself higher than for group 1 ($p < 0.0001$). Higher irradiation time showed significant increase of conversion degree of all composites in all groups except in group 3 where it is not significant for irradiation times between 10 s and 20 s.

3.2. Young's Modulus using three-point bending test

Fig. 5 compares the average Young's moduli of the three composites as a function of polymerization conditions and irradiation time. An increase in irradiation time resulted in a significant increase in Young's modulus for all composites ($p < 0.05$) except for Filtek™ Supreme XTE where it is not significant between 5 s and 10 s and between 10 s and 20 s. For Ceram.x®, after 5 s irradiation times (Fig. 5a) Young's modulus was (5058 ± 842) MPa in group 1, (7577 ± 258) MPa in group 2 and (8879 ± 405) MPa in group 3. The maximum values with 40 s of polymerization were (8856 ± 294) MPa in group 1, (9702 ± 214) MPa in group 2 and (10307 ± 186) MPa in group 3.

For Filtek™ Supreme XTE (Fig. 5b), Young's modulus values obtained with 5 s curing time were (6765 ± 551) MPa, (8851 ± 911) MPa and (11438 ± 558) MPa, in groups 1, 2 and 3, respectively. The maximum values obtained with 40 s curing time were (11230 ± 219) MPa, (11533 ± 321) MPa and (12136 ± 285) MPa, in groups 1, 2 and 3, respectively. For Ceram.x® and Filtek™ Supreme XTE composites, the manufacturer's values were met for all irradiation times in group 3, with 20 s and 40 s in group 2 and only with 40 s in group 1.

For Tetric® EvoCeram (Fig. 5c), with 5 s of irradiation, Young's modulus values were (3522 ± 310) MPa, (4445 ± 67) MPa and (6699 ± 253) MPa, in groups 1, 2 and 3, respectively. The maximum values were again with 40 s curing time (6591 ± 300) MPa, (7734 ± 351) MPa and (8016 ± 315) MPa in groups 1, 2 and 3, respectively. However, the manufacturer's value was not reached in any groups.

4. Discussion

The Young's modulus is an important parameter measuring the elastic properties and useful in the characterization of the composite materials. Many studies describe feasible tests to measure this parameter (Ilie and Hickel, 2009; Rodrigues Junior et al., 2007). The most common one is the 3-point bending test that was also used in this study. The ISO 4049 standard regulates the preparation of the specimens and the conditions of the tests in order to improve their reproducibility and comparison. Literature data show divergences despite tests carried out in accordance with this standard and some manufacturers do not necessarily give much guidance on how they obtained this parameter for their materials (Adabo et al., 2003; Palin et al., 2003; Sideridou et al., 2011; Zakir et al., 2013). The degree of conversion of a composite material is another parameter that characterises the polymerization process as it provides an indication of the degree of solidification. It was measured, at several points and on each side of all the samples, before the bending tests to exclude the samples showing a polymerization defect. The degree of conversion increases with the total irradiation time because it generates an increase in the hardness of the material, the latter also has an impact on the elastic modulus although this does not have a linear correlation with the degree of conversion. (Li et al., 2009; Versluis et al., 2004).

Therefore, the purpose of the present study was to investigate Young's modulus using the recommendations of the ISO 4049 standard and the degree of conversion of three nanotechnology composites (International Organization for Standardization, Geneva, Switzerland, 2019). The 3-point bending test was used for the former while micro-Raman spectroscopy was employed for the latter.

The maximum degree of conversion obtained for all composites did not exceed 60%. For Ceram.x® the manufacturer recommends an irradiation time of 20 s with increments not exceeding 2 mm and

with a minimum lamp power of 500 mW/cm². The recommendations remain the same for more powerful curing-light units. In these conditions, Ceram.x® composite exhibited a degree of conversion of (47.3 ± 5.2)% with 3 points without overlapping on one side of specimen (group 1). In group 2, it showed an increase of 7.5% with (50.9 ± 3.0) % and in group 3, an increase of 4.5% with (53.2 ± 1.6)% for the overlapping polymerizations on both sides of the sample. The Young's modulus values increased by 5.8% between groups 1 and 2 and by 11% between groups 2 and 3 with (8305 ± 662) MPa, (8788 ± 150) MPa and (9772 ± 195) MPa, for groups 1, 2 and 3, respectively. The changes of degree of conversion and Young's modulus values observed for Ceram.x®, between the test groups irradiated with recommended time (20 s), was less important than for the other two composites. These values were close to the value defined by the manufacturer (9000 MPa).

