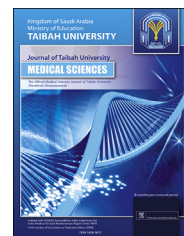




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Original Article

Dental dimethacrylate-based nanohybrid composite Kalore GC: Kinetic study of its light-curing



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المخلص

أهداف البحث: بحثت هذه الدراسة حركية التصلب الضوئي لمركب سني هجين نانوميترى جديد معتمد في تركيبته على الدايميثاكريلات، ويتكون قلبه العضوي من موحود ذي وزن جزيني عالي بالإضافة إلى مواحيد دايميثاكريلات ثنائي الفينول؛ وهي إيثايل دايميثاكريلات وبوريثان دايميثاكريلات.

طرق البحث: تم قياس أربعة خواص وهي: درجة التحول، وعمق التصلب، والانكماش بالبلمرة، ودرجة حرارة التحول الزجاجي مقابل مدة التصلب. تم قياس هذه الخصائص بواسطة التصوير الطيفي في الانعكاس الكلي الخفيف، واختبار الكشط، وقياس الكثافة والتحليل الحراري الميكانيكي الديناميكي، على التوالي.

النتائج: بعد ١٠ ثوان من التصلب الضوئي كانت درجة التحول ٢.٥٪، وعمق التصلب ١.٨٦ مم والانكماش بالبلمرة ١.٤٨٪. وأظهر المركب السني المصلب ضوئياً لمدة ١٠ ثوان درجتي حرارة للتحول الزجاجي: عند درجة حرارة مئوية ٥٦.٤ ودرجة حرارة ١١٢.٨. في هذه المرحلة لوحظ المعدل الأقصى للبلمرة. على أي حال، فإن التصلب الضوئي استمر بمعدل منخفض وأقل بكثير لمدة ١٠٠ ثانية. وعند هذا الزمن لوحظ أن الحد الأقصى من درجة التحول ٤٠٪ والحد الأقصى من عمق التصلب كان حوالي ٣.٥ مم. كما ارتفعت قيم التحول الزجاجي إلى ٥٩.٥ و ١٠٢.٣ درجة مئوية، على التوالي.

الاستنتاجات: ضمن ظروف الدراسة الحالية يبدو أن مدة التصلب الضوئي الأمثل للمركب السني تحت الدراسة هي ١٠٠ ثانية. وأظهر المركب السني المصلب ضوئياً لمدة ٣٠٠ ثانية درجتي حرارة للتحول الزجاجي وهذا يشير إلى أن المركب السني لا يزال يحتوي على روابط مزدوجة غير متفاعلة بين ذرات

الكربون وجذور ماكروية الحجم، التي استمرت بالتصلب عند التسخين في التحليل الحراري الميكانيكي الديناميكي.

الكلمات المفتاحية: درجة التحول؛ عمق التصلب؛ درجة حرارة التحول الزجاجي؛ حركية التصلب الضوئي؛ الانكماش بالبلمرة

Abstract

Objective: This study investigated the light-curing kinetic of the novel dental dimethacrylate-based nanohybrid composite (Kalore GC). Its organic matrix consists of a high molecular weight monomer called DX 511 as well as the known dimethacrylate monomers bisphenol A ethyl dimethacrylate (Bis-EMA) and urethane dimethacrylate (UDMA).

Methods: Four properties were measured: degree of conversion (DC), depth of curing (DOC), polymerization shrinkage (S) and glass transition temperature (T_g) versus curing time. These properties were measured by spectroscopic imaging in Attenuated Total Reflection (ATR-FT-IR), scrape test, density measurements and dynamic mechanical thermal analysis (DMTA), respectively.

Results: After 10s of light curing, the DC was 2.50%, DOC 1.86 mm and S 1.48%. The composite cured for 10s showed two T_g , 56.4 °C and 112.8 °C. At this stage, the maximum rate of polymerization was noticed. The curing, however, continued with much lower and decreased rate for up to 100s. There, a maximum DC of about 40% and a maximum DOC of about 3.5 mm were observed. T_g values were raised to 59.5 and 102.3 °C, respectively.

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Conclusions: Within the condition of this study, the optimum curing time of Kalore GC seems to be 100 s. The composite light-cured up to 300 s showed two T_g , indicating that this compound still contained unreacted double bonds of C=C and macroradicals, which continued to cure upon heating in DMTA.

Keywords: Degree of conversion; Depth of cure; Glass transition temperature (T_g); Light-curing kinetics; Polymerization shrinkage

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Introduction

Due to their versatility and aesthetic advantages, dental composites have found widespread application in restorative dentistry. Dental composites consist of an organic matrix, inorganic filler particles, silane coupling agents and initiators/activators for light-curing (photo-polymerization). The organic matrix typically is a mixture of two or more dimethacrylate monomers such as bisphenol A-glycidyl methacrylate (Bis-GMA), bisphenol A-ethyl methacrylate (Bis-EMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA).¹ The overall characteristics of the composite may be improved by research and optimization of either of its individual components. One factor that has received considerable attention in recent years with respect to the choice of dental dimethacrylate-based composites for direct restorations is the volumetric shrinkage, which is approximately 2–4%.² The shrinkage is due to the polymerization reaction of dimethacrylate monomers, during which the distance between monomer molecules, which are loosely bound by van der Waals forces, is reduced as the monomer molecules become tightly linked by covalent bonds forming a polymer network. Composite shrinkage is restricted by the adhesion of the material to the cavity walls, thus generating stress at the interface. Shrinkage stress development during polymerization is an important factor that may affect the longevity of a restoration; the material is bonded to tooth cavity walls; thus, the polymerization stresses are transferred to the tooth-restoration interface. The outcome of this interaction depends on the bond strength, the mechanical properties of the structures involved and the geometric configuration of the cavity.³ Frequently, marginal gap formation occurs at the interface, creating microleakage, which may in turn cause secondary caries, marginal discolouration or post-operative sensitivity.⁴

