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Thermal degradation of light-cured dimethacrylate resins
Part I. Isoconversional kinetic analysis

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Abstract

The thermal degradation of resins based on bis-phenol A glycidyl dimethacrylate (Bis-GMA), bis-phenol A ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) was investigated using thermogravimetric analysis. Four different heating rates were employed for its polymer in order to have adequate data to perform an isoconversional analysis. Activation energies were estimated as a function of the extent of degradation using a differential and an integral method. The observed differences were interpreted in terms of degradation mechanisms, which are highly depended on the structural characteristics of the corresponding resin. The existence of only a small number of defects in the network structure of Bis-GMA and Bis-EMA resins together with their stiff aromatic nuclei lead to the formation of a rigid network with high thermal stability and to decomposition in one-step. In contrast, inhomogeneities in the network structure of TEGDMA and UDMA resins, mainly due to the formation of primary cycles during polymerization, result in a two-step degradation mechanism at much lower temperatures. The hydrogen bonding ability of Bis-GMA and UDMA monomer units was also found to play an important role during thermal degradation of these resins.

Keywords: Thermal degradation; Dimethacrylate resins; Isoconversional analysis; Activation energy; TGA

1. Introduction

The thermal degradation of polymers has been at the center of thermal analysis for many years. The determination of the parameters of the thermal decomposition process provides more specific information regarding internal structures of polymeric materials [1–5]. Thermogravimetric analysis (TGA) is a common experimental method used to study the overall or macroscopic kinetics of polymer degradation. However, apart from a simple TGA scan, further computational kinetic analysis is needed to probe the degradation mechanism, as well as, to predict the thermal stability of polymers. Among others, isoconversional methods have been conceived by many researchers and widely used in thermal degradation kinetic studies [6].

As it is well-known, polymers degrade on heating forming low molecular products. The process involves breaking of the bonds between individual atoms forming a polymer chain. Study of polymer degradation becomes more difficult when the material studied does not form linear macromolecular chains but three-dimensional networks. Dimethacrylate-based resins are such materials, which find wide applications as biomaterials. In fact, dental resins require highly crosslinked three-dimensional network structures which can be produced from the photopolymerization of multifunctional monomers. The monomers typically used combine a relatively viscous dimethacrylate base monomer, such as 2,2-bis[*p*-(2′-hydroxy-3′-methacryloxypropoxy)phenylene]propane (usually referred as bis-phenol A glycidyl dimethacrylate, Bis-GMA) with a low viscosity dimethacrylate comonomer, such as triethylene glycol dimethacrylate (TEGDMA) used as reactive diluent. Other common used base monomers in commercial dental resin-based materials are the bis-phenol A ethoxylated dimethacrylate (Bis-EMA) and 1,6-bis-(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethyl hexane (usually referred as urethane dimethacrylate, UDMA). These monomers are copolymerized at ambient temperature, by using either a photoinitiation system or a redox initiation system. In the first case

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the most common photoinitiation system is a combination of camphorquinone with an amine. Polymerization kinetics and network structure formation of these resins have been extensively studied in literature [7–10].

Thermal degradation of these monomers has been described in only a few reports owing to the complexity of the process [11–14]. Pielichowski et al. [13] studied the thermal decomposition of copolymers based on long chained diol dimethacrylated and Bis-GMA/TEGDMA. One degradation step was observed using a rather high heating rate (50 K/min). Only two serious attempts to study thermal degradation of photo-polymerized Bis-GMA/TEGDMA copolymers were presented by Teshima et al. [11] and Rigoli et al. [14]. To our knowledge thermal degradation of UDMA, Bis-EMA and also of the homopolymers prepared from Bis-GMA and TEGDMA has not been reported so far in literature.

Therefore, following our recent publications on the effect of the monomer chemical structure on the degree of conversion, water sorption, modulus of elasticity, and thermal expansion characteristics of dimethacrylate-based dental resins [15–18], in this investigation the thermal degradation kinetics of resins based on Bis-GMA, Bis-EMA, UDMA or TEGDMA is examined. Thermogravimetric scans are taken at different heating rates and an isoconversional analysis is carried out to determine the change of the effective activation energy as a function of conversion for all resins. Both differential and integral isoconversional methods are examined.