The manufacturer's recommendations for Filtek™ Supreme XTE and Tetric® EvoCeram were the same as for Ceram.x® except that an irradiation time of 10 s was recommended with a curing light power > 1000 mW/cm². For Filtek™ Supreme XTE composite, the degree of conversion did not exceed (39.7 ± 9.9)% with 10 s of irradiation without overlapping on one side of specimen (group1). The Young's modulus was (7756 ± 521) MPa, i.e., 29.5% lower than the value defined by the manufacturer (11000 MPa). Overlap polymerization on one side of the specimen (group 2) generated an increase of 14.6% for the degree of conversion and of 2445 MPa for the Young's modulus. Polymerization of both sides of the sample (group 3) resulted in a 22.1% increase in conversion degree (55.5 ± 0.4)% and a 17% increase in Young's modulus (11938 ± 749) MPa compared to group 2. Using group 3 as a test group in compliance with the ISO 4049 standard, gave a Young's modulus greater than the value defined by the manufacturer (11000 MPa).

For Tetric® EvoCeram, Young's modulus values were (4448 ± 312) MPa in group 1, (5509 ± 393) MPa group 2 and (7480 ± 299) MPa in group 3. For this composite, conversion degree was 40% when an irradiation of 10 s in accordance with the manufacturer's recommendations was used on one side without overlapping (group 1). It increased by 6.8% with overlap (group 2) and by 17% with irradiation on both sides with overlapping in accordance with the ISO 4049 standard (group 3). However, this increase in the degree of conversion did not allow to reach the high Young's modulus value given by the manufacturer (10000 MPa). This showed that this low value was not due

to poor curing of the material. The maximum value of the Young's modulus obtained with this study was (8016 ± 315) MPa with an overlapping polymerization of 40 s per point on both sides of the sample. The value of Young's modulus increased with the total irradiation time for all composites but for Tetric® EvoCeram this was not enough to reach the value predefined by the manufacturer. It remained about 20% lower than this value.

In order to evaluate the pertinence of our results, we have compared some literature reports where some parts of test conditions were quite close to ours. For instance, Benetti et al. (Benetti et al., 2014) conducted studies on Filtek™ Supreme XTE composite with Optilux 501 (light tip diameter of 8 mm and power of 850 mW/cm²) that showed similar correlation between irradiation time and Young's modulus. Ilie and Hickel studied the macro-, micro- and nano-mechanical properties of some composites stored in water, saliva and alcohol for 24 hours or 4 weeks and reported a Young's modulus of 7700 MPa in water or saliva and 4900 MPa in alcohol (Ilie and Hickel, 2009). Scribante et al. studied the Young's modulus of different composites stored in an acidic beverage for 1 week or 1 month, compared with immersion in distilled water for 24 hours like in our study. They performed a 3-point bending test and reported a decrease in the Young's modulus value when the sample had spent more time in an acidic medium. Their results indicated 9450 MPa for Filtek™ Supreme XTE in distilled water and this value decreased to 7160 MPa after one month in the acidic beverage. For storage condition in distilled water, this value is less than our results (11938 ± 749) MPa and the manufacturer's value (11000 MPa). They also studied Ceram.x® and reported values of 7120 MPa and 6920 MPa for distilled water and acidic medium, respectively (Scribante et al., 2019). In a similar way, we and the manufacturer found a higher value after 24 hours in distilled water [(9772 ± 195) MPa and 9000 MPa, respectively]. This difference can be explained by variations during the production of samples and the performance of tests. The specimens produced in the dimensions defined by standard ISO 4049, but they have been polymerized 3 minutes in a light polymerization oven with the light intensity of 1200mW/cm² and a wavelength of 430-480 nm. In addition, the 3-point bending test was carried out with a span length of 21 mm instead of 20 mm as defined by the standard. Takahashi et al. (Takahashi et al., 2010) have used three points bending tests after 20 s curing on both sides of specimens with 5 overlapping polymerization points in accordance