Due to the clinical significance of polymerization shrinkage (bacteria outbreaks may occur if restoration displays cracks or holes), efforts have been undertaken to minimize it, such as filling the tooth cavity in increments and mainly making changes in composite composition, both in the inorganic portion and in the organic matrix.⁵

Polymerization shrinkage is related directly to the degree of conversion (DC, the % of C=C bonds converted into C–C). An increase in the DC leads to higher polymerization strains⁶ because more covalent bonds and more highly cross-linked networks are formed. Because a high DC value is associated with improved mechanical and chemical properties, colour stability and biocompatibility, the optimum relation between DC and shrinkage is required.⁷ According to the literature available, the most frequently used method for the kinetic study of photo-polymerization is FT-IR through DC determination. In addition, the shrinkage and depth of cure properties, DMTA and HPLC techniques can be used.

Recently, a new composite has been developed, the Kalore GC, which has shown lower polymerization stress and shrinkage values compared to conventional composites.^{8,9} The basis for the lower level of shrinkage demonstrated by Kalore GC was attributed to the high molecular mass of the basic monomer contained in its matrix, named DX-511 (Figure 1). Its molecular structure includes a long rigid core, which is claimed to rapidly reduce polymerization shrinkage and stress, whereas the flexible arms increase the activity of the monomer. The core maintains its shape and size; thus, reduced volume, deformation of the monomer and shrinkage prevail. The flexible edges increase the activity, thereby overcoming the reduced activity that is typically associated with long monomer chains. The molecular weight of the DX-511 (M.W. = 895) is twice the molecular weight of Bis-GMA or UDMA. Little information is known for the subscripts n , m , n' within the DX-511 formula. According to our knowledge and the literature data, there is no more information about the effect of DX-511 on the composite. The new monomer DX-511, licensed from DuPont for exclusive partnership agreement, is based on urethane dimethacrylate chemistry and designed to combine excellent handling and physical properties with low shrinkage (stress). The DX-511 is compatible with all current composite and bonding systems.¹⁰

For this study, a light-curing kinetics investigation of Kalore GC was performed by determining the (a) degree of conversion, (b) depth of cure, (c) polymerization shrinkage and (d) glass transition temperature versus curing time. Our interest was focused on how far the polymerization may proceed under the conditions applied and whether all of the above-mentioned properties demonstrate the same ability to attend polymerization closely, as it is theoretically known that it affects them.

The null hypothesis is that the polymerization time for the dental polymer nanocomposite Kalore GC does affect the trend of the materials' properties examined.

Materials and Methods

Material investigated

The studied material is a newly marketed product under the brand name Kalore GC, fabricated by GC Corporation (Tokyo, Japan). Its polymeric matrix is of great interest due to the chemical structure of the component DX-511, which is a large molecule, as shown in Figure 1, whereas assumptions

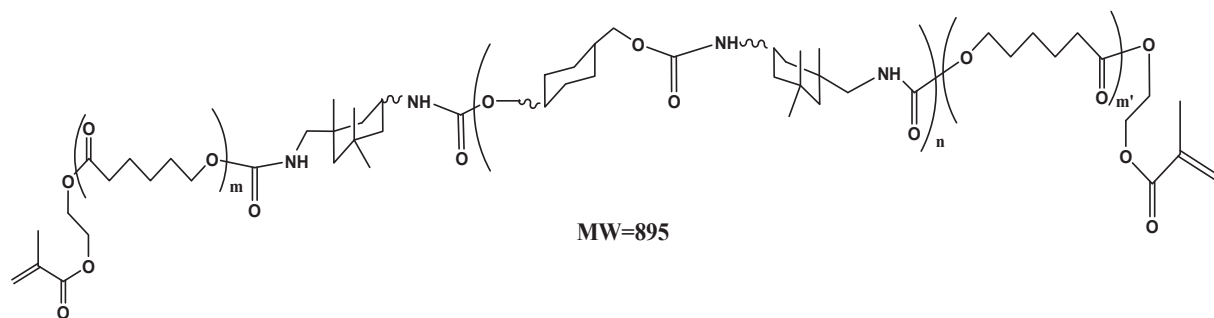


Figure 1: Chemical structure of DX-511 dimethacrylate monomer contained in the Kalore GC matrix.¹⁰

Table 1: Composition of Kalore GC according to the manufacturing company.¹⁰

Components	Weight %
Polymer matrix	18
Dimethacrylate urethane (UDMA)	6–16
Dimethacrylate urethane DX-511	5–10
Ethoxylated dimethacrylates (Bis-EMA)	<5
Filler	82
Fluoro-aluminium-silicate glass	
Prepolymerized filler	
Silicon dioxide	
Others	
Photoinitiator	<1
Pigments	<1

may only be made regarding the n , m , m' subscripts. The ingredients of the composite are shown in Table 1.¹⁰

The product (Lot. 1107201 & 1309051) was used as received with no further purification, and it should be noticed that all experiments were carried out in the absence of light. The polymerizations were performed using a 3000 XL dental curing device (Serial No. 119213, 3M Company, St. Paul, USA). This source consisted of a 75 W tungsten halogen lamp, which emits radiation between 420 and 500 nm and irradiance of 840 mW/cm² (frequently checked during the experiments), as measured using a Hilux curing light meter (Benlioglu Dental INC, Serial No. 9080935). The unit was used in direct contact with the samples. ISO 4049:2009 specifications have been taken into account.¹¹

