Fast curing of restorative materials through the soft light energy release

R. De Santis [a,*], A. Gloria [a], D. Prisco [b], E. Amendola [a], L. Puppulin [c], G. Pezzotti [c], S. Rengo [b], L. Ambrosio [a], L. Nicolais [d]

[a] IMCB-CNR, Institute of Composite and Biomedical Materials, National Research Council, P.le Tecchio 80, Naples 80125, Italy
[b] Department of Odontostomatology and Maxillofacial Science, University of Naples Federico II, Via Pansini 5, Naples 80100, Italy
[c] Ceramic Physics Laboratory and Research Institute for Nanoscience, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, 606-8585 Kyoto, Japan
[d] DIMP, Department of Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, Naples 80125, Italy

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ABSTRACT

Objective. The effect of a novel light curing process, namely soft light energy release (SLER®), on shrinkage, mechanical strength and residual stress of four dental restorative materials (DEI experience, Gradia Direct, Enamel Plus HFO and Venus) was investigated.

Methods. Composite specimens were fast cured through high level of power density and soft light energy release. Temperature, linear shrinkage and light power measurements were acquired in parallel in order to assess the effect of light modulation on temperature and shrinkage profiles during the light curing process and the following dark reaction phase. The small punch test and Raman spectroscopy were adopted to investigate the effect of SLER® on mechanical strength and on internal stress, respectively.

Results. The soft light energy release photo-polymerization allows to reduce of about 20% the shrinkage rate and to increase the strength of fast light cured specimens. In addition, a more relaxed and homogeneous internal stress distribution was observed.

Significance. Properties of fast cured restorative materials can be improved by adopting the soft light energy release process.

1. Introduction

Composite resins are the most popular bearing materials for dental restorations [1–3]. Their optical properties (i.e. translucency and color) allow attractive aesthetic restorations [2–5]. These composites comprise a polymeric matrix, an inorganic reinforcement (i.e. fillers) and a coupling agent (e.g., silane). The organic matrix is mainly based on bisphenol A and glycidyl methacrylate (Bis-GMA) and/or other monomers such as triethylene glycol dimethacrylate (TEGDMA), 1,4-butanediol dimethacrylate (BDDMA) and urethane dimethacrylate (UDMA). The polymerization process takes place *via* a photo-activated reaction involving a photoinitiator system (e.g. camphorquinone and amine) contained in the composite resins [6–12]. In clinical practice, the light curing process (LCP) is an important issue affecting the mechanical stability of a restored tooth; the clinician has not only to deal with the proper choice of materials for the specific restoration but also with the technological process

involved in the place in service and setting of the specific composite.

The polymerization process forms covalent bonds between monomer, molecules which were originally subject to interaction through weaker van der Waals forces. Average intermolecular distances are therefore reduced [13], causing a reduction in free volume [14] which is non-homogeneously distributed through the developing crosslinked network. These effects macroscopically translate into volumetric shrinkage.

The physical and chemical properties of the cured material are strongly dependent on the LCP, which strongly influences the degree of polymerization. An inadequate degree of cure leads to higher *in vivo* wear and marginal breakdown [15–16], increased cytotoxicity [17–19] and lower mechanical properties (i.e. elastic modulus and strength) *in vitro* [20–22].

On the other hand, greater degree of cure of the polymeric matrix produces higher shrinkage and contraction stress [23,24]. In clinical practice, the amount of stress building up in the composite, partially constrained by the cavity wall, depends on boundary conditions. In particular, the ratio between bonded and unbonded surfaces, the stiffness of the surrounding tissue, the photo-polymerization kinetics of the composite material in relation to its chemistry and the quality of the dentin substrate onto bond together all determine the amount of shrinkage or contraction stress developing into the material [25–28].

Free and constrained volume polymerization, investigated through shrinkage and contraction stress, respectively, represent the extremes of the infinite set of boundary conditions occurring in dental practice. Unfortunately, the variability of the physical conditions related to teeth restoration prevents to exactly define the effect of the photo-polymerization process on the mechanical stability of the involved materials (i.e. composite and tissues), however if internal stress exceeds local bond strength the resin–dentin interface and the filler–matrix interface will be jeopardized [28]. Visco-elasticity further complicates the behavior of methyl methacrylate and dimethacrylate resins transforming, through polymerization, from a viscous phase to a highly cross-linked and vitrified network; the strain rate dependence of the mechanical properties of these resins are widely documented [11,19,29–33].

In this scenario, a variety of light curing units have been developed in order to optimise the LCP of dental restorative materials [34]. Quartz–tungsten-halogen represents the most common light source for curing dental composites [35–38]. Other fonts of light source, derived from a voltaic arch generating in mercury vapor or xenon bulbs [21,22,38] and the argon LASER [39,40], have also been employed in dental practice. More recently, light emitting diode (LED) represents the alternative light source to traditional halogen units, the main advantage of the LED source is that its wavelength spectrum is narrow and can be precisely calibrated on camphorquinone absorption wavelength. Consequently, this source emits only light which is useful for curing the material thus providing high efficiency which in turns allows the design of a comfortable lightweight curing device [41,42].