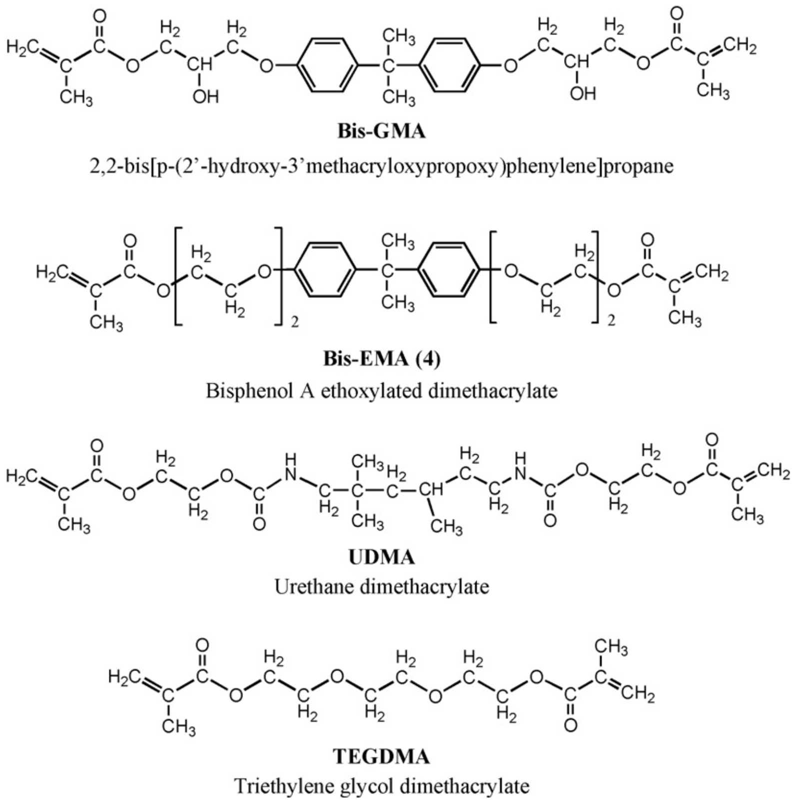
2. Experimental

2.1. Materials

The dimethacrylate monomers used were Bis-GMA (Aldrich Chem. Co., Lot no. 07210BB), UDMA (Ivoclar-Vivadent, Lot no. B00338), TEGDMA (Aldrich Chem. Co., Lot no. 09004BC-275) and Bis-EMA (Aldrich Chem. Co., Lot no. 03514 HF). The chemical structure of these monomers appears in Scheme 1. The photoinitiator system was camphorquinone (CQ) (Lot no. S12442-053) and ethyl-4-dimethylaminobenzoate (4EDMAB) (Lot no. 90909001) and they were provided from Aldrich. All the materials used in this study were used as received without further purification.

2.2. Preparation of specimens

Polymers were prepared by mixing monomer and the photoinitiator system (CQ 0.2% mass fraction and 4EDMAB 0.8% mass fraction), followed by heating in the dark at 60 ± 0.5 °C until the photo-initiator components were dissolved in the monomer. Then the mixture of monomer was cured in Teflon molds using a XL3000 dental photocuring unit (3M Company). This source consisted of a 75-W tungsten halogen lamp, which emits radiation between 420 and 500 nm and has the maximum peak at 470 nm. The samples were irradiated for 200 s on each side, time that has been found to be adequate for the polymerization to reach the limiting degree of conversion [16].



Bis-GMA

2,2-bis[p-(2’-hydroxy-3’methacryloxypropoxy)phenylene]propane

Bis-EMA (4)

Bisphenol A ethoxylated dimethacrylate

UDMA

Urethane dimethacrylate

TEGDMA

Triethylene glycol dimethacrylate

Scheme 1. Chemical structure of the dimethacrylate monomers used.

2.3. Thermogravimetric analysis (TGA)

TGA was performed on a Pyris 1 TGA (PerkinElmer) thermal analyzer. Samples of about 8 mg were used. They were heated from ambient temperature to 600 °C under a 20 ml/min nitrogen flow. TGA measurements of each sample were performed at different heating rates of 2.5, 5, 10 and 20 °C min^{-1} and sample mass versus temperature was continuously recorded.