ATR FTIR measurement of DC

A Teflon mould (1 mm thick and 15 mm in diameter) was placed between two glass slides (3 mm thick) covered by a Mylar film (Stripmat Polydentia SA, thickness 0.05 mm), and the composite material filled the empty space, taking care not to entrap air bubbles (avoid oxygen inhibition). The assembly, which was held together by spring clips, was put under irradiation (in direct contact) on both sides for several time intervals. The disk was then removed, the excess material was scratched away, and an abrasive paper was used to correct the slight side irregularities. These samples were used for ATR recordings. A Spectrum One FT-IR Spectrometer (Perkin Elmer) was involved, along with the appropriate ZnSe plate (45°) and arm-cover accessory. A wave number

range of 4000–700 cm⁻¹ was applied (32 scans, resolution 4 cm⁻¹) for structural imaging and groups/bonds identification. Later, the narrow area of 1660–1480 cm⁻¹ was found to be ideal for the constant observation of desirable peaks; 1636 cm⁻¹ and 1532 cm⁻¹ corresponding to C=C bonds that react and N–H bonds that remain unchanged (internal standard). The software allows us to obtain exact values for the peak area/height in each case. The equations used are:

$$DC_A\% = 100 \cdot \left[1 - \frac{(A_{C=C}/A_{N-H})_I}{(A_{C=C}/A_{N-H})_O} \right]$$

$$DC_H\% = 100 \cdot \left[1 - \frac{(H_{C=C}/H_{N-H})_I}{(H_{C=C}/H_{N-H})_O} \right]$$

where A is the peak area value and H is the peak height value for the particular peak and time interval. An unpolymerized composite was also characterized by the above procedure with ATR FT-IR, using, in addition, a Mylar film to avoid adhesion. Three sets of experiments were performed ($n = 3$).

Scrape test measurement of DOC

A dark-coloured straw (commercially available, 10 mm high and 4–5 mm in diameter) was firmly placed on a glass plate. The cylinder was filled with the composite material, trying to avoid trapping air bubbles, until a flat upper-side was reached; it was then covered by a piece of Mylar sheet. Photocuring was performed for certain time intervals, and then the sample was removed and the uncured excess material was carefully scratched away with a spatula from the bottom upwards. Thus, the specimen had a flat-disk side and an irregular semi-spherical edge. The length of that specimen was measured using a calliper (N° 600 Rabone Chesterman, England ± 0.001 cm) at its central axis. Then, the number was divided by two, and that result was called DOC (mm). The specimen preparation procedure was fulfilled when no substantial increases in DOC were recorded. Three replicate series were carried out. The experiment was conducted according to ISO 4049:2009, §7.10.

Density measurements of S

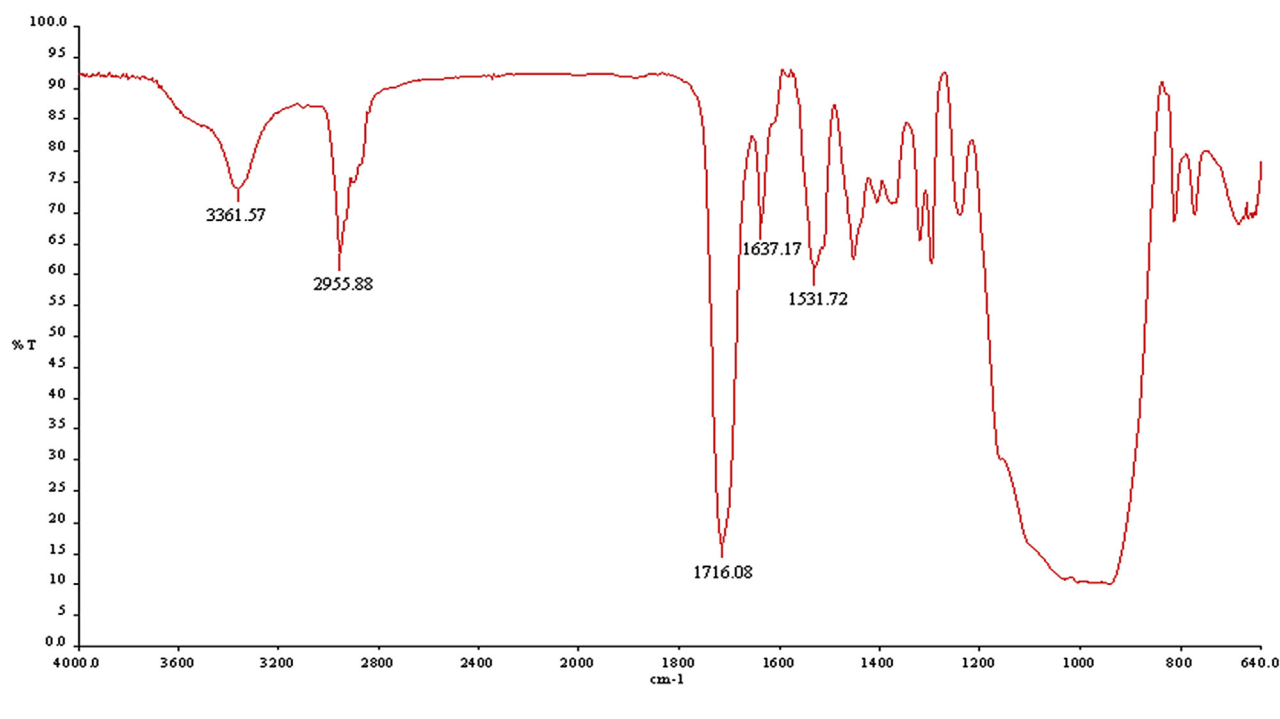
The volumetric shrinkage strain was determined using the Archimedes buoyancy principle as it is described in Refs. 12–14. Sample disks were produced as described in Section 2.2 and were measured shortly thereafter. The mass recordings of the specimens in air and water under certain

temperatures were carried out using a specially designed Mettler-Toledo AG64 balance (± 0.0001 g). Those values produced density values. Three replicate series were carried out in total ($n = 3$). The equation given below was used, where ρ_t is the material density required (g/cm^3), ρ_θ is the water density at particular certain working temperature (g/cm^3), and m_a or m_w is the disk mass (g) in air or water.

