J Therm Anal Calorim (2010) 99:263–268
DOI 10.1007/s10973-009-0521-6

Thermal and structural properties of commercial dental resins light-cured with blue emitting diodes (LEDs)

S. S. Rojas · G. J. M. Frigo · M. I. B. Bernardi ·
A. N. de S. Rastelli · A. C. Hernandes · V. S. Bagnato

Received: 19 January 2009 / Accepted: 25 September 2009 / Published online: 31 October 2009

Abstract We have investigated the thermal and structural properties of different commercial dental resins: Filtek^{TM} Z-350, Grandio$^{®}$, Tetric Ceram$^{®}$, and TPH Spectrum$^{®}$. The purpose of the present study was to evaluate quantitatively the photo-polymerization behavior and the effect of filler contents on the kinetic cures of the dental resins by using Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. We have successfully obtained the low and high glass transition T_g values of the dental composite resins from DSC curves. It was also observed a good agreement between the both T_g values, activation energies from thermal degradation, and the degree of conversion obtained for all samples. The results have shown that Tetric Ceram$^{®}$ dental resin presented the higher T_g values, activation energy of 215 ± 6 KJ mol^{-1}, and the higher degree of conversion (63%) when compared to the other resins studied herein.

Keywords Degradation · Dental resins · DSC · FT-IR · Thermal analysis

---

S. S. Rojas (✉) · G. J. M. Frigo · M. I. B. Bernardi ·
A. C. Hernandes
Grupo Crescimento de Cristais e Materiais Cerâmicos, Instituto de Física de São Carlos, Universidade de São Paulo, Avenida Trabalhador São Carlense, 400, São Carlos, SP 13566-590, Brazil
e-mail: seila@ifsc.usp.br

A. N. de S. Rastelli · V. S. Bagnato
Grupo de Óptica, Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil

Introduction

Methacrylate-based composites have been widely used as direct polymeric dental restorative materials because they have excellent aesthetic qualities and relatively high cure efficiency in free radical photo-polymerization [1, 2].

The essential phases of most polymeric dental restorative materials are the matrix, filler, and interphase [3]. The matrix, or continuous phase, is typically derived from the monomer system that includes a free radical initiating system. The filler or dispersed phase is designed to enhance the strength–modulus of the softer polymer phase and usually consists of glass or ceramic particles of different compositions, sizes, and size distributions [4]. Filler size is only one of several parameters that affect the overall properties of a composite resin. The filler type, shape, and amount, as well as the efficient coupling between fillers and resin matrix, contribute to the material performance [5].

An important point to be considered in the treatment of dental cavities with composite resins materials, in order to obtain satisfactory restorative results, is to make an adequate clinical composite filling by means of the photo-polymerization process [6].

Photo-polymerization of dental composite resins produces highly crosslinked network systems that exhibit good solvent resistance [7]. However, strong structural changes are observed during the polymerization of multifunctional methacrylate-based composites for dental restorations, which significantly affect the final properties of the materials [8].

The study of the thermal degradation processes would provide more specific information about the internal structures of the dental composite resins. Several studies have been reporting the relationships between filler content and different properties of dental composite resins, such as flexural strength [9], hardness [10], wear [11], stress [12], and thermal expansion [13]. However, there are few studies examining the effect of the filler content on the polymerization of the dental composite resins [14].

A significant characteristic of the light-cured resin-based dental composites is represented by the glass transition temperature (T_g). It is well known that incomplete polymerization which occurs in normal operative conditions determines the high level of the unreacted double bonds that may adversely affect the mechanical properties and the environmental resistance of the dental composites [15]. Moreover, an incomplete polymerization of the matrix determines a low final glass transition temperature—low T_g (16–58 °C). However, it is also known that the unreacted groups in the incompletely cured resins react to some degree after irradiation, providing a glass transition at higher temperatures—high T_g (130–178 °C) [15]. Lee et al. showed that these both glass transitions are only well determined by measuring the differential scanning calorimetry (DSC)—curve immediately after irradiation of the dental resin [15].

DSC technique allows the direct determination of the rate of polymerization reaction, assuming that the heat produced by the polymerization is proportional to the number of monomer units reacted. Therefore, DSC can also be used to the development of kinetic models, which represents a fundamental step for the optimization of conditions during application of the dental composite resins in the oral environment [16].

