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ORIGINAL ARTICLE

# Is the soft-start polymerisation concept still relevant for modern curing units?

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**Abstract** Shrinkage stress, degree of cure and mechanical properties are contradicting properties, forcing to a compromise between an adequate curing and low stress at the interface tooth-restoration. The purpose of this study was to quantify this relations for a micro-hybrid composite, by analysing in real time the development of degree of cure at depths of 2 and 6 mm, shrinkage stress and curing time until gelation, as well as the variation of micro-mechanical properties with depth, after curing with 13 regimes of one halogen and two light-emitting diode (LED) curing units. A nano-dynamic mechanical test was additionally performed on selected regimes (Ramp, Pulse and Fast Cure) of the same curing unit. The present study showed that the soft-start polymerization concept is still valid for less deep cavities (2 mm), even by curing with high-power LED curing units, since a soft-cure polymerization resulted in a delayed gel point and a lower shrinkage stress, keeping simultaneously the degree of cure and mechanical properties constant. At 6 mm depth, curing with soft-start regimes resulted in a significant decrease in degree of cure, although this decrease was less than 10%, while the mechanical properties were maintained.

**Keywords** Degree of cure · Mechanical properties · Shrinkage stress · Nano-DMA

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## Introduction

Polymerisation shrinkage stress is still considered as being the main drawback of methacrylate-based restorative dental materials, being often discussed in relation to clinical negative effects like marginal staining, restoration fractures, microleakage [1], debonding, recurrent caries or postoperative pain. However, no clear correlation between contraction stress in dental composites and the success of a composite restoration was found clinically [2, 3]. New materials having reduced internal stress as a result of low polymerization shrinkage are predicted to dominate the market in the future, even before a complete understanding of the clinical consequence of shrinkage was achieved [3].

To reduce shrinkage stress at the interface tooth-composite for a given composite material, numerous approaches are proposed, most of them being related to the chosen cavity configuration (C-factor) [1], the method of cavity reconstruction [4], the introduction of stress absorbing intermediate layers [5] or the selection of the curing method [6, 7]. The shape of a preparation is often described by means of the configuration factor (C-factor), the ratio of bonded to unbonded surface area of the restoration [8]. Good contraction stress compensation is possible only for restorations in which the material can flow during the pre-gel state from the free surfaces to the bound surface. Class IV restorations are most favourable, since they offer several free surfaces, whereas restorations of class I cavity show the most unfavourable cavity configuration; but also, a slower polymerization rate is expected to increase the ability of a material to flow, without damaging its internal structure [7]. Manipulations of curing protocols using stepped, pulsed or ramped energy delivery are therefore proposed. Among these approaches, soft-start curing, where irradiation begins with a low intensity, followed by a full light intensity, and pulse curing, being similar to soft-start curing except that a dark interval is included between the initial low intensity and the following full-intensity curing, have been the subject of extensive investigations [9–14]. The selection of the appropriate polymerization procedure for a restorative composite implies, however, a compromise between opposite material characteristics. A high degree of cure (DC) can improve the mechanical properties, chemical stability and longevity of the restorative material [15–17] but mainly stands in contrast to requirements of low polymerization stress values. It was shown that a soft-start polymerisation reduce polymerisation shrinkage and temperature rising [6] as well as lower the solubility by equivalent or even higher hardness values [18]. Also, improved integrity of the composite/tooth interface [9, 12, 19, 20] without compromising the mechanical properties of the cured dental composite were reported [12]. On the other hand, several studies found that the soft-start polymerisation reduce the polymerization shrinkage being however associated with a slight reduction in DC [11, 13, 14].

The aim of this study was to investigate the relation between DC, shrinkage stress and micro-mechanical properties in a micro-hybrid composite and to select curing protocols being able to reduce shrinkage stress and, at the same time, to maintain good mechanical characteristics and a high DC. This was done by analysing the influence of 13 different light-curing regimes—comprising one quartz-tungsten-halogen (QTH) and two light-emitting diode (LED) curing units—at different irradiation times and by simulating clinical relevant filling depth. Further, we aimed to analyse the effect of a soft-start polymerisation also at nano-scale for three selected regimes (Ramp, Pulse and Fast Cure) of the same curing unit, by mapping the nano-dynamic mechanical properties across the different composite zones.

The null hypotheses tested were:

1. That the soft-start technique would not affect the measured properties (DC, shrinkage and mechanical properties) compared to conventional high intensity irradiation by the same unit
2. That reduction of light intensity would not significantly reduce the DC as well as the mechanical properties at 2 and 6 mm depth.