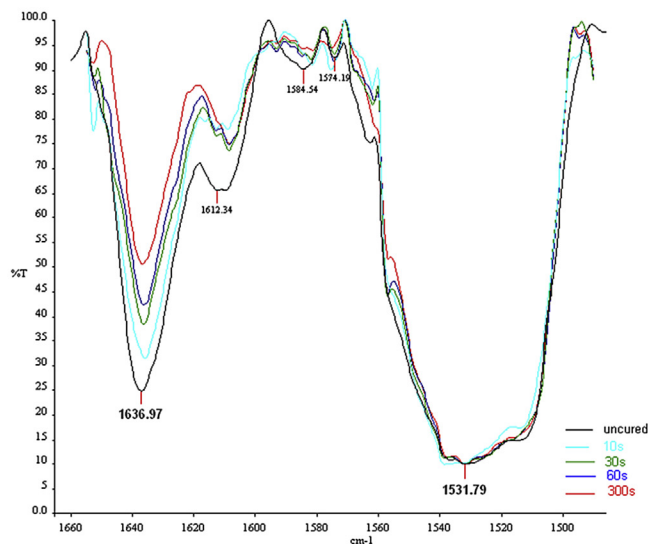
$$\rho_t = \frac{m_a}{m_a - m_w} \rho_\theta$$

The density of uncured composites was measured first. An uncured sphere-shaped specimen was carefully formed in such a way that trapping air bubbles was avoided.

Because it was rather sticky, a thin polyester film (thickness 0.05 mm) was fixed on the special holder of the balance and its mass was recorded in air and in water. Next, the sample was carefully placed on the polyester film, and the mass of the entire assembly was measured again in air and in water. Slight deformations of the materials during the test were of no importance because they do not influence density. The mass of each material was calculated by subtracting the mass of the polyester film from the mass of the entire assembly. Three replicate series were carried out in total. The below equation was used, where S is the polymerization shrinkage percentage, ρ_0 or ρ_t is the density



(a)



(b)

Figure 2: FT-IR (by ATR) spectrum of Kalore GC: (a) unpolymerized sample in $4000\text{--}600\text{ cm}^{-1}$ and (b) cured specimens in $1660\text{--}1480\text{ cm}^{-1}$ region.

(g/cm³) of the uncured or a material cured for a certain time, respectively.

$$S\% = 100 \left(1 - \frac{\rho_0}{\rho_t} \right)$$

DMTA measurements of T_g

For DMTA tests, rectangular bar specimens (sticks) were prepared by filling a Teflon mould ($2 \times 2 \times 40$ mm³, as recommended by DMTA manufacturer's instructions) with unpolymerized material, taking care to minimize the amount of trapped air. The upper and lower surfaces of the mould were overlaid with glass slides covered with a Mylar sheet to avoid adhesion with the uncured material. The completed assembly was held together with spring clips, irradiated by overlapping for specific time intervals on each side, and stored in an oven (Mettmert Model 200) at 37 ± 0.1 °C for 1 h.

DMTA tests were performed on a Diamond DMTA dynamic mechanical thermal analyser (Perkin–Elmer) in bending mode. A frequency of 1 Hz was applied (approximately average chewing rate), with a bending force of 4000 mN and an amplitude of 10 μ m. A temperature range of 25–185 °C and a heating rate of 2 °C/min were selected to cover the mouth temperature and the materials' likely glass transition temperature (T_g). Storage modulus (E'), loss modulus (E'') and tangent delta ($\tan\delta$) were plotted against temperature over this period. After the DMTA run was completed, the sample was allowed to cool naturally to room temperature, and the value of T_g was noted. This method was used for each of the samples, and the mean values were calculated ($n = 3$).

The values reported in the tables and figures represent mean values \pm standard deviation of three replicates. One-way analysis of variance (ANOVA) and Tukey's test for multiple comparisons between means to determine significant differences were used at a significance level set at

$p \leq 0.05$ for analysis of the results (by Origin Pro 8, Origin Lab Corporation on Microsoft Windows).

Results

Figure 2a shows the FT-IR spectrum at 4000–600 cm⁻¹ of the uncured, as-received sample, and Figure 2b shows the FT-IR spectrum at 1660–1480 cm⁻¹ of samples light-cured for 10, 30, 60 or 300 s. The characteristic absorption of C=C methacrylate double bonds observed at 1636 cm⁻¹ decreases over time due to their polymerization and conversion to C–C single bonds.

The area and the height of the peak in relation to those of the peak at 1532 cm⁻¹, which is stable and attributed to N–H bending, can be used as an internal standard for the determination of the DC of C=C bonds to C–C bonds during the curing time. The results obtained are shown in Table 2.

Figure 3a represents the dependence of DC on curing time when calculated based on the FT-IR peak areas. Next, the rate of change of the DC ($R_{DC\%}$) was calculated by taking the first derivative of the DC with respect to time [$d(\text{DC})/dt$]. The dependence of R_{DC} on the curing time and the DC is shown, respectively, in Figure 3b,c. The trend for DC values calculated based on the FT-IR peak heights is analogous.

In Table 2, the results obtained from the determination of depth of cure (DOC), the shrinkage (S) and the glass transition temperature (T_g) over the curing time are presented. The dependence of DOC% versus time is shown in Figure 4a. The rate of change of DOC (R_{DOC}) versus time or versus DOC is shown, respectively, in Figure 4b,c.

Figure 5a shows the dependence of the volumetric shrinkage of composite (S) versus time, whereas Figure 5b,c show the dependence of the rate of shrinkage R_S corresponding to time or S.

In Table 3, the values of the properties determined in the present study are given along with the data published by GC Corporation.¹⁰

Table 2: Summary presentation of the resulting properties values for each technique (mean \pm s.d., $n = 3$).