A reciprocal relationship between light power density and exposure time on conversion of resin based composites has been observed [35]. Accordingly, the advantage of using high power curing devices is that the time required for the polymerization process may be reduced, hence both the patient and the clinician benefit from a fast curing process. Moreover, errors related to the positioning of the light guide tip on the tooth to be restored are reduced, if compared to positioning errors occurring over a prolonged exposure time. Unfortunately, the hypothesis of reciprocity between light power density and exposure time on mechanical properties is not fully satisfied, especially when high power units are used [21]; mechanical properties of fast cured composites are lower than those obtained using similar energy level by means of low power density [21,22]. Modulation of light intensity has been widely investigated in order to improve the performance of both light curing units and the cured dental composites. The main attempts in order to optimize the light curing process through the modulation of light intensity are based on soft start, pulsed and delay photo-polymerization [39,43,44]. The main effect of the soft start, pulsed and delay photo-polymerization modulation is to shift in a time domain the gel point [45,46], that is the point at which the resin is cross-linked into a three dimensional network. However, the advantage of using a light delay is controversial [47,48]. Increased softening after ethanol storage has been measured [49], but a remarkable reduction of shrinkage stress has been detected through two light step curing involving the soft pre-curing [46]. Although the marginal gap and the stress raising at the dental tissue–composite interface may benefit from the soft start light modulation [46,49], a decrease of the degree of cure is also recognized [50]. In the last decades a strong effort has been devoted to measure shrinkage or contraction stress developing in dental composites as a function of the light source and light modulation process [25,43,51–54]. Interestingly, shrinkage and stress profiles recorded during LCP [46,51–54] present a marked discontinuity as the light source is switched off, and this discontinuity is more pronounced as the light power is increased [53]. It is important to point out that as the light source is switched off the polymeric matrix of the composite is already cross-linked and possibly vitrified, and it behaves as a visco-elastic solid or a composite whose matrix is in a glassy state [11]. Therefore, the material has a low damping capability, especially if high rate of building-up stress is developed [24]. Moreover, in clinical trials, the composite material interacts with the surrounding dental tissues [55], therefore high rate of stress contraction rising as the light is switched off will be directly transferred to the adhesive layer and to tissues, thus compromising the dentin–composite interface [28].

In order to reduce the rate of contraction stress or shrinkage developing as the light is switched off, we investigated the effect of a novel curing process [56] based on the Soft Light Energy Release (SLER® [57]) on the composite shrinkage, strength and residual stress. Briefly, through the SLER® process, light density is gradually reduced before the curing unit switches off (Fig. 1a). This light modulation allows to control the cooling process of the composite (Fig. 1b). This novel approach aims to reduce the thermal effect on shrinkage (Fig. 1c), by slowly reducing the light energy at the end of a high power LCP. Within all the restrictions of this *in vitro* investigation, it will be shown that by avoiding sharp cooling effects through SLER®, mechanical strength and stress distribution into the composite improve.
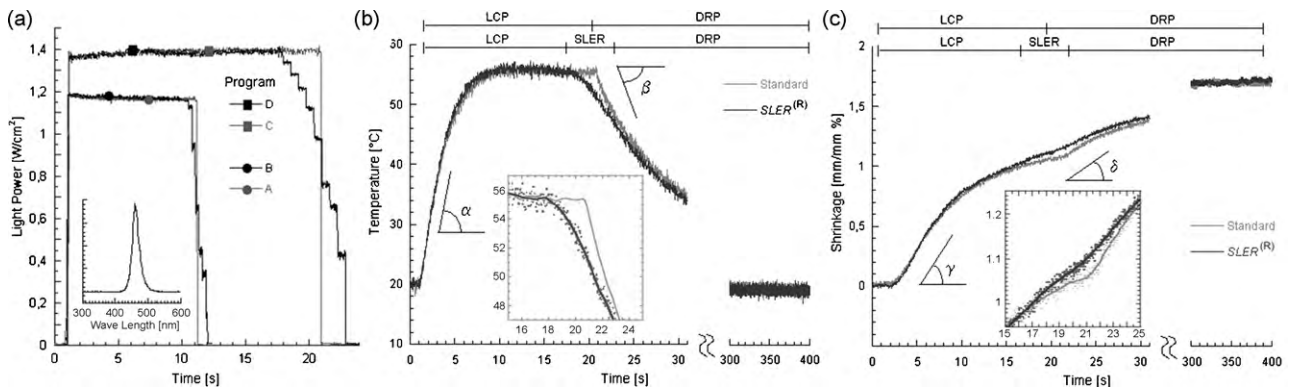
Fig. 1 – Power curves of the Mectron Starlight unit incorporating the SLER® process, the inner box depicts the wavelength distribution (a); effect of the SLER® process on temperature profile (b); effect of the SLER® process on shrinkage profile (c).