## Materials and methods

The curing behaviour of a micro-hybrid composite (EsthetX®, Dentsply, Caulk, Milford, DE, USA; LOT: 0505002629) was evaluated by assessing the DC, variation of hardness and modulus of elasticity, as well as shrinkage stress after polymerizing the material with 13 curing regimes using one halogen and two LED curing units (Table 1). The composite matrix consists of Bis-GMA adduct, Bis-EMA adduct and triethylene glycol dimethacrylate TEGDMA, whereas the filler comprise barium fluoro-alumino-borosilicate glass with a mean particle size below 1 μm and nanofiller silica with a particle size of 0.04 μm. The total inorganic filler content of the composite is 77 wt.% and 60 vol.%, respectively.

**Table 1** Curing units and curing regimes, degree of conversion at 2 and 6 mm depth as well as shrinkage stress as function of the curing regime

| Type | Curing unit | Curing mode | Time (s) | $DC_{2mm}$ (%) | $DC_{6mm}$ (%) | Shrinkage stress (MPa) |
|---|---|---|---|---|---|---|
| LED | Mini L.E.D (Satelec)<br>Serial No.:114-6064 | Fast Cure | 10 | 52.0 bcd (2.0) | 51.8 bc (1.6) | 3.8 a (2.1) |
| | | | 20 | 54.1 defgh (1.3) | 54.5 efgh (2.9) | 4.5 d (2.4) |
| | | | 40 | 55.3 ghi (3.5) | 54.6 efgh (0.8) | 5.0 e (2.3) |
| | | Pulse | 12 | 54.2 defgh (2.0) | 46.3 a (1.8) | 4.0 ab (2.7) |
| | | | 24 | 55.3 ghi (1.3) | 52.6 bcdef (1.4) | 4.6 d (0.7) |
| | | | 48 | 55.7 hi (1.0) | 54.0 defgh (2.6) | 4.5 cd (2.4) |
| | | Ramp | 20 | 52.4 bcde (1.3) | 48.1 a (1.2) | 4.2 bc (1.7) |
| | Bluephase (Ivoclar Vivadent)<br>Serial No.:1547581 | HIP | 10 | 54.0 cdefgh (1.1) | 51.7 b (1.0) | 5.1 e (3.3) |
| | | | 20 | 55.0 ghi (2.5) | 55.6 hi (1.8) | 6.0 f (1.9) |
| | | | 40 | 57.1 i (2.7) | 56.0 hi (3.0) | 6.5 g (3.1) |
| Halogen | Astralis 10 (Ivoclar Vivadent)<br>Serial No.:013336 | HIP | 10 | 54.8 fgh (1.2) | 53.3 bcdefg (2.5) | 6.0 f (4.5) |
| | | | 20 | 54.8 fgh (1.3) | 55.4 ghi (1.6) | 7.4 h (3.0) |
| | | | 40 | 55.1 ghi (3.2) | 55.7 hi (0.9) | 7.9 i (3.3) |

Lowercase letters indicate statistically homogeneous subgroups (Tukey's honestly significant difference test, $\alpha=0.05$). The Pulse program of the curing unit MiniLED emit ten pulses in 12 s, equivalent with a 10-s continues exposure

*HIP* high intensity program

## Curing units and curing conditions

Two of the tested curing units, the LED Bluephase and the QTH Astralis 10, were equipped with a light-concentrating (Turbo) guide tip, whereas the LED unit MiniLED was equipped with a standard light guide tip. Besides a Fast Cure regime at a constant maximum light intensity, the MiniLED curing unit also provided two other curing modes: ramped light intensity within 10 s followed by an addition 10 s at maximum intensity, as well as an intermittent pulsed light emission. As for the Bluephase and Astralis 10 curing units, they were used in the standard curing mode (high intensity program).

Spectral distributions and irradiance of the tested curing units were determined by means of a calibrated fibre optic, spectrally resolving radiometer equipped with an integrating sphere (S2000, Ocean Optics, Dunedin, FL, USA; Fig. 1). Total irradiance was obtained by integrating the irradiance as a function of the wavelength over the entire wavelength range, divided by the effective area of the curing unit tip. Diameter of the tip was measured with a digital micrometer, whereby effective area was defined as the area of the tip without cladding. To determine the energy density, the irradiance was multiplied by the curing time for each curing unit and regime.

## Degree of cure (DC)

To evaluate the DC, two different sample geometries were considered:

1. One 2-mm high increment in a white Teflon mould of 2 mm height and 4 mm diameter, cured by applying the curing unit directly on the sample surface ($n$=5);
2. Three consecutive increments—each 2 mm high—in a white Teflon mould of 6 mm height and 4 mm diameter, cured by applying the curing unit on each increment surface from the top of the 6-mm high mould ($n$=5).