Thus, the purpose of this study was to evaluate quantitatively the photo-polymerization behavior of the different commercial dental composite resins using the DSC technique and the effect of filler content on the cure kinetics and degree of conversion (DC%) of the dental composites by means of FT-IR technique. The low and high T_g values were determined by measuring the DSC curves of the light-cured and uncured dental composite resins, respectively.

Experimental

The information about fillers and resins matrix of the commercial dental composite resins, analyzed in this work, is summarized in Table 1.

The samples were made with a metallic mould (4 mm diameter and 1 mm thickness). The mould was placed on a glass plate of 10 mm of thickness. The composite resin was packed in a single increment and the top and base surfaces were covered by a mylar strip. A glass sheet with 1 mm thickness was positioned, and a 1 kg weight was used to pack the composite resin. After that, the top surface of the samples was placed in contact with the light-curing tip.

The dental composite resins were photo-activated for 40 s of irradiation by using one LED LCU (LEC 1000/MMOptics, São Carlos, SP, Brazil). The LED LCU was used in standard mode (continuous, constant power density) and power density value of 400 mW cm^{-2}. The power output was measured using a power meter Fieldmaster (Coherent Commercial Products Division—model number FM, set no WX65, part number 33-0506 made in USA) and the power densities values were determined by the equation:

$$I = \frac{P}{A} \tag{1}$$

where P is defined as the power in mW and A is the area of the light tip in cm^2.

DSC measurements were performed with a DSC 2910 (TA Instruments). The samples were heated at 5, 10, and 15 °C min^{-1} constant rates, from 25 to 500 °C, under

Table 1 Basic characteristic of the commercial dental composite resins

Composite resin	Resinous matrix	Filler type loading (vol%)	Batch number
Filtek^{TM} Z-350 (3M/ESPE Dental Products Division, St. Paul, MN 55144-1000, USA)	Bis-GMA, Bis-EMA, UDMA, and TEGDMA	59.5 vol% silica no aglomerate 20 nm and silica/zirconia aglomerate (0.6–1.4 μm)	7HL6018
Grandio® (Voco, (Cuxhaven, Germany)	Bis-GMA, TEGDMA	71.4 vol% spherical nano-particules (silicium dioxide, 20–50 nm) and glass ceramic particles	0809115
Tetric Ceram® (Ivoclar Vivadent, Liechtenstein)	Bis-GMA, UDMA, TEGDMA	60 vol% barium aluminofluorosilicate glass filler of 0.04–3.0 μm (average 0.7 μm)	G25986
TPH Spectrum® (Dentsply/Caulk, Milford, DE, USA)	Urethane modified Bis-GMA dimethacrylate	57 vol% barium aluminoborosilicate glass and highly dispersed silicon dioxide of submicron filler (0.8 μm)	E391965

nitrogen flowing at 40 mL min^{-1} in order to observe the degradation peak of the different dental composite resins. A mass of ~6.5 mg of the samples was used in an aluminum sample pan. The reference pan contained 5 mg of aluminum. All cured dental composite resins were previously heated until 100 °C in order to eliminate the thermal history of the resins and after that the DSC curves were performed.

In order to understand the thermal behavior of the dental composite resins, all uncured samples were submitted to DSC measurement in two steps at 10 °C min^{-1}. In the first step, the samples were heated up to the exothermal peak, which means that the composite resins reached their thermal cure during the DSC measurement and were cooled down. In the second run, subsequently done, the samples were heated until reaching their thermal degradation temperatures. These curves were compared to the DSC curve of the light-cured composite resins at 10 °C min^{-1}. All DSC curves presented herein are the experimental results without fit or smooth.

The samples used for FT-IR measurements were prepared 24 h after the photo-activation. The composite resins were pulverized into a fine powder and maintained in a dark room until the moment of the FT-IR analysis. The ground powders (10 mg) were thoroughly mixed with KBr powder salt (100 mg). These mixtures were pressed with a load of 10 tons during 1 min to obtain a pellet.

The number of double carbon bonds which are converted in single bonds provides the degree of conversion (DC%) of the composite resin. In order to measure the degree of conversion values for the samples, the FTIR spectra (Nexus—470) for both uncured and cured samples were analyzed. The measurements were recorded in the absorbance mode operating under the following conditions: 32 scans, 4 cm^{-1} of resolution, in the range of 400–4000 cm^{-1}.