Photocuring t (s)	ATR-FTIR		Scrape test	Density measurements	DMTA	
	DC _A (%)	DC _H (%)	DOC (mm)	S (%)	T_{g-1} (°C)	T_{g-2} (°C)
0	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	–	–
10	24.96 \pm 4.00 ^a	26.04 \pm 4.76 ^a	1.86 \pm 0.06	1.48 \pm 0.24	56.4 \pm 0.4 ^a	112.8 \pm 3.9
20	27.45 \pm 3.85 ^a	28.00 \pm 5.47 ^a	2.20 \pm 0.12	1.92 \pm 0.14 ^a	56.5 \pm 0.5 ^a	116.1 \pm 2.2 ^a
30	29.72 \pm 1.63 ^a	31.69 \pm 4.62 ^a	2.50 \pm 0.08	2.09 \pm 0.04 ^a	57.2 \pm 0.1 ^a	116.4 \pm 0.7 ^a
40	34.77 \pm 2.65 ^b	33.67 \pm 6.01 ^b	2.61 \pm 0.16 ^a	2.13 \pm 0.01 ^b	57.5 \pm 0.3 ^a	117.4 \pm 0.2 ^a
50	38.75 \pm 3.24 ^b	36.37 \pm 6.28 ^b	2.80 \pm 0.18 ^a	2.14 \pm 0.03 ^b	57.2 \pm 1.3 ^a	117.3 \pm 1.2 ^a
60	40.27 \pm 4.15 ^c	36.97 \pm 6.58 ^b	2.88 \pm 0.21 ^a	2.18 \pm 0.03 ^b	57.7 \pm 0.5 ^a	119.1 \pm 2.5 ^b
80			3.13 \pm 0.12		58.8 \pm 1.5 ^b	121.3 \pm 1.2 ^b
90	41.25 \pm 4.19 ^c	39.28 \pm 6.47 ^b		2.16 \pm 0.05 ^b		
100			3.33 \pm 0.08 ^b		59.5 \pm 3.7 ^b	120.3 \pm 1.4 ^b
120	45.60 \pm 1.34 ^c	41.72 \pm 5.98 ^b	3.36 \pm 0.08 ^b	2.19 \pm 0.03 ^b	59.5 \pm 1.9 ^b	121.4 \pm 1.2 ^b
150	46.93 \pm 0.74 ^c	43.44 \pm 5.78 ^c	3.46 \pm 0.14 ^b	2.23 \pm 0.07 ^b	60.6 \pm 2.4 ^b	119.5 \pm 0.7 ^b
180	48.52 \pm 0.45 ^d	45.44 \pm 6.77 ^c	3.65 \pm 0.33 ^c	2.19 \pm 0.03 ^b	60.1 \pm 3.2 ^b	121.7 \pm 0.8 ^b
210	49.48 \pm 1.81 ^d	46.80 \pm 6.25 ^c	3.78 \pm 0.38 ^c	2.20 \pm 0.05 ^b		
240	49.96 \pm 2.81 ^d	47.33 \pm 5.87 ^c	3.93 \pm 0.15 ^c	2.19 \pm 0.06 ^b	60.0 \pm 3.3 ^b	121.2 \pm 0.8 ^b
270	50.62 \pm 3.80 ^d	47.88 \pm 6.23 ^c	4.01 \pm 0.14 ^c	2.21 \pm 0.07 ^b		
300	51.88 \pm 3.00 ^d	49.01 \pm 7.16 ^c	4.03 \pm 0.16 ^c	2.28 \pm 0.10	59.5 \pm 3.2 ^b	122.1 \pm 0.1 ^b

A common lowercase letter in the same column indicates no significance difference at $p < 0.05$ value.

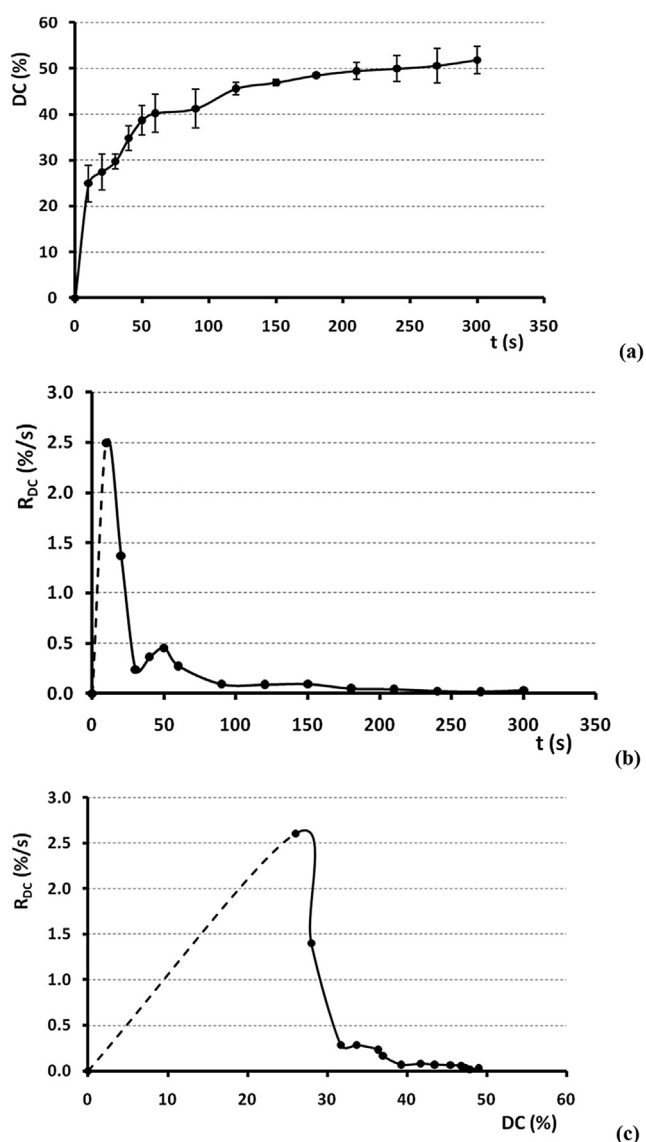


Figure 3: Dependence curve of DC (a) or R_{DC} (b) versus time and R_{DC} versus DC (c) (based on peak area).