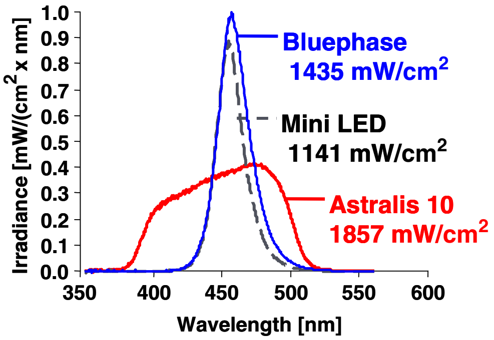

**Fig. 1** Normalised spectral emissions of the tested curing units. In addition, total irradiance is indicated

Real-time measurements were made with a Fourier transform infrared (FTIR) spectrometer with an attenuated total reflectance (ATR) accessory (Nexus, Thermo Nicolet, Madison, WI, USA). Therefore, the non-polymerized composite paste was put directly on the diamond ATR crystal in the mould as described above. FTIR spectra were recorded in real time for 20 min at the bottom of the samples irradiated according to the curing protocol presented in Table 1. Diameter of measured surface was 800 µm, wave number of the spectrum ranged between 4,000 and 650 cm$^{-1}$, and the FTIR spectra were recorded with four scans at a resolution of 8 cm$^{-1}$.

To determine the percentage of the remained unreacted double bonds, the degree of conversion (DC) was measured by assessing the variation in peak height ratio of the absorbance intensities of methacrylate carbon double bond peak at 1,634 cm$^{-1}$ and that of internal standard peak at 1,608 cm$^{-1}$ (aromatic carbon double bond) during polymerization, in relation to the uncured material.

$$\mathrm{DC}_{\mathrm{Peak}}\% = \left[1 - \frac{\left(1{,}634/1{,}608\ \mathrm{cm}^{-1}\right)_{\text{Peak height after curing}}}{\left(1{,}634/1{,}608\ \mathrm{cm}^{-1}\right)_{\text{Peak height before curing}}}\right. \times 100$$

## Micro-mechanical properties

To analyse the quality of polymerization within the 6-mm high samples, hardness and modulus of elasticity profiles ($n$=5) through the middle of the samples were measured. For this purpose, samples were stored in distilled water after curing for 24 h at 37°C, sectioned in the middle prior to testing with a slow-speed diamond saw (Isomet low speed saw, Buehler, Germany) under water and polished with a diamond suspension (mean grain size: 1 µm). Measurements were made with an automatic microhardness indenter (Fischerscope H100C, Fischer, Sindelfingen, Germany) starting from 0.1 mm under the surface, with 100-µm intervals between the measuring points. The test procedure was carried out force-controlled, where the test load increased and decreased with constant speed between 0.4 and 500 mN. Load and penetration depth of the indenter were continuously measured during the load–unload hysteresis. Universal hardness is defined as the test force divided by the apparent area of indentation under the applied test force. From a multiplicity of measurements stored in a database supplied by the manufacturer, a conversion factor between Universal hardness and Vickers hardness was calculated and input into the software, so that the measurement results were indicated in the more familiar Vickers hardness units. Indentation modulus was calculated from the slope of the tangent of indentation depth curve at maximum force. Hardness and modulus of elasticity variations with depth were calculated for each group as a curve-fitted line, based on data from five samples (300 measuring points; Table 2).

### Shrinkage stress and gel point

Further, the shrinkage stress ($n$=8) of the tested material was investigated with a Stress–strain Analyzer (SSA T80, Engineering Consultancy Peter Dullin Jr, Munich, Germany), which measured continuously the contraction force generated by polymerizing the restorative material, with compensation of the compliance of the machine. The tested curing units (Table 1) were positioned directly on the samples' surface. The composite specimens were placed between two aluminium attachments with a distance of 4 mm and a height of 2 mm. One attachment was connected to a load sensor and the other to a Piezo-actuator. A PTFE-coated plastic tray was attached to the testing machine. Two opposing attachments together with the plastic mould simulate a 4×4×2-mm cavity with a C-factor of 0.3. The functional surfaces of the two attachments were cleaned and coated with ROCATEC-Pre, -Plus (3M-ESPE, Seefeld, Germany), followed by further application of a silane-coupling agent (ESPE-Sil, 3M-ESPE, Seefeld, Germany). The tested composite was then applied in one 2-mm increment. The contraction force generated by polymerizing the composite was continuously measured and recorded for 300 s after photo-initiation. Each experiment was conducted at room temperature and repeated eight times for each material. Further, the time needed to exceed a force threshold of 0.5 N—arbitrarily defined as the time until gelation—was expressed as gel point.