3. Kinetic analysis of TGA data according to isoconversional methods

The kinetics of polymer degradation are usually described by the following single-step kinetic equation [1,6]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

where α represents the extent of reaction, which can be determined from TGA runs as a fractional mass loss, t is time, $k(T)$ a temperature-dependent rate constant and $f(\alpha)$ denotes the particular reaction model, which describes the dependence of the reaction rate on the extent of reaction. If an Arrhenius-type expression is used to describe the temperature dependence of $k(T)$, then Eq. (1) yields:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

with A and E the pre-exponential factor and the activation energy, respectively.

According to the isoconversional principle, at a constant extent of reaction, the reaction rate is a function only of the temperature. So Eq. (2) can be written as:

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}(1/T)}\right]_\alpha = -\frac{E_\alpha}{R} \tag{3}$$

where the subscript α denotes value at a specific extent of reaction.

Isoconversional methods employ multiple temperature programs (e.g., different heating rates) in order to obtain data on varying rates at a constant extent of conversion. Thus, isoconversional methods allow complex (i.e., multi-step) processes to be detected via a variation of E_α with α [6].

Simple rearrangement of Eq. (2) leads to the following equation, which forms the foundation of the differential isoconversional method of Friedman [19]:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln\left[A_\alpha f(\alpha)\right] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{4}$$

The subscript i denotes different heating rates.

Application of the Friedman method to the integral part (e.g., TGA data) requires numerical differentiation of the experimental α versus T curves. This is typically carried out by the software of the instrument used and in sometimes results in quite noisy rate data and thus, unstable activation energy values. This problem of numerical differentiation could be avoided by using integral isoconversional methods. For nonisothermal conditions, when the temperature is raised at a constant heating rate β, integration of Eq. (2) involves solving the temperature integral in the following equation:

$$g(\alpha) \equiv \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_\alpha} \exp\left(\frac{-E}{RT}\right)\mathrm{d}T = \frac{A}{\beta}I(E,T) \tag{5}$$

Since the integral $I(E,T)$ in Eq. (5) does not have an analytical solution it can be solved using either approximations or numerical integration. One of simplest approximations by Doyle [20] gives rise to the following equation, which is used in the popular isoconversional methods of Flynn [21] and Wall and Ozawa [22]:

$$\ln(\beta_i) = \text{const.} - \frac{1.05E_\alpha}{RT_{\alpha,i}} \tag{6}$$

The use of a more precise approximation by Coats and Redfern [23] yields the equation:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha,i}}\right) = \text{const.} - \frac{E_\alpha}{RT_{\alpha,i}} \tag{7}$$

Further increase in precision of the integral methods can be accomplished by using numerical integration, a method developed and extensively used by Vyazovkin [24–26]. In this investigation the methods of Friedman, Flynn, Wall and Ozawa (FWO) and Coats and Redfern were used.

4. Results and discussion

4.1. Effect of heating rate

Figs. 1a–4a show the TGA scans of Bis-GMA, Bis-EMA, UDMA and TEGDMA resins, respectively at different heating rates of 2.5, 5, 10 and 20 °C min^{-1}. The corresponding differential TGA (DTGA) plots of all these resins at different heating rates appear in Figs. 1b–4b, respectively. In all cases studied, it was observed that an increase in the heating rate shifts the TGA curves and peak temperatures to higher values, as it was expected and is common in different types of polymers [2–4,14]. Decomposition of crosslinked polymers in an inert atmosphere occurs in such a way that they tend to conserve the structure of their matrix, thus bond breaking inside the polymer matrix requires a large amount of energy [27]. In this investigation, almost all resins exhibited high thermal stability with very small degradation even at 300 °C. The values measured at the heating rate 10 °C min^{-1} were 2.3, 3.1, 5.5 and 34.5% for Bis-GMA, Bis-EMA, UDMA and TEGDMA, respectively. It is obvious that only the TEGDMA resin degraded significantly at this temperature. From Figs. 1–4 it can be observed that either one-step or a two-step degradation mechanism may occur depending on the resin type. The temperature where degradation starts together with that where the maxima appears for all resins at different heating rates are provided in Table 1. An explanation of the results, taking into consideration the degradation mechanism, follows.