In Figure 6a, the correlation between DC and DOC is shown; in Figure 6b the correlation between DC and S, whereas in Figure 6c the correlation between S and DOC are illustrated.

Discussion

The FT-IR spectrum of the uncured, as-received sample (Figure 2a) showed peaks of the characteristic groups of dimethacrylate monomers contained in the composite matrix. The evaluation of the peaks formed should first be discussed. From left to right in the spectrum, we observe the 3361 cm^{-1} peak (medium, broad), which corresponds to the stretching vibration of the N–H group contained both in UDMA and in DX-511; we also observe the medium 2955 cm^{-1} peak(s) typical of C–H stretching vibrations. The strong and narrow peak at 1716 cm^{-1} is attributed to the C=O group of all methacrylates; the medium, narrow

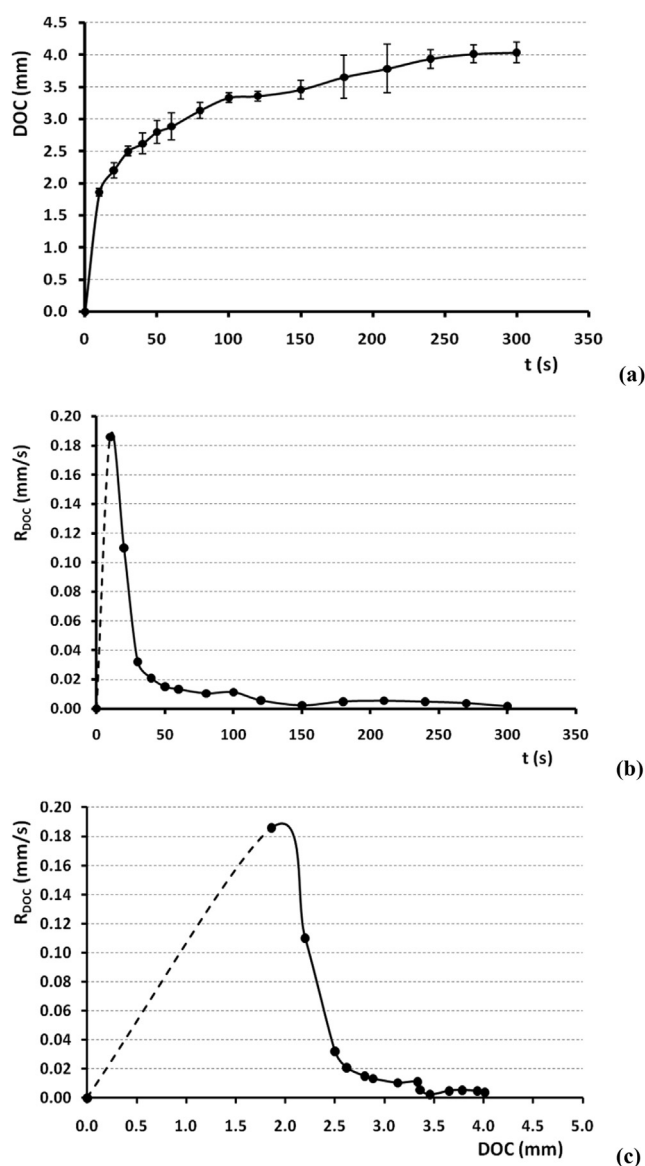


Figure 4: Dependence curve of DOC (a) or R_{DOC} (b) versus time and R_{DOC} versus DOC (c).

peak at 1637 cm^{-1} is attributed to the stretching vibration of C=C. Nearby, an absorbance at 1612 cm^{-1} is faintly shown (mainly as a shoulder of the peak at 1637 cm^{-1}), which is attributed to the aromatic C–C bonds of Bis-EMA present in the composite matrix in small amounts (<5 wt%, Table 1). The medium and wide peak at 1532 cm^{-1} is due to the N–H bending vibration.

C=C vinyl bonds decrease over time; this is noted in the elimination of the 1636 cm^{-1} peak. The stretching vibration of C–C aromatic bonds at 1612 cm^{-1} was taken first as an internal standard for the DC determination because this does not change during the curing and is used frequently (Figure 2b). However, the results obtained by the use of this internal standard were not reliable because of the very low intensity of this peak (due to the low Bis-EMA content). The choice of a peak as the internal standard is typically based on the baseline absorption, the intensity, the shape,