### Nano-dynamic mechanical properties

To analyse the effect of soft-start polymerisation on the polymer matrix, a nano-dynamic mechanical test (Triboindenter, Hysitron Inc., Minneapolis, MN, USA) was performed on a sample area of $5\times5$ μm$^2$ of the samples cured with the miniLED unit in the 20 s regimes (Fast Cure, Pulse, Ramp, $n$=3). The measurements were performed at the bottom of the 2-mm samples. During a test, the indenter—a Berkovitch diamond indenter with a 100-nm tip radius—scanned on the surface in a raster mode to image the sample. A lock-in amplifier was then sending a dynamic signal to the drive plate of a transducer, causing the tip to oscillate during the image. The frequency of the sinusoidal force was 120 Hz and the dynamic force, 5 μN. This dynamic load was subsequently analysed using the lock-in amplifier to measure the amplitude (X) and phase shift (Φ) of the signal, which allowed to calculate the nano-dynamic mechanical parameter: storage-modulus (SM), loss-modulus (LM), complex-modulus (CM) and loss-factor tan δ as described in Asif et al. [21] and Ilie et al. [22].

During the imaging process, the system continuously monitored the stiffness of the sample and plotted this stiffness as a function of the position on the sample. The dynamic mechanical parameters mentioned above are so calculated at each pixel in the image. This is the equivalent of performing an indentation test at each pixel in a 256×256 image, or 65,536 tests in a single image.

Results were compared using one-way analysis of variance (ANOVA) and Tukey's honestly significant difference (HSD) post hoc test as well as a multivariate analysis ($\alpha$=0.05; Statistical Package for the Social Sciences 15.0).

**Table 2** Curing units and curing regimes, Vickers hardness (HV) at 0.1, 2 and 6 mm depth

| Curing unit | Curing mode | Time (s) | HV 0.1mm | HV 2mm | HV 6mm |
|---|---|---|---|---|---|
| Mini L.E.D (Satelec)<br>Serial No.:114-6064 | Fast Cure | 10 | 95.4 efg (3.2) | 92.7 bcdefg (9.6) | 91.3 bcdefg (7.2) |
| | | 20 | 92.2 bcdefg (6.7) | 97.1 efg (7.0) | 89.6 efg (5.2) |
| | | 40 | 93.6 cdefg (3.8) | 93.6 cdefg (2.8) | 88.8 bcdefg (8.3) |
| | Pulse | 12 | 88.9 bcdefg (4.4) | 88.9 bcdefg (21.8) | 72.6 a (16.5) |
| | | 24 | 87.6 abcdefg (18.2) | 87.4 abcdefg (24.3) | 85.0 abcdefg (9.9) |
| | | 48 | 87.1 abcdefg (10.9) | 86.1 abcdefg (14.0) | 81.0 abcde (7.9) |
| | Ramp | 20 | 87.3 abcdefg (9.1) | 86.6 abcdefg (12.0) | 78.7 abcd (9.5) |
| Bluephase (Ivoclar Vivadent)<br>Serial No.:1547581 | HIP | 10 | 94.1 defg (7.5) | 87.3 abcdefg (8.5) | 78.1 abc (5.6) |
| | | 20 | 87.2 abcdefg (7.8) | 85.6 abcdefg (6.3) | 77.4 ab (5.0) |
| | | 40 | 95.0 efg (3.3) | 95.6 efg (4.5) | 84.2 abcdefg (14.5) |
| Astralis 10 (Ivoclar Vivadent)<br>Serial No.:013336 | HIP | 10 | 94.6 efg (3.0) | 91.2 bcdefg (10.9) | 91.6 bcdefg (7.0) |
| | | 20 | 95.7 efg (2.7) | 99.8 g (8.0) | 89.9 bcdefg (5.0) |
| | | 40 | 91.3 bcdefg (4.8) | 86.5 abcdefg (8.0) | 80.9 bcde (7.8) |

Lowercase letters indicate statistically homogeneous subgroups (Tukey's honestly significant difference test, $\alpha$=0.05)

*HIP* high intensity program

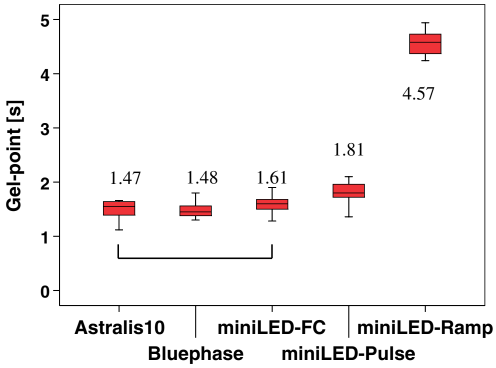

**Fig. 2** Gel point as a function of curing unit; *FC* Fast Cure

## Results

Normalised spectral emissions of the four tested curing units are presented in Fig. 1. Highest irradiance was measured for the halogen curing unit, Astralis 10 (1,857 mW/cm$^2$), whereas LED curing units, Bluephase and MiniLED, with a narrow band spectral output, achieved irradiances of 1,435 and 1,141 mW/cm$^2$, respectively.