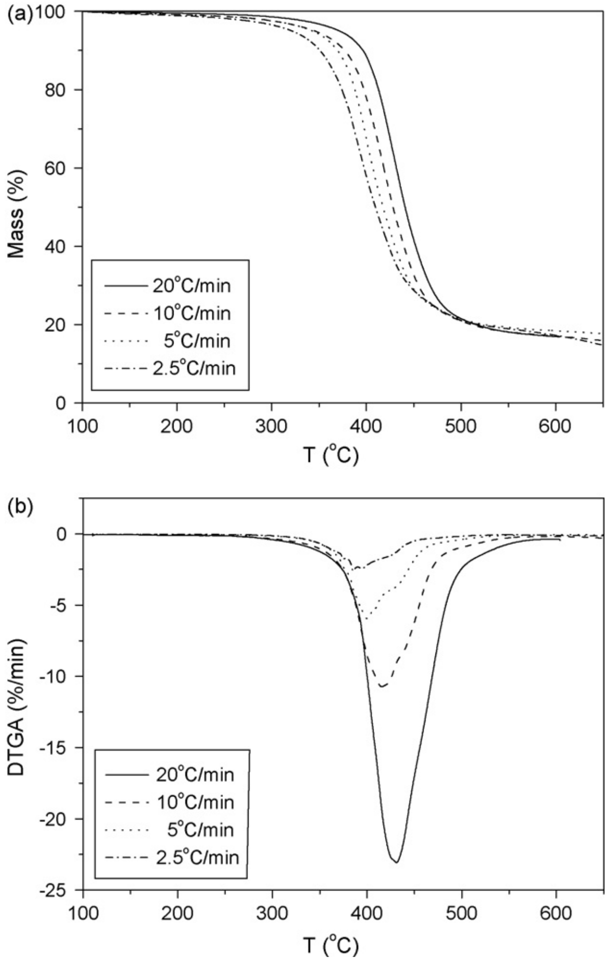


Fig. 1. Effect of heating rate on the TGA scans (a) and DTGA curves (b) of Bis-GMA resin.

Table 1
Temperatures where thermal degradation starts (T_0) and at the first (T_1) and second (T_2) maximum of thermal decomposition, as well as residual mass at 600 °C for each sample studied at different heating rates

Sample	Heating rate (°C min^{-1})	T_0 (°C)	T_1 (°C)	T_2 (°C)	Residual mass at 600 °C (%)
Bis-GMA	2.5	250	394	–	17.2
	5	248	400	–	18.4
	10	250	415	–	17.1
	20	255	431	–	17.0
Bis-EMA	2.5	242	414	–	5.3
	5	244	414	–	5.3
	10	245	424	–	4.1
	20	246	441	–	4.2
UDMA	2.5	209	321	417	1.5
	5	209	340	434	1.7
	10	217	357	444	1.0
	20	222	372	454	1.3
TEGDMA	2.5	201	277	370	2.0
	5	203	284	371	1.2
	10	204	306	403	1.9
	20	206	320	416	1.8