with ISO 4049 standard and compared Young's modulus of different conventional direct restoration composites at 15 min after polymerization and after 24 hours of storage in water. They found that Tetric® EvoCeram had Young's modulus around 4000 MPa at 15 min and < 9000 MPa at 24 hours of storage in water. We obtained (7480 ± 299) MPa in distilled water at 24 hours, which is lower than Takahashi's results and manufacturer's value (10000 MPa). In most of the studies (Belli et al., 2014; Scribante et al., 2019; Takahashi et al., 2010), some variations are observed in comparison with the manufacturer's values. In our study, we observed that the results were similar to manufacturer's value for two of the composites (Filtek™ Supreme XTE and Ceram.x®) and not for Tetric® EvoCeram. This implies that respecting the manufacturer's recommendations and ISO 4049 standard test conditions may give expected results for some composites but not for all. The degree of conversion values described for conventional direct restoration composites were between 25% to 75% and 100% was never achieved (Imazato et al., 2001; Kopperud et al., 2013; Mohamad et al., 2007; Pianelli et al., 1999; Soh et al., 2004; Vaidyanathan et al., 2017). Durner et al. described the similar results and a statistically significant increase in conversion degree of Tetric® EvoCeram from (38.2 ± 2.0)% with 5 s of curing time to (47.4 ± 2.1)% with 40 s of curing time (Durner et al., 2012). For Filtek™ Supreme XTE, they observed an increase from (22.4 ± 1.9)% with 5 s of polymerization to (46.5 ± 2.6)% with 40 s. These results showed that a small variation in the number of irradiation points or in the curing time during samples preparation induced a variation in the Young's modulus and the degree of conversion values. Similar protocols can be found in the literature (Alsharif et al., 2014; Atai et al., 2012; Bijelic-Donova et al., 2016) but divergences due to protocol discrepancies complicated the comparison. In some studies, irradiation was done with 3 points, the overlap of the irradiation windows was zero or partial depending on the dimensions of the tip of the curing light (Beun et al., 2012; Hong et al., 2017; Manhart et al., 2000; Palin et al., 2003; Sideridou et al., 2007). This was different from the ISO standard which mention an overlap of half the diameter of the tip. It is therefore important that when using standardized test, the conditions of realization of the samples are meticulously respected. The old version of ISO 4049 (2009) did not illustrate at all the polymerization method. The new version, published in May 2019, allows authors to visualize the correct polymerization method with an illustration, facilitates understanding and will avoid any errors during

the sample preparation. The visualization by a clear illustration excludes errors of interpretation concerning the standard test conditions and avoids compromising the reproducibility and the comparison of studies reported in the scientific literature (International Organization for Standardization, Geneva, Switzerland, 2019). The overlapping photopolymerization protocol described in ISO 4049 has been criticized by some authors who believe that areas of overexposure interfered with the characteristics of materials (Randolph et al., 2016). But this standard protocol remains a simple, reproducible and recommended method to test composites (Della Bona et al., 2011). Standards are important for test calibration and for a good reproducibility. The thickness of the specimens is clearly mentioned (2 mm x 2 mm x 25 mm) but it was not the case for the photopolymerization parameters and the machines and tools used. The standard remains unclear regarding the wavelength or the characteristics of the curing-light tip, the homogeneity and the divergence of the beam and the use of the mono or polychromatic source, whereas these points are important parameters when producing samples (Ceballos et al., 2009; Harlow et al., 2016; Michaud et al., 2014; Price et al., 2010; Sampaio et al., 2017; Shimokawa et al., 2016). The manufacturers do not wish to give information on the precise photo initiator composition of their composites. This also complicates the comparison of studies, because the coupling of photo-initiators and their concentration can be the cause of variations on the degree of conversion results and consequently on Young's modulus (Bruschi Alonso et al., 2013; Fornaini et al., 2015; Grohmann et al., 2017; Kostylev et al., 2016; Maciel et al., 2018; Santini et al., 2012; Van Landuyt et al., 2011). The standard is also unclear about the composite shade which interferes with the degree of conversion of the samples (Ferracane et al., 1986; Guiraldo et al., 2009; Jeong et al., 2009). All these points, present in the literature, generate bias in the comparison of different studies. Moreover, the question of clinical conditions arises regularly. ISO standard propose to produce 3-point bending test specimens in compliance with the manufacturer's recommendations but in the clinical conditions, practitioners cannot cure restoration material on both sides. They can modify the thickness of the incrementation, irradiation point number, polymerization time as well as the power and the type of the light source used. However, composites are very operator dependent materials and the slightest variation of these parameters can influence the final material features. The results of this study showed that it was necessary to increase the exposure