One-way ANOVA analysis of the shrinkage stress results is listed in Table 1. Homogenous subgroups can be identified by the same superscript. Post hoc multiple pairwise comparisons with Tukey's HSD test revealed significant differences ($p<0.05$) in maximum contraction stress among the curing unit types and regimes. Within one curing unit, a significant increase in shrinkage stress with increased curing time was measured. The halogen curing unit, Astralis 10, caused the highest shrinkage stress after a curing time of 20 and 40 s, respectively. The effect of soft-start polymerization on the curing behaviour of the composite was assessed with three curing regimes of the LED curing unit MiniLED: Fast Cure 20 s, Ramp 20 s, and Pulse 20 pulses (24 s). The time needed to exceed a force threshold of 0.5 N was arbitrarily defined here as time until gelation. For both soft-cure regimes Pulse (gel point=1.81 s) and Ramp (gel point=4.57 s), a significant delay in the gel point compared to the other regimes was measured. As for the halogen curing unit Astralis 10, the LED curing unit Bluephase and the Fast Cure regime of MiniLED, no statistically significant differences in their gel points were recorded (Fig. 2). The delayed gel point in the Ramp regime caused reduced final polymerization shrinkage in comparison to the Fast Cure regime, whereas the Pulse and Fast Cure regime had a similar effect on the final shrinkage stress. The slow initiation of polymerization in the Ramp regime also caused a slower rise of the degree of conversion in the first seconds, but nonetheless approached the other regimes as light intensity increased. The Pulse regime, on the other hand, caused a similar development in the degree of conversion as the Fast Cure regime with a continuous light emittance (Fig. 3). The shrinkage rate development in time (Fig. 4a) for the above-mentioned regimes also emphasises the delay in shrinkage for the Ramp regime, showing at the same time a comparable maximum shrinkage rate at the end of polymerization for the three regimes. As for the shrinkage rate, dependency with time within one curing unit (Fig. 4b), the maximal rate increased with increased curing time, whereas the curve shape during polymerization followed the same pattern for all curing times. For a given curing time, the shrinkage rate increased with increased irradiation of the used curing unit (Fig. 4c).

One-way ANOVA analysis of the FTIR spectroscopy (Table 1) revealed for the soft-start polymerization regimes Pulse at all measured curing times, for the Ramp regime, as well as for the 10 s regime of the LED unit Bluephase, a significantly lower degree of conversion (DC) at 6-mm

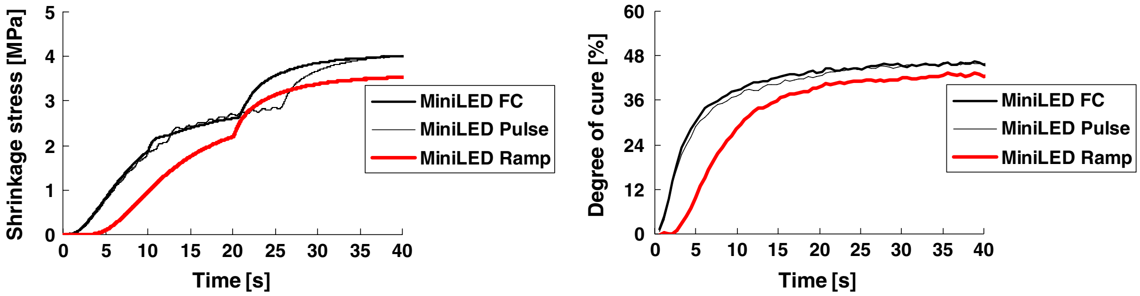

**Fig. 3** Influence of the soft-start polymerisation on the shrinkage force and degree of cure at 2-mm depth. Three curing regimes of the light-emitting diode (LED) curing unit MiniLED: Fast Cure 20 s, Ramp 20 s and Pulse 20 pulses (24 s) were compared. The time needed to exceed a force threshold of 0.5 N is arbitrarily defined as the time until gelation. The Ramp regimes caused a delay of the gel point and, consequently, a reduced final polymerization shrinkage in comparison to the Fast Cure regime, whereas the effect of the Pulse and Fast Cure regime were similar. Regarding the degree of cure, there are no statistically significant differences between the three regimes; the slower initiation of cure in the Ramp program becomes clearly visible as a slower rise of the degree of cure, whereas the Pulse regime causes a similar development of the degree of conversion as the continuous Fast Cure regime