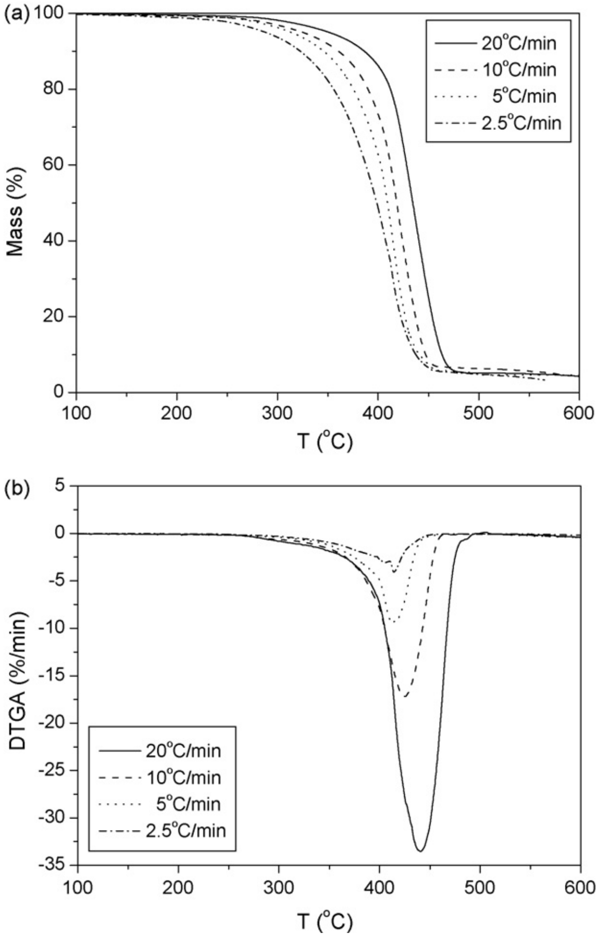


Fig. 2. Effect of heating rate on the TGA scans (a) and DTGA curves (b) of Bis-EMA resin.

4.2. Effect of the resin chemical structure

Thermal degradation of radically polymerized mono-methacrylate polymers like poly(methyl methacrylate), PMMA, usually shows two or three mass loss steps during decomposition [2]. The decomposition reaction is a radical depolymerization where the chain backbone of the polymer is split by a radical reaction mechanism [28]. Depending on polymer type and experimental conditions either end-chain, or random scission of the macromolecules occurs [28] leading to the production either of the monomer in a large amount (i.e., in PMMA degradation [29]) or in other secondary products [30]. During thermal degradation of PMMA at low temperatures (330–400 °C) end-chain scission is favoured, which is replaced by random main-chain scission at higher temperatures (>400 °C) [31]. Thus, initial degradation is initiated at vinylidene end groups resulted from the termination by disproportionation reaction taking place during polymerization. Once the vinylidene-terminated chains have unzipped, further degradation is initiated by random scission that corresponds to the second mass loss step in TGA experiments [2]. Furthermore, random main-chain scission may start at abnormal head-to-head linkages formed as a result of termination by combination of growing polymer chains [31,32]. During this step two radicals are formed by the action of heat

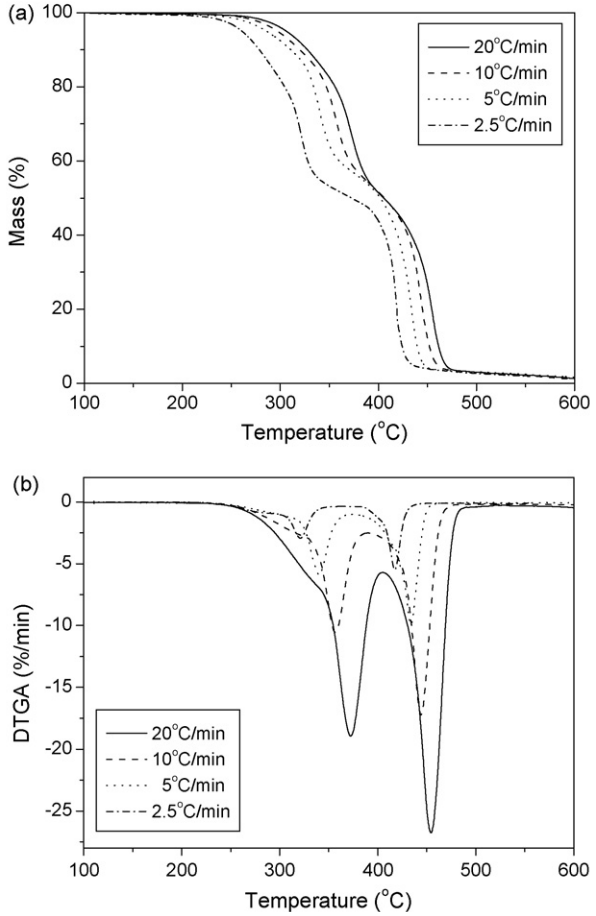


Fig. 3. Effect of heating rate on the TGA scans (a) and DTGA curves (b) of UDMA resin.