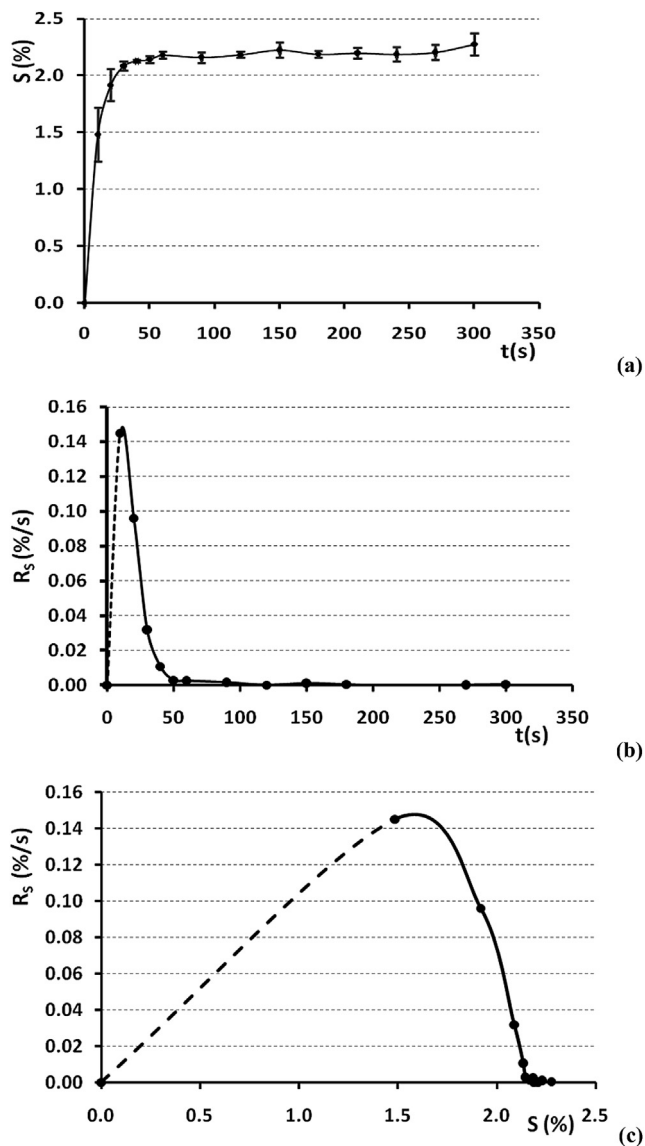


Figure 5: Dependence curve of S (a) or R_S (b) versus time and R_S versus S (c).

the size and the position of the peak that should be unchanging. The neighbouring peak at 1532 cm^{-1} , due to N–H bending, was found to be more suitable in this case for use as an internal standard, which is also reported in the literature.¹⁵

The obtained values of DC for various curing times are presented in Table 2. These were determined, as described in Section 2.2, based on both the area and height of peaks. It is generally stated that the values based on the peaks' area

(DC_A) are more accurate because they take into account the entire space underneath the peaks. Indeed, the standard deviations of values obtained from the peak area are lower than the standard deviations of values obtained from the height of the peak (Table 2). Attempts were also made to determine the DC using transmittance FT-IR on composites pressed between two NaCl crystal windows or by KBr discs. These were, however, unsuccessful due most probably to the dense structure of the composite.

Next, the rate of change of the DC (R_{DC}) was calculated by taking the first derivative of the DC with respect to time [$d(\text{DC})/dt$]. Figure 3a represents the dependence of DC on curing time. A plateau region of the curve is drawn at approximately 200 s. The rate of change per degree of conversion ($R_{DC}^{\%}$) gives a clearer picture of the curing process; a maximum rate is achieved ($R_{DC} = 2.50\%/s$) within 10 s of curing, and an abrupt decrease is then observed ($R_{DC} = 0.24\%/s$) up to 30 s (Figure 3b). The curing is continued at a much lower and decreased rate for up to approximately 100 s. Figure 3c shows that at R_{max} , DC = 25%, and this value then slowly increases up to approximately DC = 40%. The shape of the rate curve (Figure 3b) is typical for the free radical copolymerization of dimethacrylates. In the high crosslinking regime caused by the presence of the two methacrylate groups, autoacceleration of polymerization is apparent from the beginning of polymerization, and the mobility of molecules is restricted upon the immediate onset of gelation. Shortly after the polymerization reaches its maximum rate, autodeceleration begins due to vitrification, and the rate gradually tapers off to zero.¹⁶

Figure 4a shows that at approximately 200 s, a maximum DOC is obtained at approximately 4 mm. The rate of change of DOC (R_{DOC}) takes a maximum value ($=0.186\text{ mm/s}$) after 10 s of curing; then, an abrupt decrease in R_{DOC} is observed to 0.015 mm/s up to 50 s. The rate is slowly reduced practically to zero at approximately 100 s (Figure 4b). Figure 4c shows that when the rate of depth of cure reaches a maximum value ($R_{DOC} = 0.186\text{ mm/s}$), the DOC = 1.858 mm and slowly increases to approximately 3.5 mm. Kalore GC successfully passes the limit of 1.5 mm of curing depth recommended by ISO specification from the first 10 s of irradiation (Table 2). Many researchers agree that halogen-lamp curing devices are no longer suitable for detailed experimental work because the energy emitted by LED units may accurately be determined. The results above reinforce the claim that lamp devices, which remain widely used,^{12,17} may also perform meticulous work on dental materials' presentation of reasonable data.

Figure 5a demonstrates that the volumetric shrinkage of the composite (S) achieves a maximum value of approximately 2.2% after 40 s of curing; it then remains constant. The rate of shrinkage achieves a maximum value

Table 3: Comparative apposition for some parameters calculated in the present study and values published by GC Corporation.¹⁰

Property	Present study	Information brochure of GC Corporation
Degree of conversion	DC = 50% at t = 210 s	DC = 52.44% at t = 20 s
Depth of cure	DOC = 4 mm at t = 240 s	DOC = 3 mm at t = 40 s
Shrinkage	S = 2.2% t = 60 s	S = 1.72% at t = 40 s

By ATR (*different conditions*) (University of Siena)
 By a scratch method (GC Corporation)
 By mercury dialometer (GC Corporation)