The percentage of unreacted carbon–carbon double bonds (C=C%) was determined from the ratio of absorbance intensities of the aliphatic C=C, which corresponds to the IR peak at 1638 cm^{-1}, against internal standard before and after curing of the specimen: aromatic C–C, IR peak observed at 1608 cm^{-1} [17]. This experiment was carried out in triplicate. The degree of conversion was determined by subtracting the C=C% from 100%, according to the formula:

$$\mathrm{DC\%} = 1 - \frac{(1638\mathrm{cm}^{-1}/1608\mathrm{cm}^{-1})\mathrm{cured}}{(1638\mathrm{cm}^{-1}/1608\mathrm{cm}^{-1})\mathrm{uncured}} \times 100 \qquad (2)$$

Results and discussion

A representative result obtained by DSC measurements of two commercial dental composite resins TPH Spectrum® and Filtek™ Z-350, without and with photo-polymerization, is shown in Fig. 1. The inset in the Fig. 1a, b shows the T_g values observed at low and high temperatures.

It has been observed, in Fig. 1a for the first run (dashed line), a high T_g value (102 °C) and an exothermal peak in a range of 160–193 °C, that can be attributed to the thermal cure of the TPH® Spectrum composite resin. In the second run of DSC measurement (dotted line) the thermal degradation of the composite resin, represented by the endothermic peaks, was observed. The first degradation was observed between 250 and 350 °C, and a second degradation in a range of 400–475 °C, which represents the main chain degradation of the polymer. The peak value of the main degradation was observed at 433 °C. The solid line in Fig. 1a represents the DSC curve of THP® Spectrum composite resin, previously cured with blue LED, and in this curve was observed the low T_g value (52 °C), and its main thermal degradation peak was observed at 436 °C.

Figure 1b shows the results of DSC curves from Filtek™ Z-350 composite resin. It has been observed a similar behavior in the thermal events as obtained for TPH Spectrum®, as well as to the other resins. The characteristic

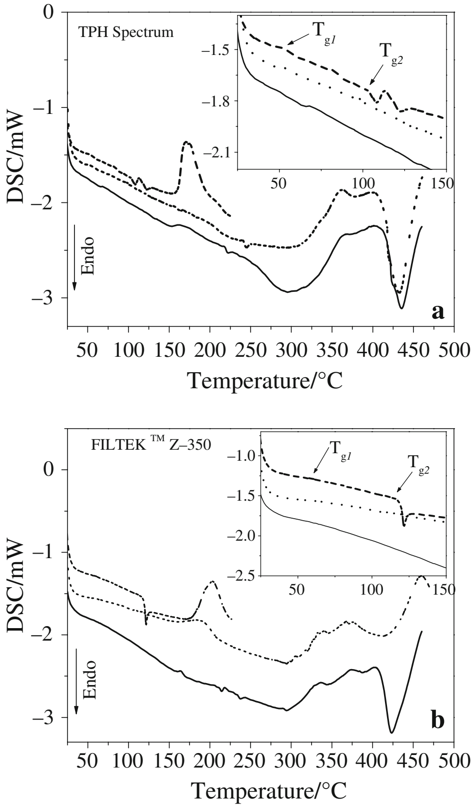

Fig. 1 DSC curves from **a** TPH Spectrum® and **b** Filtek™ Z-350 dental composite resins under different conditions, uncured (two runs: *dashed and dotted lines*) and light-cured with blue LED (*solid line*) at 10 °C min^{-1}, in N_2 atmosphere

Table 2 Thermal parameters obtained from DSC curves and degree of conversion of the dental resins

Resin	Low T_g (at 10 °C min^{-1})	High T_g (at 10 °C min^{-1})	ΔE/KJ mol^{-1}	R^2	Degree of conversion (%)
Filtek™ Z-350	61	118	217 ± 14	0.991	54
Grandio®	50	103	173 ± 10	0.994	51
Tetric Ceram®	84	140	215 ± 6	0.998	63
TPH Spectrum®	52	102	204 ± 10	0.995	52

R^2 fit parameter

temperatures as low and high T_g for all resins studied herein are summarized in Table 2.