time but also overlap the irradiation points to ensure a good polymerization of the composite. This is even more important for occluso-proximal restoration because the distance with the proximal composite increment is greater, especially when the light beam is not perpendicular to the cavity and consequently that part of the proximal restoration is not irradiated (Price et al., 2011). Dewaele et al. demonstrated that the increase in the total photopolymerization energy resulted in an increase of the Young's modulus values of the photopolymerizable composites (Dewaele et al., 2009). In contrast, curing with multiple phases separated with time intervals did not impact on Young's modulus values if the total irradiation time was long enough. Moraes et al. demonstrated the importance of the degree of conversion for the stability and mechanical properties of composites (Moraes et al., 2008). The degree of conversion also modified the materials hardness. Haenel et al. showed that the higher the irradiation, the harder was the composite (Vickers hardness) (Haenel et al., 2015).

We observed that even minimal changes in the composite curing conditions have an impact on the results. It is important to have a good overview of the test protocol proposed by the ISO 4049 standards and employed by the manufacturers to elaborate reproducible and comparable studies.

5. Conclusion

The indirect relationship between the degree of conversion and the irradiation time was confirmed by our results. For the sample produced in accordance with ISO 4049, the values of Young's modulus were close to those given by the manufacturer for Filtek™ Supreme XTE and Ceram.x® when the recommended irradiation time has been applied, however, for Tetric® EvoCeram, the value of Young's modulus described by the manufacturer has not been reached despite an increase in irradiation time and number of irradiation points.

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Table 1: Materials characteristics

Commercial name	Composite category	Shade	Composition	Recommended exposure time (for 2 mm of composite)	Young's Modulus given by manufacturer (MPa)
Ceram.x® mono Universal (Dentsply De Trey GmbH, Konstanz, Germany)	Nanofilled composite	A3	Methacrylate modified polysiloxane, Dimethacrylate resin, Fluorescence pigment, UV stabilizer, Stabilizer, Camphorquinone, Ethyl 4 (dimethylamino) benzoate, Barium-aluminium-borosilicate glass, Methacrylate functionalised silicon dioxide nano filler (10 nm), Iron oxide pigments and titanium oxide pigments and aluminium sulfo silicate pigments according to shade, Filler: 76% by weight (57% by volume)	≥ 500mW/cm²: 20 s	9 000
Filtek™ Supreme XTE Universal (3M ESPE, St. Paul, MN, USA)	Nanofilled composite	A3 Body Shade	Bisphenol A, Diglycidyl methacrylate, Triethyleneglycol dimethacrylate, Urethane dimethacrylate, Bisphenol A polyethylene glycol diether dimethacrylate, Camphorquinone, Tri-fluorure d'ytterbium (0.1 to 5.0 μm), Non-agglomerated/non-aggregated 20 nm silica and zirconia filler, Aggregated zirconia/silica cluster filler (comprised of 20 nm silica and 4 to 11 nm zirconia particles), Cluster particle size : 0.6 to 10 μm, Filler :78.5% by weight (63.3% by volume)	≥ 500–1000 mW/cm²: 20 s ≥ 1000 mW/cm²: 10 s	11 000
Tetric® EvoCeram Universal (Ivoclar Vivadent, Schaan, Liechtenstein)	Nano-hybrid composite	A3	Dimethacrylate resin 16.8%(v/v), Bisphenol diglycidylmethacrylate (Bis-GMA) 5–10%, Urethane dimethacrylate (UDMA) 5–10%, Barium glass, Ytterbium trifluoride, Mixed oxide prepolymer 82–83 wt%, 75–76 wt% or 53–55 vol% inorganic fillers, Particle size of inorganic fillers 40–3000 nm, with mean 550 nm, Camphorquinone and monoacylphosphine oxide (Lucirin® TPO), Additives, initiators, stabilizers and pigments (<1.0 wt.%).	≥ 500–1000 mW/cm²: 20 s ≥ 1000 mW/cm²: 10 s	10 000

Table 2: Irradiation conditions for each composite

Group	Specimen number per composite for micro-Raman spectroscopy	Specimen number per composite for 3-point bending test	Irradiation time per point (s)	Number of irradiation point	Total irradiation time per specimen (s)
1	3	6	5	3	15
			10		30
			20		60
			40		120
2			5	5	25
			10		50
			20		100
			40		200
3			5	10	50
			10		100
			20		200
			40		400