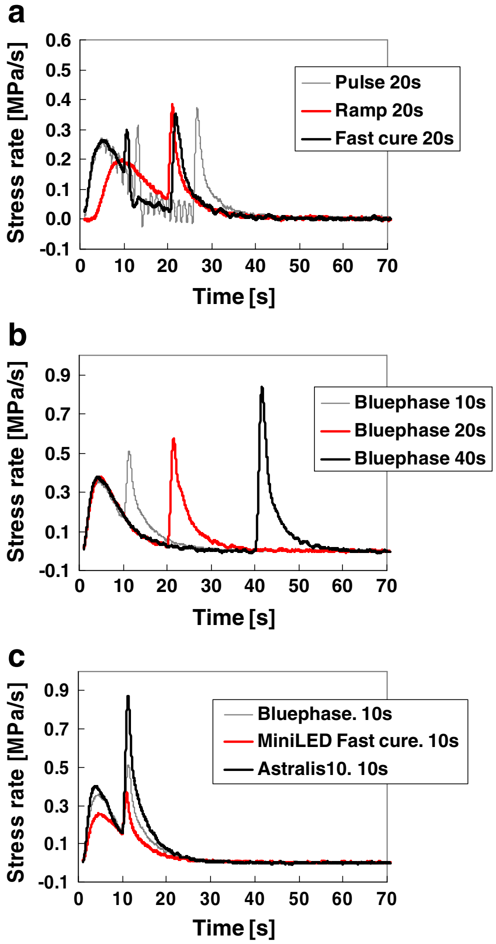

**Fig. 4** Shrinkage stress rate development with time (mean curves, $n$= 8); **a** Three curing regimes of the light-emitting diode (LED) curing unit MiniLED: Fast Cure 20 s, Ramp 20 s and Pulse 20 pulses (24 s) were compared. The Fast Cure and the Pulse programs have durations of 10 and 12 s, respectively; the curing unit must therefore be started again for a polymerisation time of 20 s, 20 respective pulses. This effect becomes visible in the curve caused by the drop in temperature after the end of the light exposure. **b** Curing unit Bluephase with three different curing times. The maximum shrinkage stress rate (Peak) increased with increased curing time. **c** Comparison of all continuous 10-s regimes. A lower shrinkage stress rate was observed at lower irradiation

depth compared to the DC at 2-mm depth. For all other regimes, the differences in DC as function of composite depth measured 20 min after photo-initiation was not significant, although the real-time measurements of the variation of DC in time showed significant differences during the first seconds after photo-initiation (Fig. 5).

At 2-mm depth—except the unit Astralis 10, where the DC was comparable for all curing times—no significant differences were found between a 10- and 20-s, respectively, between a 20- and 40-s curing. A 40-s curing resulted in significant higher DC values then a 10-s polymerization. In 6-mm samples, an extension of curing time from 10 to 20 s caused a significantly higher DC for all curing units.

The variation of hardness and modulus of elasticity with depth for the 6-mm samples layered in three increments, after curing for 10, 20, and 40 s exemplified for the LED curing unit Bluephase, is presented in Fig. 6. The profile of hardness and modulus versus depth showed a continuous distribution also at lower curing time, with only a slight decrease at the bottom of the third increment. This behaviour was representative for all curing units.

As regards the nano-dynamic mechanical analysis, in the four delimitated zones—filler (I), filler-interphase (II), matrix-interphase (III) and matrix (IV; Fig. 7)—the complex (CM) and storage moduli (SM) increased, while loss-modulus (LM) and loss-factor tan δ decreased from the matrix (IV) to the filler (I). The organic matrix, comprising the zones III and IV, reached a CM of 8.9 (1.7) GPa, an SM of 8.3 (1.7) GPa, an LM of 0.97 (0.22) GPa and a tan δ of 0.25 (0.06), showing no significant differences between curing with the soft-start programs—Pulse and Ramp—and the continuous regime Fast Cure.

A Pearson correlation analysis reveal that at 2-mm depth, DC correlates significantly with shrinkage stress (0.3), gel point (−0.2) and the micro-mechanical properties E (0.2) and HV (0.2). The energy density also correlates with all measured properties, presenting the best correlation with the shrinkage stress (0.8) followed by DC (0.4), gel point (−0.3) and micro-mechanical properties (0.3).

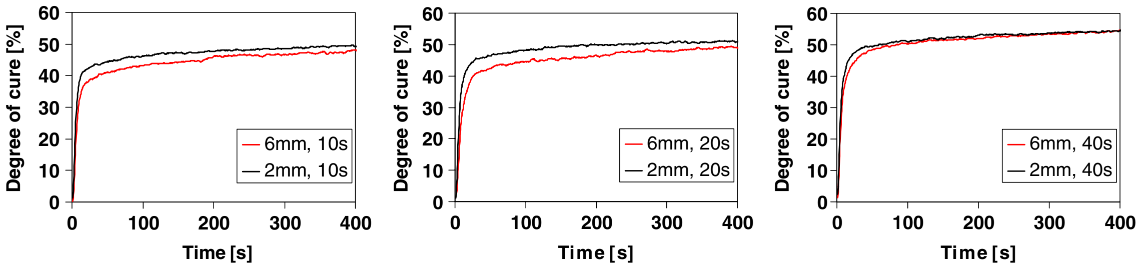

**Fig. 5** Development of the degree of cure at 2 and 6 mm depth by curing with the curing unit miniLED Fast Cure regime for 10, 20 and 40 s, respectively