Recently, Achillias et al. [18] published a report about degradation of the Bis-GMA, Bis-EMA, UDMA, and TEGDMA resins. It has been shown that only TEGDMA presented significant degradation of 34.5% at 300 °C, by heating it at 10 °C min^{-1}. All other resins presented very small degradation in the same conditions, however, the Bis-GMA and Bis-EMA degraded in two steps, while, UDMA and TEGDMA degraded in three steps.

It has been demonstrated, in a former paper [19] that different commercial composite resins presented three steps for degradation before be light-cured with the blue LED, and after that all composite resins presented only two steps of degradation. Those previous results were observed by thermogravimetric measurements [19], which are in accordance with the DSC curves obtained in this study. The differences observed among the commercial composite resins studied herein and those studied by Achilias et al., can be attributed to the presence of the different fillers at high concentration (57–70%), which can stabilize the resins under its thermal degradation.

When the composite resins are light irradiated, the radicals generated broken the double bonds of the monomers, creating cross-linked three-dimensional network polymers. However, the conversion of double bonds inside the polymerized samples cannot be easily measured directly by using the FT-IR technique. Representative FT-IR measurement obtained for Tetric Ceram® dental composite resin is shown in Fig. 2.

Figure 3 shows the degree of conversion obtained for all dental composite resins. The degree of conversion values were calculated by applying Eq. 2.

The comparison between the thermal and structural characteristics of the cured resins was carried out by measuring the activation energy required for decomposition of the dental composite resins and the degree of conversion obtained by FT-IR. Higher activation energy suggests a greater degree of polymerization, and increased cross linking.

Figure 4 shows representative curves of DSC obtained for all composite resins, studied at three different heating rates: 5, 10, and 15 °C min^{-1}.

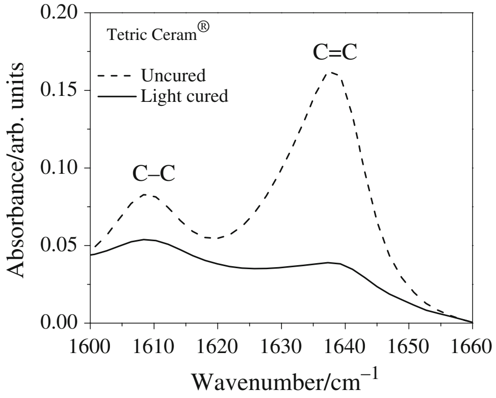

Fig. 2 FT-IR measurement obtained for Tetric Ceram® dental composite resin, IR bands at 1608 and 1638 cm^{-1} correspond to the C–C and C=C vibrations, respectively, [17]

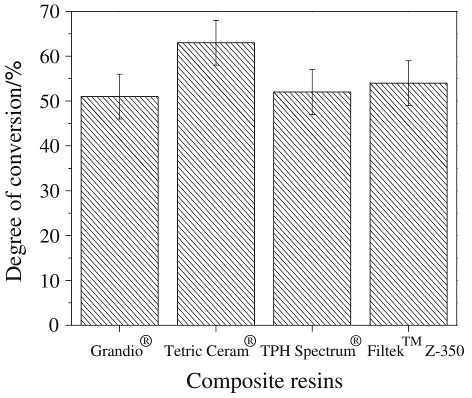

Fig. 3 Degree of conversion of the dental composite resins obtained from FT-IR measurements

All endothermic peak values were obtained at higher temperatures for faster heating rates. These curves were used to obtain the activation energy values associated to the thermal degradation of the main chain of the polymer matrix. It was calculated by the endothermic curves created from the decomposition of dental resins during DSC measurements. The reaction-rate analysis was performed by using Ozawa's method [20, 21], which is applied to the peak value of the endothermic curves. The chemical reaction is described by