Black and white figures list

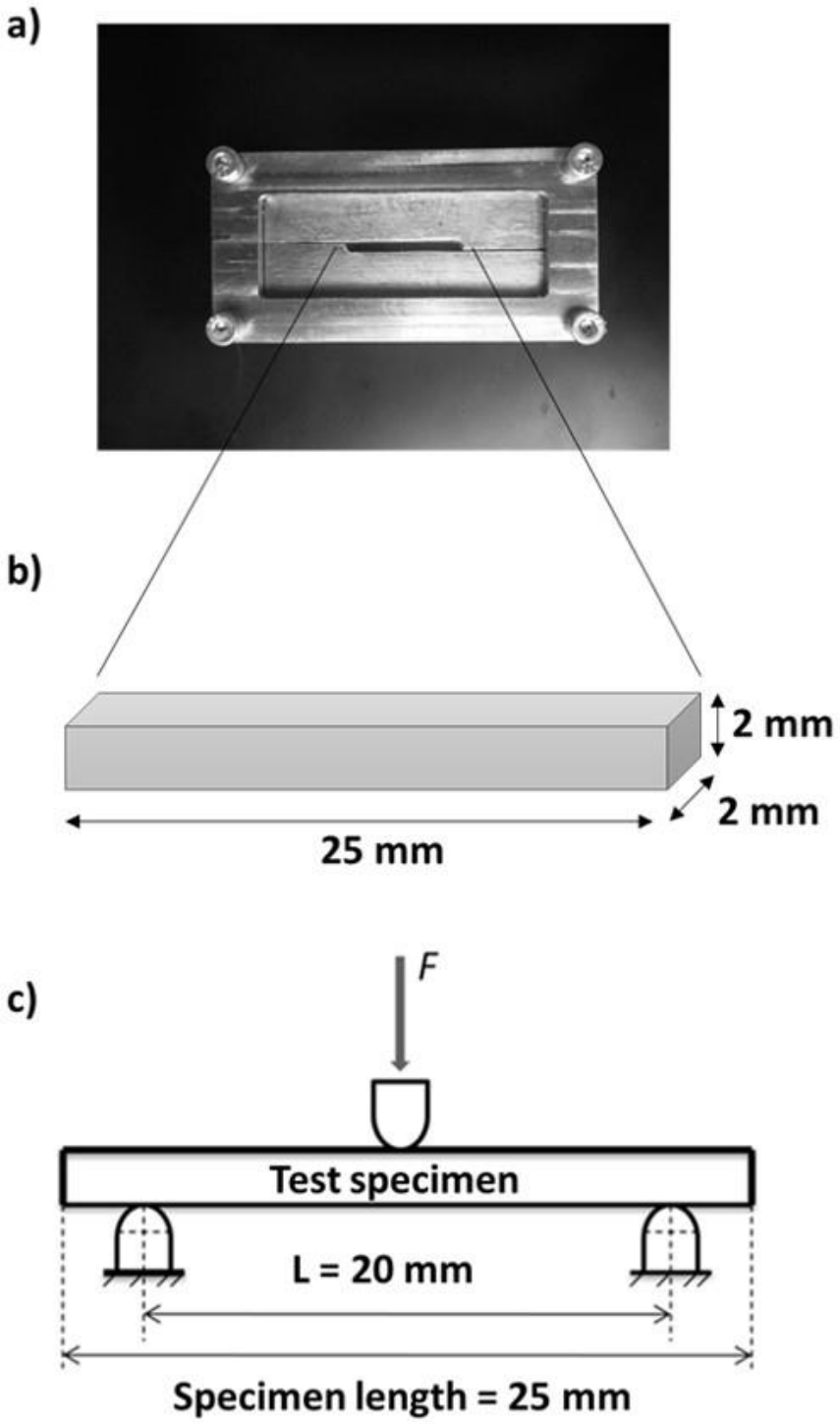


Fig. 1: Illustration of materials for producing a specimen. a) top view of steel split mold, b) schematic of fabricated specimen and its dimensions and c) three-point bending test conditions with span length (L) and specimen positioning. F is the applied force (in N).