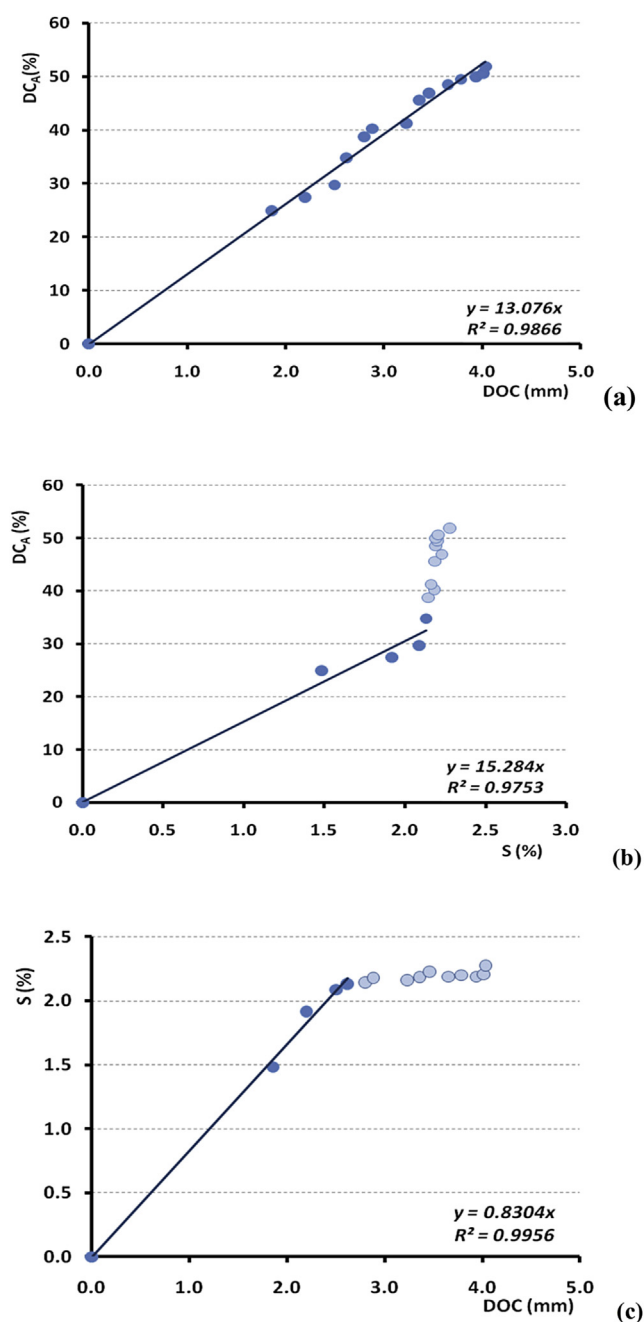


Figure 6: (a) Correlation between DC and DOC, linear regression for the sum of the experimental data. (b) Correlation between DC and S, linear regression for the first 40 s of curing. (c) Correlation between S and DOC, linear regression for the first 40 s of curing.

of 0.14%/s after 10 s of curing; it then decreases, almost to zero, until approximately 40–50 s (Figure 5b). It is interesting to notice that while curing continues beyond 50 s, the shrinkage remains constant. At the maximum rate of shrinkage, the shrinkage is 1.5%; it then increases to 2.2% (Figure 5c). The total volumetric shrinkage is reported to relate to the number of methacrylate groups that have been reacted before the system enters the glassy state.¹⁸ Thus, in our case, the composite reaches the glassy state at approximately 40 s. Subsequently, although the

reaction between the functional groups slowly continues, no further shrinkage is observed. Our results are in agreement with available research data on Kalore GC.¹⁹

Figure 6a shows a linear regression between DC_A and DOC ($R^2 \approx 0.99$) for the full-curing procedure. However, Figure 6b,c exhibit two regions: a linear one (curing time 0–40 s) and a curvy one (for longer curing times). A linear correlation between the degree of conversion and the volumetric shrinkage has been found in several studies.^{6,20,21} It must be noted, however, that this correlation occurs before the system enters the glassy state.

T_g determined by DMTA indicates the polymerization progress of a cross-linked polymer material because the temperature, where transition from the glassy to the rubbery state occurs, shifts higher when the material becomes stiffer.²² An analyst would expect that the most photocured sample would show the highest T_g . In the case at hand, two T_g were found: the first one is attributed to the composite as received after light curing, and the second is attributed to the composite post-cured during the heating of the instrument of DMTA (Table 2). It is interesting to note that even 10 s of light-curing, during which the maximum rate of DC occurred, was enough to produce a composite in the glassy state with a $T_g = 56.4$ °C. However, according to the volumetric shrinkage measurements, the composite enters the glassy state after approximately 40 s. This apparent discrepancy is because the macroscopic rate of volumetric shrinkage is much slower than the rate at which carbon double bonds (C=C) are consumed; the polymerization proceeds more rapidly than the volume relaxation. This is also confirmed by the fact that the maximum rate of change of degree of conversion is achieved within 10 s of curing, whereas the maximum rate of volumetric shrinkage was observed after 40 s of curing. The T_g of the light-cured composite was increased up to 59.5 °C upon light curing for 100 s, indicating that in the glassy state, curing continued somewhat.

Conclusions

A light-curing study of Kalore GC showed that a maximum rate of degree of conversion and a maximum rate of depth of cure were observed within 10 s of curing. Additionally, this composite, cured for 10 s, showed a $T_g = 56.4$ °C and a second $T_g = 112.8$ °C due to extra thermal curing upon heating in the DMTA instrument. The volumetric shrinkage of the composite (S) showed a maximum value of approximately 2.2% after 40 s of curing due to volume relaxation and then remained constant. The curing continued at a much lower and decreased rate up to 100 s. A maximum degree of conversion of approximately 40% and a maximum depth of cure of approximately 3.5 mm were observed. This composite showed a slightly higher $T_g = 59.5$ °C. It is interesting to note that the composite light-cured up to 300 s showed two T_g , revealing that it still contained unreacted carbon double bonds (C=C) and macro-radicals that continued to cure upon heating in DMTA. Finally, the presence of the DX-511 monomer restrains the shrinkage effect when cured, while keeping DC at intermediate levels. The null hypothesis that the polymerization time

for the dental polymer nanocomposite Kalore GC affects the trend of the materials' examined properties is thus verified.

Conflict of interest

The authors have no conflict of interest to declare.

Authors' contributions

All authors have made substantial contributions to the conception, design, acquisition of data and interpretation. They participated in drafting the article, revising it critically for important intellectual content, and approved the final version submitted. They are responsible for the content and similarity index of the manuscript.

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