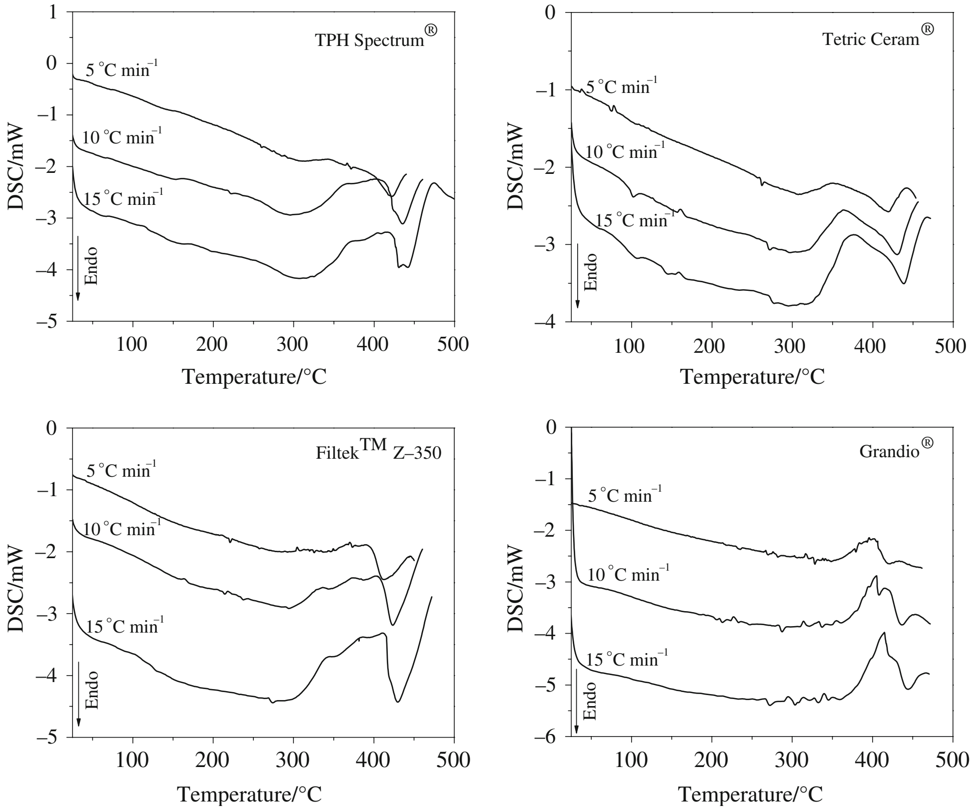

Fig. 4 DSC curves from commercial dental composite resins under three different heating rates

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\exp\left(\frac{-\Delta E}{RT}\right)(1-x)^n \tag{3}$$

Here x is the reaction rate, t is time, A is the frequency factor, ΔE is the activation energy, R is the gas constant, T is the absolute temperature, and n is the order of reaction. As the reaction rate (x) is considered to be constant at lower peaks, the reciprocal temperatures of the endothermic peaks (T_n) are related to the logarithm of the heating rates (a_n),

$$\begin{aligned}\log a_1 + 0.4567\frac{\Delta E}{RT_1} &= \log a_2 + 0.4567\frac{\Delta E}{RT_2}\\ &= \log a_3 + 0.4567\frac{\Delta E}{RT_3} = \ldots\end{aligned} \tag{4}$$

The activation energy can be approximated from the slope of the regression line in an Arrhenius plot,

$$\Delta E \approx \frac{\sim R(\mathrm{Slope})}{0.4567} \tag{5}$$

Representative Arrhenius plot for Filtek™ Z-350 resin, obtained by applying Ozawa's method, is shown in Fig. 5.

Table 2 summarizes the thermal parameters obtained from DSC experiments and the degree of conversion obtained from FT-IR measurements. It has been observed a good agreement among the T_g values (for low and high temperatures), the activation energies and the degree of conversion for all samples. The higher values of the studied parameters and consequently major stability were observed for Tetric Ceram® dental composite resin.

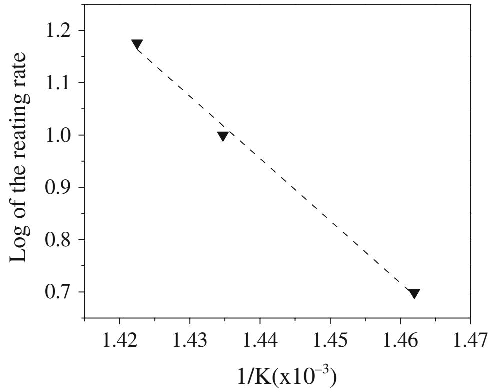

Fig. 5 Arrhenius plot of the reciprocal peak temperature versus the logarithm of the heating rate, obtained for Filtek™ Z-350 dental composite resin

Conclusions

In the present work we have confirmed that there was a good agreement between the two T_g values, at low and high temperatures, activation energies from thermal degradation of the main chain of the polymer matrix, and the degree of conversion obtained for all samples. The results observed by DSC measurements showed that Tetric Ceram® dental resin presented the higher T_g values (low T_g at 84 °C and high T_g at 140 °C) and the higher activation energy value (215 ± 6 KJ mol^{-1}), associated to the thermal degradation from the main chain of the polymer. It was confirmed by the degree of conversion (63%) obtained by FT-IR absorption, which implies that Tetric Ceram® dental resin presents the major stability when compared to the other commercial resins studied.