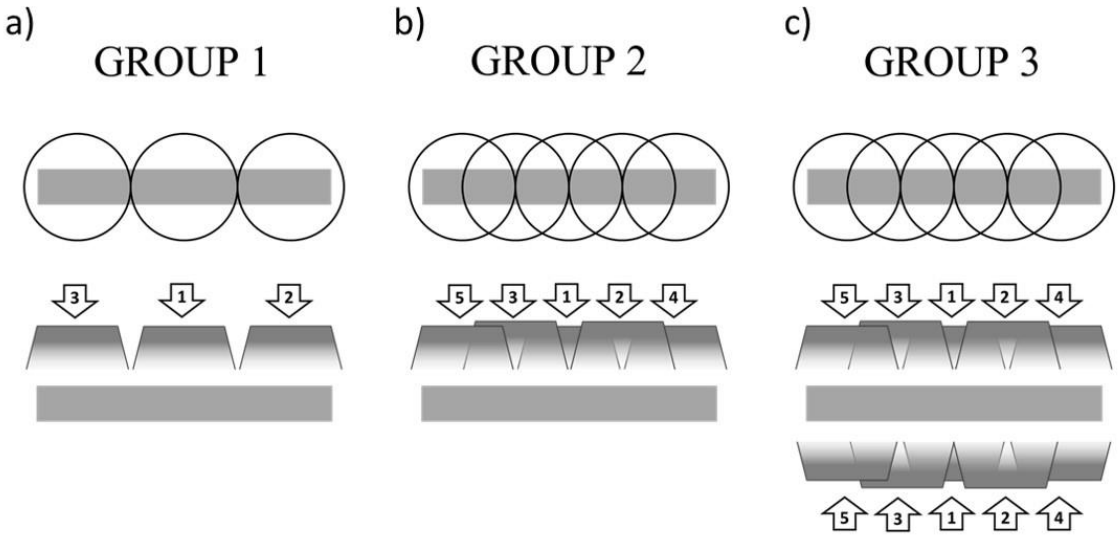


Fig. 2: Irradiation protocol scheme. a) group 1: irradiation on one side with 3 non overlapping points, b) group 2: irradiation on one side with 5 overlapping points and c) group 3: irradiation on both sides with 5 overlapping points.

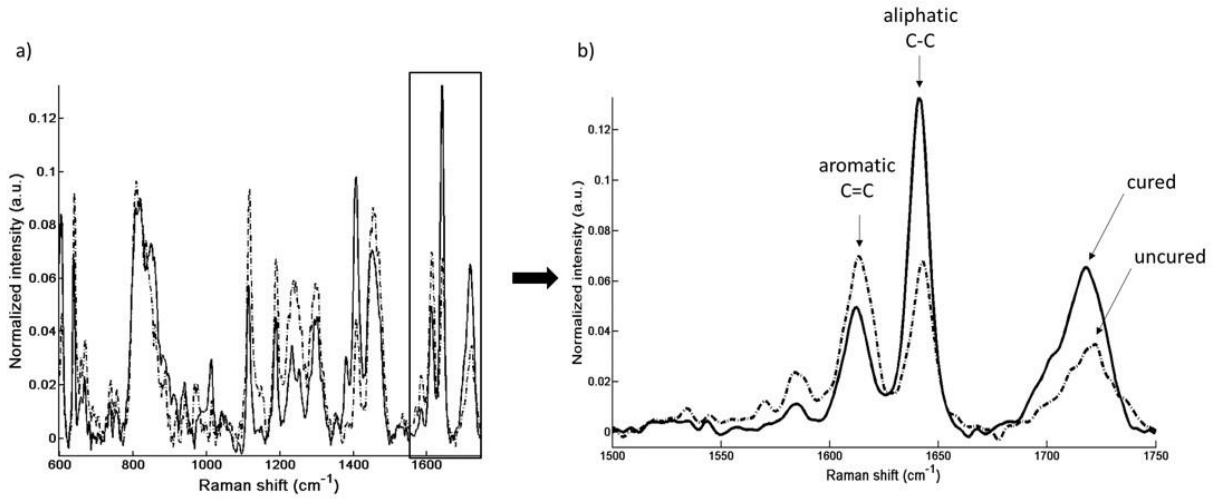


Fig. 3: Micro-Raman spectroscopy of cured and uncured Filtek™ Supreme XTE specimen. a) spectra of an uncured (dotted line) and cured (solid line) sample from group 3 (irradiation of 40 s on both sides with 5 overlapping points) and b) highlight of the 1500 – 1750 cm^{-1} frequency range showing the peaks at 1610 and 1640 cm^{-1} used for calculating the degree of conversion.