2. Materials and methods

The Mectron Starlight curing unit (Mectron Spa Genova, Italy) incorporating the SLER® process was used (Fig. 2a). The maximum power output measured by the Demetron LED radiometer (Kerr Corporation, USA) was 1400 mW/cm². This curing unit allows to supply a standard or a SLER® power curve. The standard curing conditions consists of a constant power output at the maximum intensity level, while the SLER® power curve consists of a constant step at the maximum
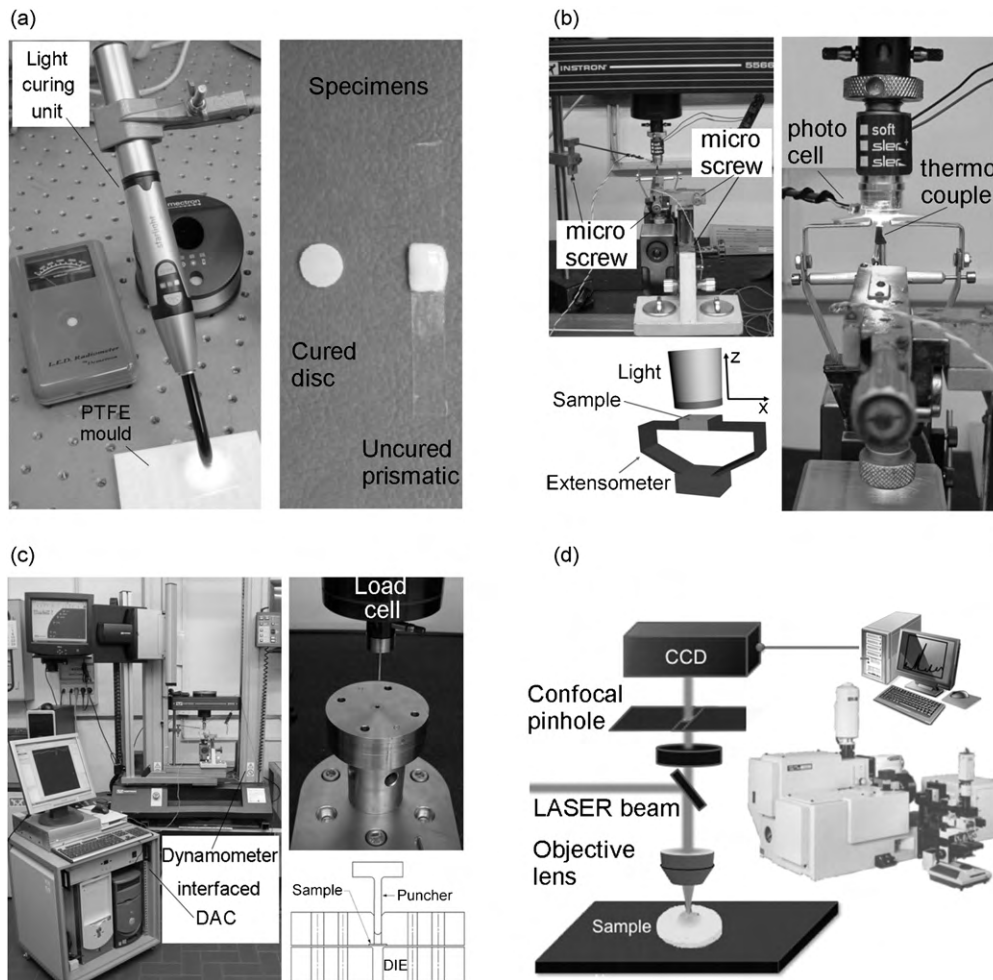

Fig. 2 – Experimental set-up. Mectron Starlight Sler unit and PTFE moulds used to realise prismatic and disc specimens (a); shrinkage testing set-up showing sensors used for on line light power and temperature measurements (b); stainless moulds and mechanical set-up used to perform the small punch test (c); RAMAN equipment showing the set-up procedure (d).

Table 1 – Light curing conditions used to polymerize composite materials.

LCP	Power (mW/cm^2)	Exposure time (s)	SLER time (s)	Energy dose (J/cm^2)
A	1200	10	–	12
B	1200	9	2	12
C	1400	20	–	28
D	1400	17.5	5	28

power followed by a soft light energy release (Fig. 1a). Table 1 reports light curing conditions adopted to polymerize composite materials.

Shade A2, DEI Experience (DEI Italia, Italy), Gradia Direct (GC, Japan), Venus (Heraeus Kulzer, Germany) and Enamel Plus HFO (Micerium, Italy), composite materials were used. The polymeric matrix of Gradia Direct is UDMA, while the other composites are based on a mixture of Bis-GMA, TEGDMA, and BDDMA. Table 2 reports the polymeric matrix composition and weight amount of the investigated composites.

Linear shrinkage was investigated up to 400 s using composite specimens obtained from prismatic PTFE moulds of 5.0 mm × 5.0 mm × 1.5 mm (Fig. 2a). A Mylar strip (Fig. 2a) was used to handle the composite and to position this specimen between the mechanical arms (Fig. 2b) of a modified Instron extensometer (Instron, UK). The C-factor [25], that is the ratio between bonded and unbonded surfaces, was 0.2. Programs C and D (Table 1) provide an energy of 28 J/cm^2 were used to polymerize composite materials. Shrinkage measurements were performed in the direction perpendicular to the light curing front (direction x of Fig. 2b) Shrinkage, temperature and light power measurements were performed in parallel. A filtered photocell obtained from a Demetron LED radiometer (Kerr Corporation, USA) was used to monitor light power level (Fig. 2b). This approach has already been adopted to trigger shrinkage measurements [58]. Disposable K-type thermocouples were used to measure temperature profiles during LCP and DRP. The mini-screws of a micromanipulator facilitated the gentle and precise positioning of the thermocouple in the side of the specimen opposite to the light tip guide (Fig. 2b). On line light power, linear shrinkage and temperature measurements were performed using the National Instrument DAC (National Instruments, USA) driven by Signal Express software (National Instruments, USA). Data were acquired at a speed of 50 p/s. For each composite 20 specimens were used equally divided into two sub-groups according to the LCP (i.e. standard or SLER® process).