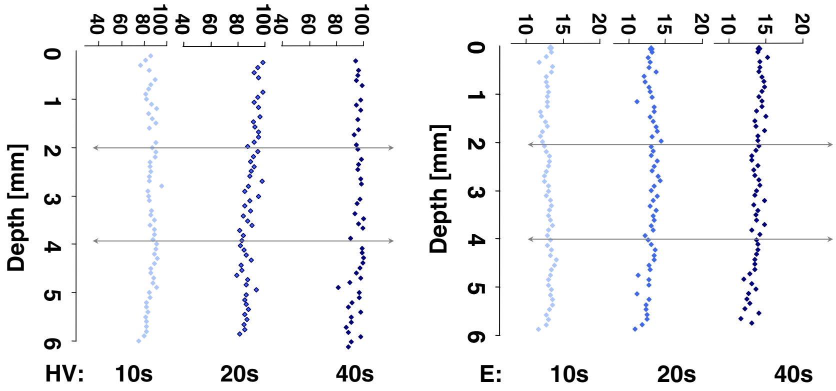

**Fig. 6** Variation of the hardness and modulus of elasticity with the depth after curing for 10, 20 and 40 s, exemplified for the light-emitting diode-curing unit Bluephase. Transferred to a large filling restored in three increments, these results show a continuous variation of the hardness with the depth for all polymerisation times

The influence of the parameters: "irradiation", "energy density", "curing time" and "composite depth" as well as their interaction product, were analysed in an ANOVA multivariate test. The shrinkage, gel point, DC and micro-mechanical properties were selected as dependent variables. The significance values of these four main effects were less than 0.05, indicating that they all contributed to the model. The partial eta squared statistic (Table 3) reports the practical significance of each term, based upon the ratio of the variation accounted for by the effect. Larger values of partial eta squared indicate a greater amount of variation accounted for by the model effect, to a maximum of 1. The cure-time performed the highest effect on the shrinkage, whereas the effect on DC was low, being even not significant regarding the micro-mechanical properties. Since the gelation occurred within the first seconds of photo-initiation, the measured polymerisation time—10, 20 and 40 s—was also not significant. The effect of sample depth on DC was low but significant, whereas on the micro-mechanical properties, no effect was measured.

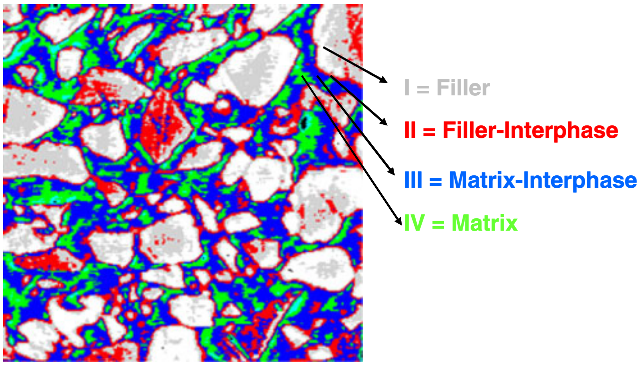

**Fig. 7** Variation of the dynamic mechanical properties (tan δ) exemplified for the Rampe regime, differentiating between four different zones: *I*=filler, *II*=filler-interphase, *III*=matrix-interphase and *IV*=matrix

## Discussion

For a given chemical composition of a light-curing resin-based composite, handling with antagonist properties like DC, mechanical properties and shrinkage could additionally improve the final quality of a restoration. The modulation of light intensity, implemented in the most commercial available curing units in use today, and the appliance of soft-start polymerisation protocols are nowadays well accepted by practitioners. However, the literature presents contradictory results in view of the effect of soft-cure protocols on reducing shrinkage stress. Besides positive effects by using a soft-start polymerisation [6, 9, 12, 18–20], also a decrease in final conversion was stated as a predominant reason for reduced shrinkage stress [11]. To judge these contradicting results, a closer view into the studies design must be done, since not only the sample geometry and volume but also the light intensity of the measured curing units differs consistently. The above-mentioned study, noting a decrease in final conversion after soft-start polymerisation [11], used, for example, curing protocols with a rather low light intensity (450 mW/cm$^2$), representing thus less than the half of the curing protocols analysed in the current work (>1,141 mW/cm$^2$).