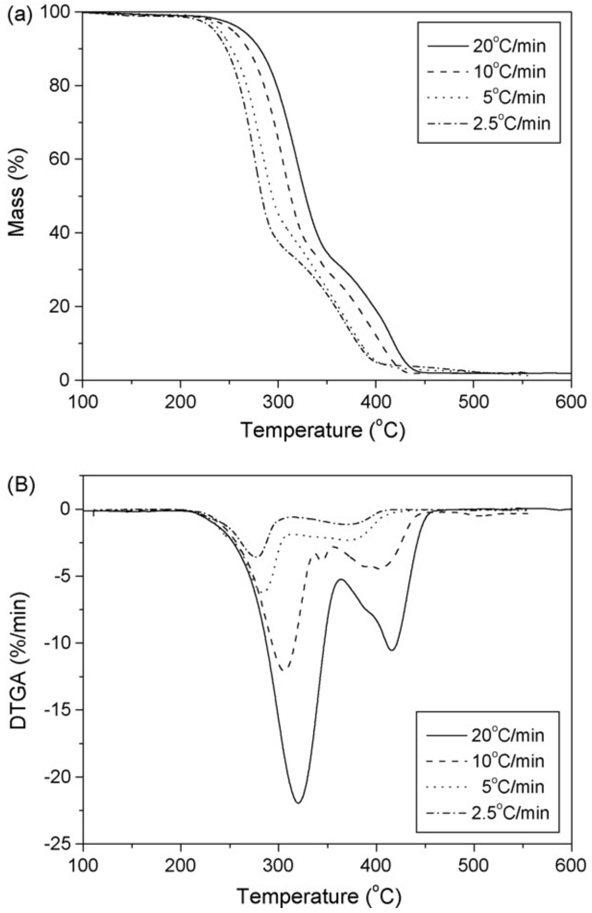


Fig. 4. Effect of heating rate on the TGA scans (a) and DTGA curves (b) of TEGDMA resin.

on the polymer chain, which both can undergo a number of different reactions such as depolymerization, hydrogen abstraction or interaction with another radical giving either coupling or disproportionation. Considering the isobutyryl macroradical it is general accepted that it will depolymerize to form monomer molecules in a process which is the reverse of polymerization. However, the second primary radical formed does not depolymerize efficiently. Therefore, different mechanisms, such as β-scission to form a methoxycarbonyl radical, or side-group scission, have been proposed to describe the degradation of these radicals and predict the different products obtained during the process [32].

For the Bis-GMA resin, the temperature at which degradation starts is near 250 °C and does not seem to depend much on the heating rate. Thermal degradation seems to stop at approximately 500 °C, where afterwards it continuous, but at a much slower rate. The solid residual weight at 600 °C was not much affected by the heating rate used, with a char yield of carbonization high enough and approximately equal to 17–18%. The degradation is completed in only one-step and the temperature at which maximum degradation occurs ranges between 394 and 431 °C, as the heating rate increased from 2.5 to 20 °C min^{-1} (Table 1).

Bis-EMA resin exhibits a similar to Bis-GMA behaviour with only one degradation step starting at 242–246 °C and completing at approximately 450 °C. The solid residual weight at 600 °C was again not much affected by the heating rate used, with a char yield of carbonization much lower than that of Bis-GMA and approximately equal to 4–5% (Table 1).

Thermal degradation of TEGDMA resin seems to complete in two steps, starting at rather low temperatures of 201–206 °C increasing with the heating rate. The first degradation rate maximum occurs at 277–320 °C (increasing with the heating rate) and the second at 371–416 °C (increasing with heating rate). The degradation stops at a temperature interval between 400 and 450 °C, leaving a very small amount of char approximately equal to 2% (Table 1).

Finally, UDMA resin shows also a two step thermal degradation mechanism starting at temperatures higher than those of the other aliphatic resin TEGDMA, i.e., from 210 to 220 °C and completing at 430–470 °C, leaving again a very small amount of solid residue around 1–1.7%. The first maximum in the degradation rate ranges from 321 to 372 °C (increasing with the heating rate) while the second at 417 to 454 °C (increasing with the heating rate). Both maxima are higher than the corresponding measured for TEGDMA, while the values of the second maximum seem to be close to those found for Bis-EMA.