Mechanical properties were investigated using the small punch test set-up (ASTM F 2183) which covers the determination of mechanical behavior by small punch testing of miniature disk specimens (Fig. 2a) having a thickness of 0.5 mm and diameter of 6.4 mm. The diameter of these specimens is lower than the diameter of the light guide tip of the curing unit, therefore specimens have been light cured through a single step light shot. These specimens were polymerized providing a light energy of 12 J/cm^2 using programs A and B (Table 1). The rationale for using an amount of energy lower than that used for shrinkage specimens is based upon on specimen thickness [59,60]. Stainless steel moulds were manufactured to perform small punch tests (Fig. 2c) at a speed 0.5 mm/min. For each composite, 20 specimens were used equally divided into two sub-groups each of which underwent one of two different LCPs, i.e. the standard or SLER® process.

For the DEI composite, internal stress of disc specimens (Fig. 2a) was detected through Raman piezo-spectrometry, the consistency of this technique relies on a linear correlation existing between Raman band broadening and stress reported for polymers such as polyethylene [61,62]. Briefly, a probe volume is identified into the material through the focal point of a LASER beam (Fig. 2d). The observed intensity of Raman band is interpreted as an intensity distribution of scattered light around the focal point, described by the probe function. Raman band broadening is related to the frequency distribution of the light scattered by each aromatic ring, thus depending on the deformation distribution of benzene groups inside the probe volume [63,64]. The T64000 Horiba/JobinYvon spectrophotometer equipped with a green argon LASER (wavelength of 514 nm) was used. Spectra were collected from the surface of each specimen down to a maximum depth of 150 μm at step of 25 μm (position accuracy of 0.1 μm). Disc specimens were polymerized in PTFE moulds (Fig. 2 a) using programs A and B (Table 1) defining the standard and the SLER® samples, respectively. A Mylar strip was used to cover the side of the composite during the LCP in order to prevent air inhibition. 10 specimens were used equally divided in two sub-groups according to LCP (i.e. standard and SLER® process). Control specimens were represented by relaxed specimens obtained from a sample of standard cured specimens and a sample of SLER® cured specimens which underwent a heating step up to 100 °C and a slow cooling (relaxation step) to room temperature at 1 °C/min. The not-cured composite paste was used as reference or blank control. Data were expressed through full width at half maximum (FWHM) of the Raman band located at 1610 cm^{-1} associated to the in-plane stretching vibration mode of the aromatic ring.

Table 2 – Polymeric matrix composition of the investigated restorative materials.

Material	Code	Polymeric matrix	Weight amount (%)
DEI Experience	DEI	BisGMA, UDMA, TEDMA	22.5
Gradia Direct	GRD	UDMA	25
Enamel Plus HFO	EPH	Bis-GMA, UDMA, BDDMA	25
Venus	VNS	Bis-GMA, TEGDMA	25

Table 3 – Thermal, shrinkage and mechanical properties of restorative materials polymerized through standard curing process. Values within columns displaying different superscript letter were significantly different ($p < 0.05$).

Composite	Standard light curing						
	LCP			DRP			
	Temperature rate α (°C/s)	Shrinkage rate γ (%/s)	Peak temperature (°C)	Temperature rate β (°C/s)	Shrinkage rate δ (%/s)	Shrinkage at 400 s (mm/mm%)	Mechanical strength (N)
DEI	9.4 (0.4)[a]	0.09 (0.01)[a]	55.8 (2.9)[a,b]	−3.5 (0.4)[a]	0.041 (0.006)[a]	1.75 (0.11)[a]	18.1 (1.8)[a,b]
GRD	9.5 (0.5)[a]	0.17 (0.02)[b]	53.0 (1.9)[a]	−2.7 (0.3)[b]	0.050 (0.005)[b]	1.84 (0.17)[a]	12.9 (1.6)[c]
EPH	12.1 (0.6)[b]	0.19 (0.02)[b]	57.2 (2.8)[b]	−3.4 (0.5)[a]	0.043 (0.005)[a]	2.17 (0.15)[b]	21.0 (1.5)[a]
VNS	8.4 (0.4)[c]	0.13 (0.01)[c]	52.7 (2.5)[a]	−2.7 (0.3)[b]	0.044 (0.004)[a]	1.81 (0.16)[a]	16.4 (1.7)[b]

One-way ANOVA at a significance level of 0.05 was used to assess differences in a fixed group (i.e. a specific composite of Table 2) cured through standard or SLER® process. Two-way ANOVA at a significance level of 0.05, followed by the Tukey post hoc test, was used to compare properties of the investigated set of composites.