Our data showed that some soft-start polymerization regimes like Pulse (10 s) and Ramp (20 s) lowered only at 6-mm depth significantly the degree of conversion, compared to the equivalent continuous regime of the same curing unit. At 2-mm depth, the polymerisation time and not the curing protocols influenced the DC. Within one curing regime, significantly lower DC values at 6-mm depth, compared to 2-mm depth, were found for the soft-start polymerization regimes, whereas for the continuous regimes, DC was not influenced by the curing depth. The differences in DC measured 20 min after photo-initiation were, however, too low to affect the micro-mechanical properties measured after storing the samples for 24 h in distilled water, which proved to be independent from the curing regime, performing a continuous distribution across

**Table 3** Influence of curing time, irradiation, energy density and composite depth on shrinkage, gel point, degree of cure (DC) and micro-mechanical properties; Vickers hardness HV and modulus of elasticity E (partial eta squared statistic)

| | Shrinkage | Gel point | DC | HV/E |
|---|---|---|---|---|
| Time | 0.711 | Not significant | 0.147 | Not significant |
| Irradiation | 0.911 | 0.207 | 0.216 | Not significant |
| Energy density | 0.722 | 0.911 | 0.267 | 0.227/0.373 |
| Depth | | | 0.01 | Not significant |

the depth. Since unreacted monomers could act in time as plasticizer of the polymer matrix, an increased DC is nevertheless preferable.

The development of DC at 2 and 6 mm depth within 20 min after polymerisation (Fig. 5) also demonstrated that a significant amount of polymerization occurred after the light was extinguished. When the irradiation stops, the remaining free radicals continue to propagate and terminate, although no new radicals are generated from initiation. The post-polymerization capability depends not only on the remaining monomer and on the system's cross-linking density and reacting species' mobilities but also on the radical concentrations and their lifetime after photo-initiation. Owing to the decreased light intensity and thus decreased radical concentrations at 6 mm depth, compared to 2 mm depth, the soft-start polymerization regimes Pulse at all measured curing times as well as the Ramp regime were nevertheless not able to compensate the differences in DC between 2- and 6-mm depths. Similar was valid also for a short curing time (10 s) with the unit Bluephase, leading thus to the recommendation to increase the curing time to at least 20 s in deeper cavities as well as to use therefore continuous curing programs. This recommendation is also assured by the observation that the variation of the micro-mechanical properties across the depth in simulated deep cavities, measured under similar curing and storage conditions, is material dependent, showing frequently a continuous distribution only for curing times of at least 20 s [10].

The efficiency of a soft-start polymerisation concept was analysed also at nano-scale. Therefore, the effect of the curing programs Fast Cure—20 s at a constant maximum light intensity—Ramp—ramped light intensity within 10 s followed by an addition 10 s at maximum intensity—and Pulse—intermittent pulsed light emission for 24 s—were compared. The amount of energy delivered from the Fast Cure and Pulse regime is equivalent (16.5 J/cm$^2$), making a direct comparison possible, whereas the energy density in the Ramp regime reached only 75% of the former two regimes (12.4 J/cm$^2$).

Since the mechanical characteristics at small dimensions differ substantially from the characteristics at micro and macroscopic range, it was necessary to include new experimental techniques to distinguish between the mechanical characteristics of nano-structures. In addition, the viscoelastic behaviour of composite materials must also be considered. The nano-dynamic mechanical analysis was found to be a suitable method to elucidate these aspects [22]. Considering a composite material, the interaction of the filler with the organic matrix cause local characteristics in the material, being theoretically explained by the concept of the boundary layer formation around the particles. Generally, the boundary layer thicknesses are determined by the kind and the degree of the reciprocal effect between the reinforcing particle surfaces and the polymer chains of the matrix, i.e. either by a physical (loops of molecule chains) or a chemical (e.g. by the coupling agent—silane) interaction. Owing to the very high filler loading rate (60 vol.%) in the analysed composite, the interparticle distance is extremely small, which means that the boundary layers around the particles touch themselves. A consequence of this fact is that the local ability of the matrix to deform is strongly lowered, since no or only less polymer material between the nano-particles stands ready for the initiation of such deformation processes. Thus, despite the high plastic polymer content, the brittle behaviour of resin-based composites can be explained. Within one curing regime, all measured dynamic mechanical parameters were found to be influenced by the region were they were measured. Proceeding from matrix (IV) to filler locations (I), the complex and storage moduli increased while loss-modulus and loss-factor tan δ decreased. However, at 2-mm depth, the differences between the nano-dynamic mechanical properties of the matrix after curing the composite with the three regimes of the unit miniLED—Fast Cure, Pulse and Rampe—at equivalent curing time, was found to be not significant, sustaining thus the results obtained at micro-scale as well as the DC-measurements.

## Conclusion

The tested null hypotheses were partially rejected: The soft-start polymerization concept is still valid, even by using high-power LED curing units. A soft-cure polymerisation resulted at 2 mm depth in reduced shrinkage stress compared with the continuous regime of the same curing unit, while simultaneously keeping the DC and mechanical properties constant, suggesting clinically a benefiting effect for less deep cavities. However, at 6 mm depth, the DC decreased slightly after using soft-cure regimes, while the mechanical properties remained constant.

**Conflict of interest** The authors declare that they have no conflict of interest.

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