Acknowledgements The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq, PRONEX/FINEP, and CAPES.

References

1. Antonucci JM, Stansbury JW. In: Arshady R, editor. Desk reference of functional polymers. Washington, DC: American Chemical Society; 1997.
2. Moszner N, Salz U. New development of polymeric dental composites. Prog Polym Sci. 2001;26:535–76.
3. Gatti A, Rastelli ANS, Ribeiro SJL, Messaddeq Y, Bagnato VS. Polymerization of photocurable commercial dental methacrylate-based composites—Photocalorimetry study. J Therm Anal Calorim. 2007;87:631—4.
4. Wilson KS, Zhanga K, Antonuccia JM. Systematic variation of interfacial phase reactivity in dental composites. Biomaterials. 2005;26:5095–103.
5. Masouras K, Silikas N, Watt DC. Correlation of filler content and elastic properties of resin-composites. Dent Mater. 2008;24:932–9.
6. Conti C, et al. Spectroscopic and mechanical properties of dental resin composites cured with different light sources. J Mol Struct. 2005;744–747:641–6.
7. Anseth KS, Newman SM, Bowman CN. Polymerization kinetics and volume relaxation behavior of photopolymerized multifunctional monomers producing highly crosslinked network. Adv Polym Sci. 1995;122:177–217.
8. Watts DC. Reaction kinetics and mechanics in photo-polymerised networks. Dent Mater. 2005;21:27–35.
9. Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water—effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res. 1998; 42:465–72.
10. Li Y, Swartz ML, Phillips RW, Moore BK, Roberts TA. Materials science effect of filler content and size on properties of composites. J Dent Res. 1985;64:1396–401.
11. Lim BS, Ferracane JL, Condon JR, Adey JD. Effect of filler fraction and filler surface treatment on wear of microfilled composites. Dent Mater. 2002;18:1–11.
12. Razak AA, Harrison A. The effect of filler content and processing variables on dimensional accuracy of experimental composite inlay material. J Prosthet Dent. 1997;77:353–8.
13. Soderholm KJ. Influence of silane treatment and filler fraction on thermal expansion of composite resins. J Dent Res. 1984;63: 1321–6.
14. Mohsen NM, Craig RG, Filisko FE. Effects of curing time and filler concentration on curing and postcuring of urethane dimethacrylate composites: a microcalorimetric study. J Biomed Mater Res. 1998;40:224–32.
15. Lee JK, Choi JY, Lim BS, Lee Y, Sakaguchi RL. Change of properties during storage of a UDMA/TEGDMA dental resin. J Biomed Mater Res B Appl Biomater. 2004;68B:216–21.
16. Tanimoto Y, Hayakawa T, Nemoto K. Analysis of photopolymerization behavior of UDMA/TEGDMA resin mixture and its composite by differential scanning calorimetry. J Biomed Mater Res B Appl Biomater. 2005;72B:310–5.
17. Rastelli ANS, Jacomassi DP, Bagnato VS. Effect of power densities and irradiation times on the degree of conversion and temperature increase of a microhybrid dental composite resin. Laser Phys. 2008;18:1074–9.
18. Achilias DS, Karabela MM, Sideridou ID. Thermal degradation of light-cured dimethacrylate resins: part I. Isoconversional kinetic analysis. Thermochim Acta. 2008;472:74–83.
19. Bernardi MIB, Rojas SS, Andreeta MRB, Rastelli ANS, Hernandes AC, Bagnato VS. Thermal analysis and structural investigation of different dental composites resins. J Therm Anal Calorim. 2008;94:791–6.
20. Kanbe H, Ozawa T. Thermal analysis. Tokyo: Kohdansha; 1992. p. 57–64.
21. Hatakeyama T, Quinn FX. Thermal analysis—fundamentals and applications to polymer science. 2nd ed. New York: Wiley; 1999. p. 82–4.