3. Results

Fig. 2 depicts typical temperature (Fig. 2a) and shrinkage (Fig. 2b) profiles after standard or SLER® light curing process. A steep temperature profile characterized by the slope α (Fig. 2a) is detected as the light is turned on, while a delay of about 1 s is
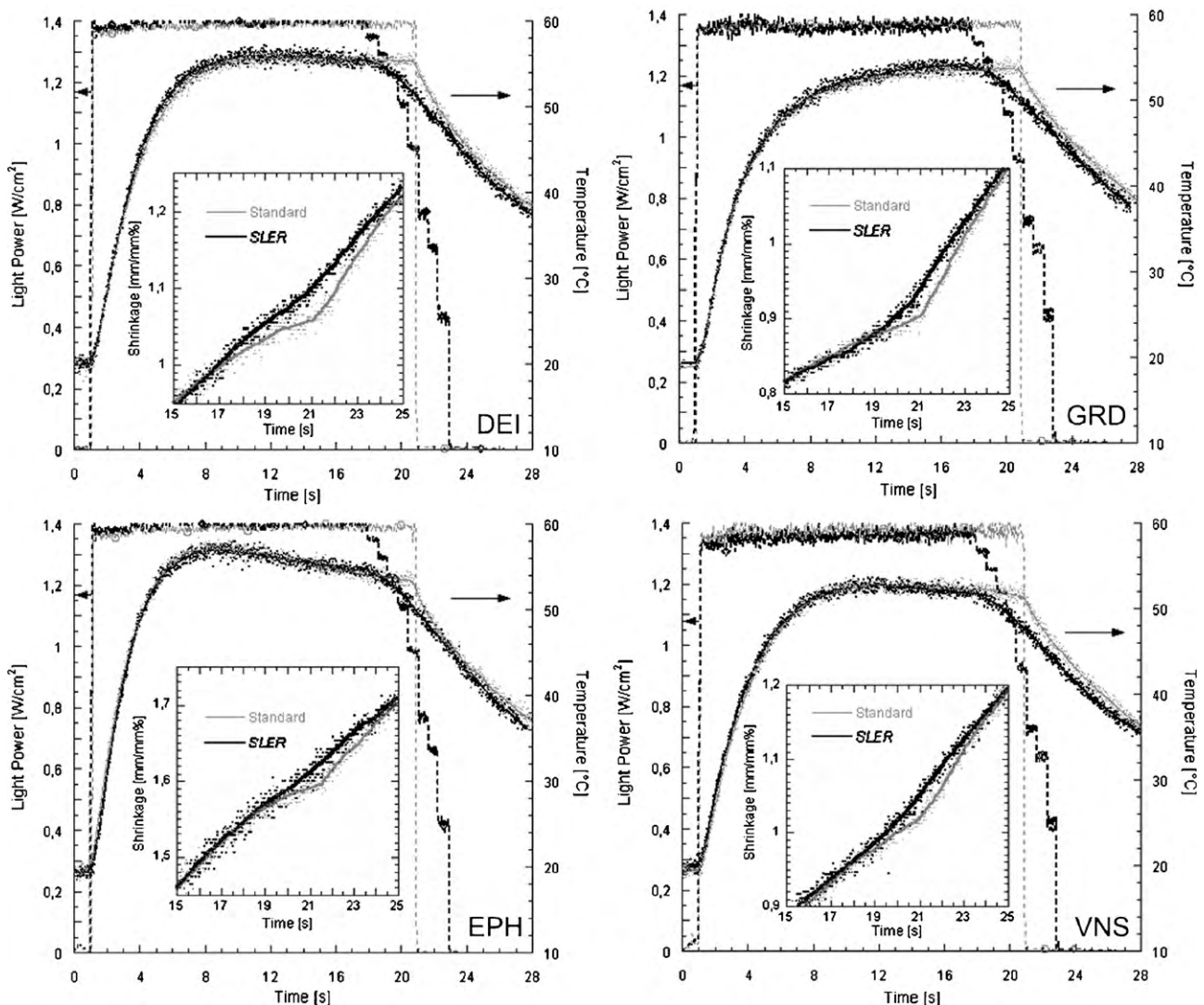

Fig. 3 – Light power, temperature and shrinkage profiles due to standard or SLER® light curing process for DEI (a), Gradia (b), Enamel Plus (c) and Venus (d) composites.

Table 4 – Thermal, shrinkage and mechanical properties of restorative materials polymerized through the SLER® process. Values within columns displaying different superscript letter were significantly different ($p < 0.05$).

Composite	SLER® light curing						
	LCP			DRP			
	Temperature rate α (°C/s)	Shrinkage rate γ (%/s)	Peak temperature (°C)	Temperature rate β (°C/s)	Shrinkage rate δ (%/s)	Shrinkage at 400 s (mm/mm%)	Mechanical strength (N)
DEI	9.4 (0.5)[a]	0.11 (0.01)[a]	55.7 (2.8)[a,b]	−2.1 (0.2)[a,b]	0.032 (0.005)[a]	1.78 (0.12)[a]	21.9 (2.0)[a,b]
GRD	9.6 (0.4)[a]	0.15 (0.01)[b]	53.8 (2.4)[a,b]	−1.7 (0.2)[c]	0.042 (0.004)[b]	1.85 (0.15)[a]	15.1 (1.7)[c]
EPH	12.4 (0.6)[b]	0.20 (0.02)[c]	57.3 (3.0)[b]	−2.3 (0.4)[a]	0.033 (0.004)[a]	2.19 (0.17)[b]	26.0 (1.8)[a]
VNS	8.3 (0.5)[c]	0.14 (0.02)[b]	52.8 (2.7)[a]	−1.9 (0.3)[b,c]	0.035 (0.004)[a]	1.83 (0.15)[a]	20.1 (1.9)[b]