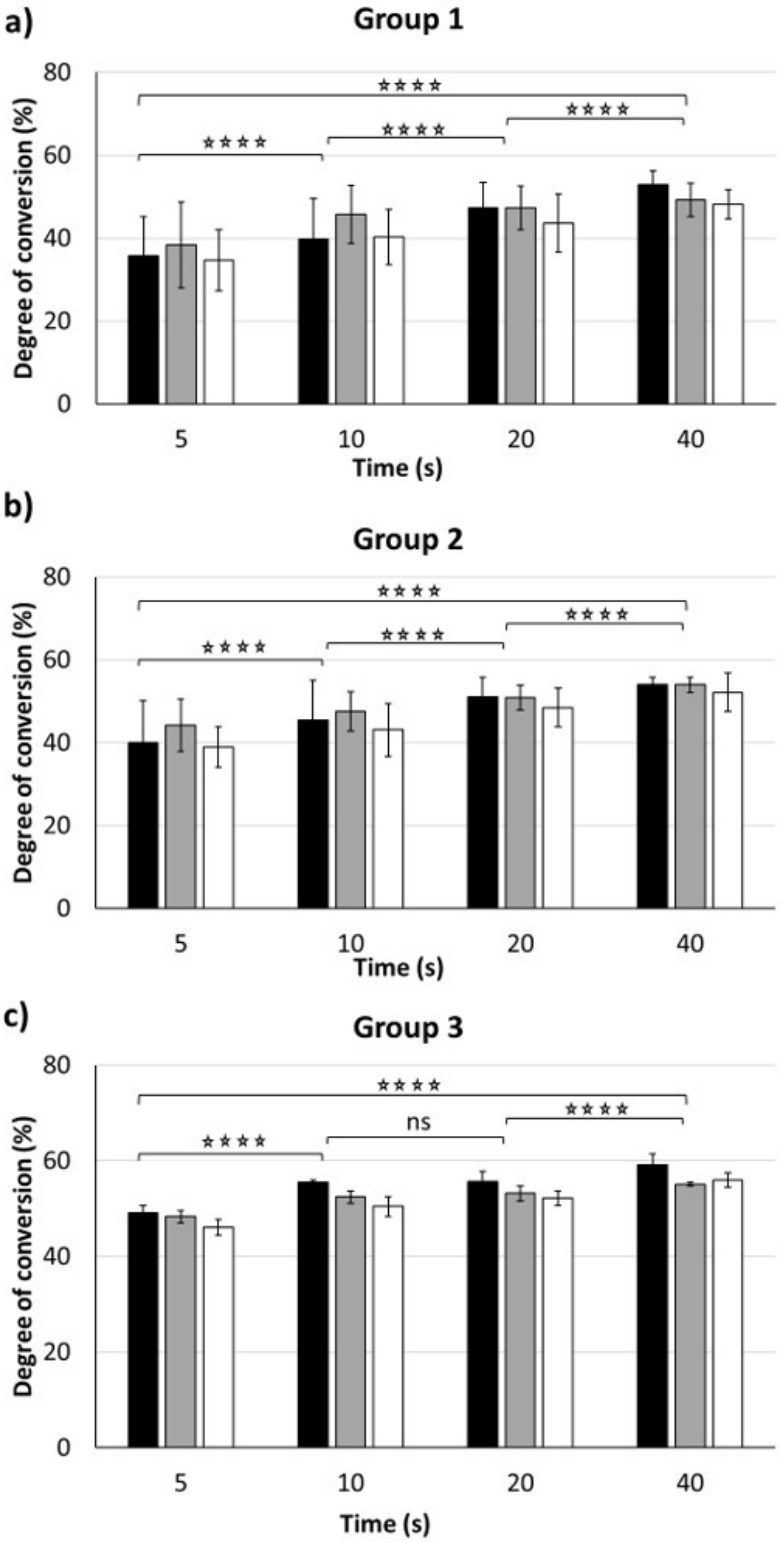


Fig. 4: Histograms of mean degree of conversion (n=3) for Filtek™ Supreme XTE (black bars), Ceram.x® (grey bars) and Tetric® EvoCeram (white bars) in terms of irradiation time and polymerization conditions for a) group 1, b) group 2 and c) group 3. Different number of asterisks indicate statistically significant differences between irradiation time groups using Wilcoxon test with 0.05 significance level (****$p < 0.00001$, ***$p < 0.001$, **$p < 0.01$, *$p < 0.05$, (ns) $p > 0.05$).