observed in the shrinkage profile before a steep contraction at a rate γ occurs (Fig. 2b). During LCP temperature increases to a maximum level. However, no difference is observed between standard and SLER® temperature and shrinkage profiles during LCP. As the light is switched off, temperature decreases to room temperature (20 °C) during the dark reaction phase (DRP). A fast temperature decrease at a rate β (Fig. 2a) is detected for standard curing process at the beginning of the DRP, as a consequence of this cooling, a steep shrinkage at a rate δ is observed (Fig. 2b). The effect of the SLER® process is a reduction of the rate of temperature decrease (Fig. 2a) and hence a reduction of the rate of shrinkage (slope δ of Fig. 2b) due to thermal cooling. Shrinkage continues to increase during the DRP and a complete cooling is observed after 400 s for both standard and SLER® cured materials. However, for each composite material, no difference was observed in the final value of shrinkage. Shrinkage values after 400 s are reported in Table 3, and the EPH composite showed significantly higher final shrinkage values.

Simultaneous time measurements of light power, temperature and shrinkage through the transition between LCP and DRP are reported in Fig. 3. Similar temperature profiles are detected for DEI, EPH and VNS composites. In particular, a maximum temperature after about 7 s can be clearly detected for the EPH (Fig. 3c). Instead, a monotonic temperature increase during the LCP is observed for the GRD composite (Fig. 3b). Temperature rate, maximum temperature and shrinkage rate values recorded during the LCP for each material are reported in Table 3. Higher temperature and shrinkage rates values were measured for the EPH, also peak temperature (Table 3) of this material resulted statistically higher than the other composites.

All materials cured through the standard curing method show a fast cooling as the light is switched off (Fig. 3), and this rate of temperature decrease derived from the slope β (Fig. 2) is reported in Table 3. As a consequence, composites cured through the standard method show a sharp rise in the shrinkage profile through the switch between LCP and the DRP. In particular, higher shrinkage rate were measured for GRD and EPH composites. The shrinkage rates derived from the slope δ (Fig. 1c) of each restorative material are reported in Table 3. The effect of the SLER® process on the shrinkage profile and rate is evident for all the investigated materials (Fig. 3, Tables 3 and 4).

The effect of light modulation through the SLER® process on temperature profile is a reduction of about 30% of the rate of cooling. Each material cured through the SLER® process shows temperature rate lower than the standard cured composite

($p < 0.05$). This decrease of the temperature rate determines a decrease of about 20% of the resulting shrinkage rate. Each material cured through the SLER® process shows shrinkage rate lower than standard cured composite ($p < 0.05$).

Mechanical strength of composites according to the small punch test are reported in Tables 3 and 4. Both SLER® and standard cured specimens show a brittle behavior characterized by a linear relationship between the applied load and deformation up to the break point. Similar behavior and strength were measured for the DEI and VNS materials. Higher strength values were recorded for EPH, while lower strength was detected for GRD. For each composite material, the strength of SLER® cured specimens was higher than those cured according to the standard procedure ($p < 0.05$). This strength increase corresponds to about 20%.

FWHM values obtained from Raman spectroscopy of the DEI composite are reported in Fig. 4. Increase of FWHM values represent the elasto-plastic strain stored in the material and depend on the amount of contraction stress locally developed into the composite. The non-cured paste (blank control) is used as reference. It shows lower values than cured and relaxed specimens. Relaxed specimens (standard control and SLER control of Fig. 4) show an almost uniform distribution along the depth of the specimens, however, even after the relaxation step through a thermal process, a remarkable difference is observed between superficial and sub-surface measurements. Below a depth of 100 μm, SLER® cured specimens show FWHM values close to the quenched control, thus suggesting a structure which is more relaxed than standard cured specimens. Below a depth of 100 μm, FWHM values of the SLER® cured sample are lower ($p < 0.05$) than standard cured specimens. It is also notable that, down to a depth of 50 μm (Fig. 4), the residual stress of SLER® cured specimens is higher than that for standard cured specimens ($p < 0.05$).

4. Discussion

The degree of conversion and mechanical properties of dental composites depend on the modality by which light energy is supplied to the material [21,26]. The energy dose provided through constant power density is directly given by the product between power and exposure time and a reciprocal relationship between power and time is observed for some restorative materials [35] although other materials do not display a full exposure reciprocity, especially when high power density are concerned [21,60]. In order to investigate
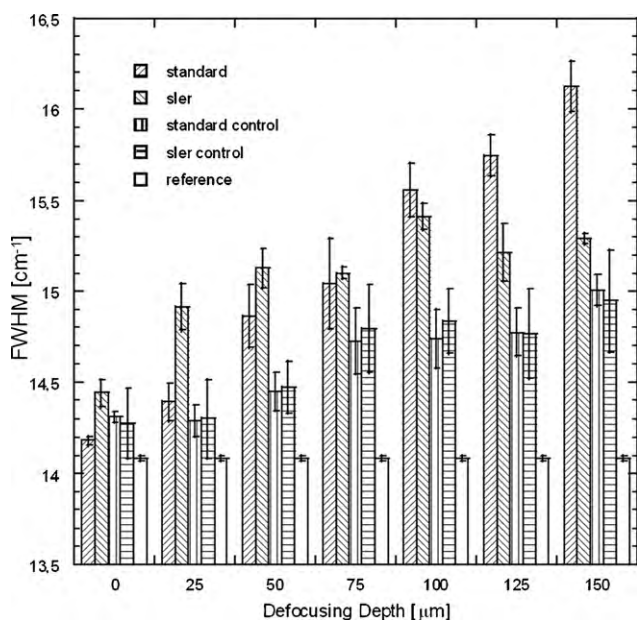
Fig. 4 – Full width at half maximum (FWHM) intensity profiles obtained from Raman spectroscopy for the DEI composite. Controls are represented by specimens quenched from 100 °C and to room temperature at 1 °C/min. The blank control is represented by the not-cured composite paste. The vertical bar represent the standard deviation.

the effect of light modulation on the composite properties, similar energy doses were provided through the standard curing method and the SLER® process (Table 1). Fast light curing was achieved using high power density levels, thus short exposure time were considered. Light modulation was obtained by gradually reducing the power provided to the LED (Fig. 1b).

As a consequence of the methacrylate matrix polymerization, the composite material undergoes a fast temperature and shrinkage increase (Figs. 1 and 3). However, as the light is switched on, a delay of about 1.5 s is observed before shrinkage occurs (Fig. 3). This delay can be addressed to several factors. At the beginning of the LCP, the consumption of inhibitor delays the onset of shrinkage and thermal expansion occurs due to the heat generated attendant to the absorption of light. This thermal expansion is particularly evident as halogen source, irradiating light over an extended wavelength range, are used [52,60]. Therefore, at the beginning of the LCP, shrinkage is partially compensated by the expansion of the material. However, further research is needed in order to address the effects involved at the beginning of the LCP.

Shrinkage itself is directly related to the degree of conversion of dental composites [11]. Given the amount and the thickness of resin to be cured, temperature and shrinkage rate during the LCP increase by increasing the power output depending also on the quality of the emitted light spectra [23,25,43,53]. Soft start, pulsed and delay photopolymerization represent the main attempts in order to improve composite properties through the modulation of the LCP, while pulsed and delayed units provide to the material

more time to dissipate thermal energy with the environment [34,39,43,44], thus lowering the maximum temperature developing into the material. Light modulation at the beginning of the LCP provides relevant reduction of shrinkage stress [46], but a reduction of degree of conversion [50] and hardness after conditioning [49] have also been observed. It is notable that the rate of both shrinkage stress and strain recorded at the end of the soft start light modulation is very similar to traditional continuous irradiation [46]. Therefore, the soft start modulation has a negligible effect on the stress build-up in the restorative material during the sharp cooling step at the end of the LCP.

In our experiments we used a LED curing unit reaching a maximum temperature into the material higher than 50 °C (Table 3). This peak temperature level is reached at about half of the whole LCP for the DEI, EPH and VNS composites (Fig. 3a, c and d), and similar temperature profile have been detected through fast curing of dental composites [42]. Instead, a monotonic temperature increase was observed for the GRD composite (Fig. 3b). Differences in thermal profiles among the investigated materials can be ascribed to the matrix composition (Table 2). GRD composite is based on UDMA polymer matrix, while the other composites are based on Bis-GMA. As the curing light is switched off, the DRP begins and temperature drops to the level of the environment while shrinkage continues to increase (Fig. 1c). The main limit to the level of light power for *in situ* fast curing is represented by thermal injury thresholds of dental tissues, and LED light source produces lower temperature increase than halogen source [42].

In accordance with kinetic parameters detected for UDMA and Bis-GMA/TEGDMA based resins [32], shrinkage rate through the LCP (slope γ in Fig. 1c) of GRD is significantly higher than VNS (Table 3). Shrinkage occurring through the DRP is due to further material curing (shrinkage due to polymerization) and to material cooling (thermal shrinkage). The former is very slow as a result of the limited diffusion of molecules inside a vitrified polymer. Thermal shrinkage is particularly evident at the beginning of the DRP as a result of temperature difference between the material and the environment (Fig. 3). Similar profiles have been detected in stress build-up and shrinkage experiments [51–54]. Shrinkage or stress occurring through the transition between LCP and DRP is particularly dangerous in clinical practice because the transition of the composite matrix from viscous gel to visco-elastic solid network already occurred [24,29,32], hence the low capability of relaxing or damping suggests a stress rise at the filler–matrix and dentin–composite interfaces.

Steep stress contraction at the beginning of the DRP is already evident when using power curing of 600 mW/cm² [65]. Huge thermal contraction force is evident using high power curing unit and, interestingly, pulsed unit also shows a steep stress contraction as the light is switched off [52]. Steep shrinkage at the beginning of the DRP is also documented when using middle power units [66]. In clinical practice the restorative composite is partially constrained by the cavity wall, hence the amount of stress building-up into the material may compromise the resin–dentin interface [55] and the filler–matrix interface [28]. The SLER® technology has a direct effect on temperature and shrinkage profiles by reducing the rate of cooling and the rate

of shrinkage as the light is switched off (Fig. 3 and Table 4).