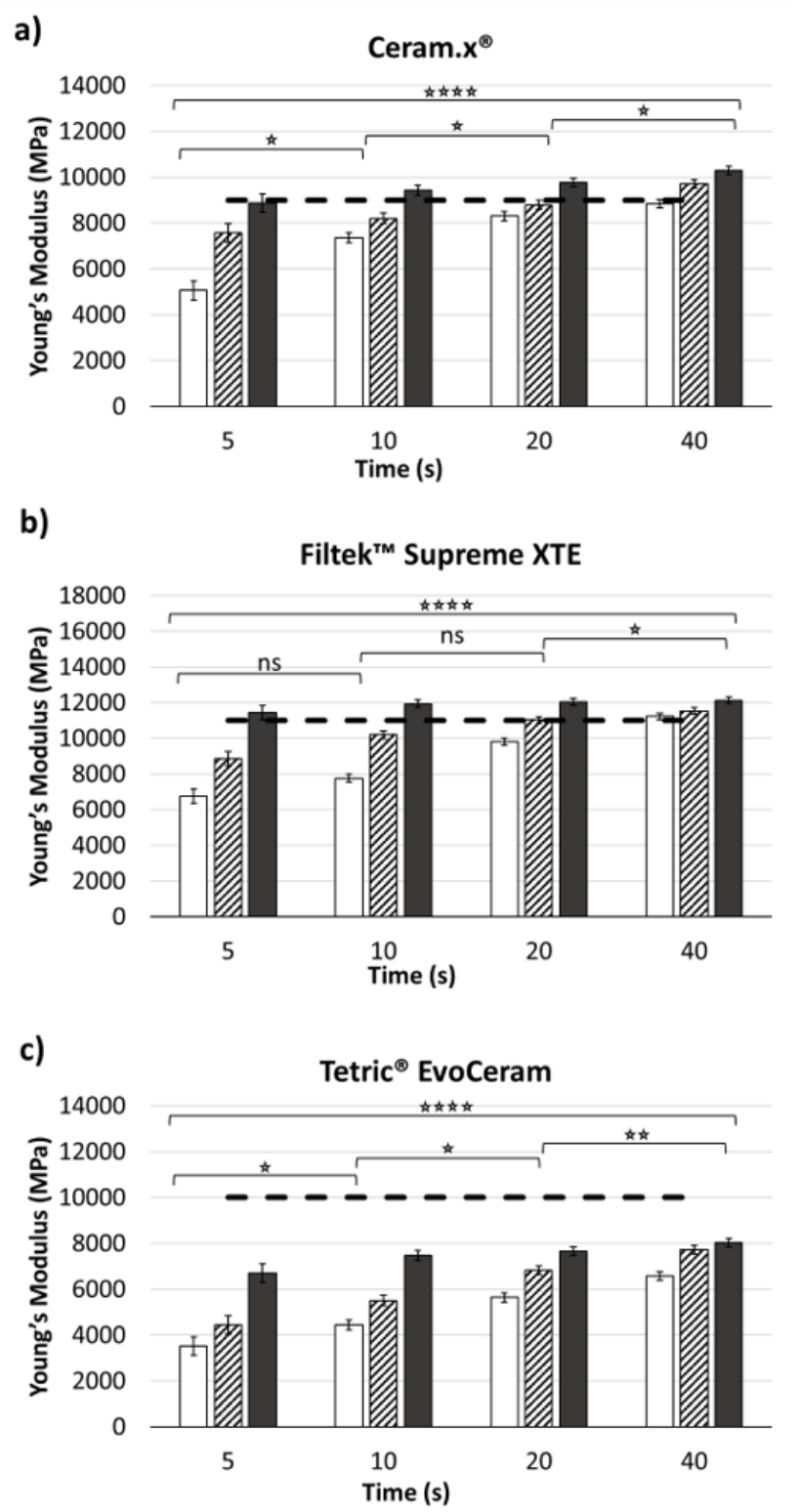


Fig. 5: Histograms of mean Young's modulus (n=6) in terms of polymerisation condition group (group 1: white bars, group 2: hatched bars and group 3: black bars) and irradiation time, in comparison with the value defined by the respective manufacturers (dashed line) for a) Ceram.x®, b) Filtek™ Supreme XTE and c) Tetric® EvoCeram. Different number of asterisks indicate statistically significant differences between irradiation time groups using Wilcoxon test with 0.05 significance level (****$p < 0.00001$, ***$p < 0.001$, **$p < 0.01$, *$p < 0.05$, (ns) $p > 0.05$).