For each composite, no difference was observed in the final value of shrinkage according to the standard or to the SLER® LCP (Table 3 and Table 4). In particular DEI (Fig. 3a) and VNS (Fig. 3d) present similar shrinkage and curing profiles and also similar final shrinkage values (Table 3). The slightly lower values of shrinkage at 400 s recorded for the DEI composite can be ascribed to the lower amount of the polymeric matrix (Table 2). On the other hand, the shrinkage value after 400 s for EPH, based on a Bis-GMA/BDDMA matrix (Table 1), is statistically higher than the other composites (Table 3), and this result is consistent with previous volumetric shrinkage [67] and contraction stress measurements [37].

The small punch test is a relatively novel standardized test. This test has already been validated for acrylic based bone cements [68]. The small punch test is particularly suitable for dental composite since specimens can be cured through a single step light shot, thus preventing artefacts due to the polymerization of long specimens through several steps of light curing. Mechanical strength of EPH is significantly higher than the other composite cured using similar conditions (Tables 3 and 4), and this result is consistent with micro-hardness measurements [69]. On the other hand, the lower strength observed of GRD is consistent with four-point bending strength [70] and three-point bending strength of composites with similar amounts of reinforcement and matrix based on a Bis-GMA or UDMA combined with TEGDMA [12], although similar fracture toughness values have been reported for GRD and VNS [35].

Mechanical strength data (Tables 3 and 4) clearly indicate that the SLER® process allows to increase the strength of fast cured dental composites. This increase is about 20%. In particular, the strength of EPH cured through the SLER® process (26 N) is 25% higher ($p < 0.05$) than that measured using standard curing modality. On the other hand, the strength of GRD composite seems to be less sensitive to the SLER® process. Similar strength values have been measured for DEI and VNS which have similar polymer matrix composition (Table 2). The slightly higher strength of the DEI composite can be ascribed to the higher amount of fillers. However, an increase of the strength is recorded for both materials as the SLER® process is employed. Since the SLER® process has no effect on the final shrinkage of composites (Tables 3 and 4), the strength increase may be ascribed to lower internal stress distribution affecting the quality of the filler–matrix interface.

FWHM values obtained from Raman spectroscopy of the DEI composite (Fig. 4) clearly indicate that the distribution of contraction stress into the composite is not uniform. Therefore, literature values related to contraction stress measured through dynamometers [28,43,54] have to be interpreted as averaged measurements. Instead, FWHM values reflect the amount of contraction stress locally developed into the composite. Aromatic rings can be considered randomly oriented in the structure of Bis-GMA; the total frequency distribution of the Raman band depends on the distribution of deformation of benzene group inside the *probe volume*. As long as the stress increases, the heterogeneous distribution of the aromatic rings deformation becomes wider and leads to Raman band broadening [61,62].

Relaxed specimens (controls of Fig. 4) show a more uniform distribution along the depth of the specimens, however, even after thermal relaxation, remarkable difference can be observed between superficial and deeper FWHM measurements. Therefore, contraction stresses into the composite specimens are not completely relaxed. In the hypothesis that the time–temperature superposition principle is satisfied [31], this result suggests that in clinical practice composite restorations will present internal stress even after a prolonged time period of service.

FWHM values recorded for both SLER® and standard cured specimens suggest that residual stress increases along the depth of the specimen. It is interesting to notice that for all cured specimens the layers of composite closer to the external surface are less stressed than layers positioned closer to the bulk of the composite (Fig. 4). Several factors can justify this phenomenon. First, it is known that the outer surface of a specimen is shear stress free, therefore the total stress in the external layer of the investigated composites is likely lower. However, differences in stress distribution between external and internal layers are also due to the LCP. In fact, models to predict polymerization rate profiles developing inside a resin during LCP suggest that a higher rate level occurs below the most external layer [71], therefore higher residual stress values are expected below this layer due to polymerization rate and thermal effects. It is also notable that down to a depth of 50 μm (Fig. 4) the residual stress of SLER® cured specimens are higher than standard cured specimens ($p < 0.05$). However, the amount of this stress is much lower than the stress recorded for standard cured specimens below a depth of 100 μm.

FWHM values recorded below 100 μm for SLER® cured specimens at each investigated depth are lower ($p < 0.05$) than standard cured samples. Considering the uncured sample (reference of Fig. 4) as base line, this reduction is about 40%. FWHM values recorded below a depth of 100 μm for SLER® cured specimens are close to the quenched control, thus suggesting a structure which is more relaxed than standard cured specimens. Therefore, also Raman spectroscopy results suggest that stress build-up distribution of light cured composites benefits from the SLER® process.

It is important to note that the advantages of using the SLER® process observed here relate only to these laboratory results. The inevitable differences between this *in vitro* investigation and the clinical situation have to be taken into account. In clinical practice, during the light curing process, the composite will shrink and heat in a different manner than that observed in our *in vitro* testing. Moreover, data which have been given through the results of this investigation represent only a picture of the composite material at a give time point. Significant changes are to be expected when a wet conditioning environment is considered [33,49,60]. Further research needs to be carried out.

5.   Conclusions

A novel light curing process, namely soft light energy release (SLER®), has been developed in order to improve mechanical properties of dental composites. The SLER® process reduces the rate of temperature decrease as the light curing unit is

switched off. Consequently, a reduction of the rate of shrinkage occurring into the composite is obtained, and the effect is an improvement of the mechanical strength and a reduction of contraction stress locally developed into the restorative material.

Acknowledgements

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