A comparative plot of TGA scans for all the polymers studied at a heating rate of 10 °C min^{-1} is shown in Fig. 5.

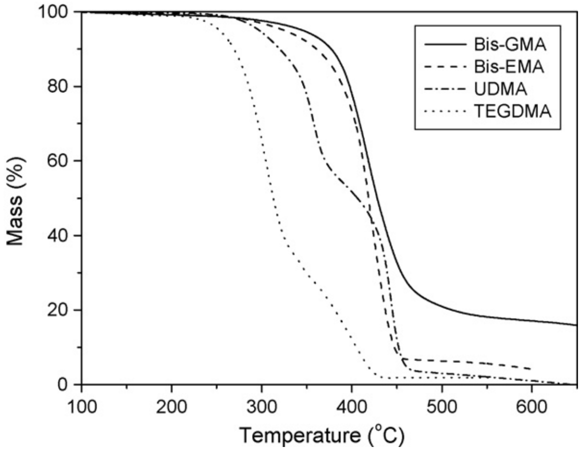
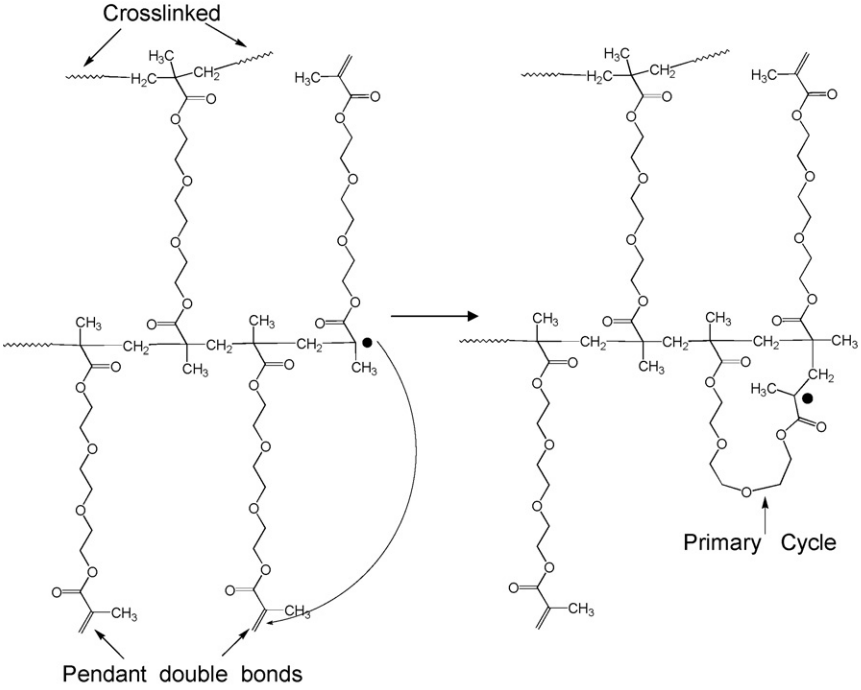
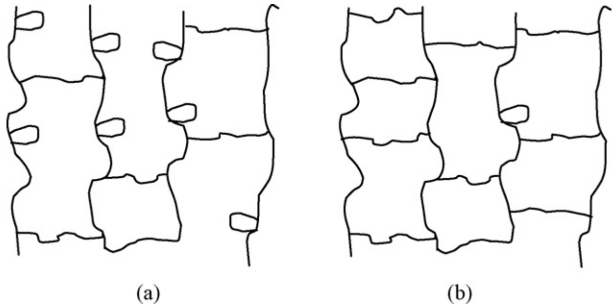


Fig. 5. Effect of the resin structure on the TGA scans at 10 °C min^{-1}.

In order to explain the aforementioned observations, at this point it is interesting to examine the features of network formation of these highly crosslinked systems. It has been reported that such phenomena as microgel formation and primary cyclization usually occur in the creation of crosslinked networks [33–36]. Since photoinitiated free radical reactions form multiple initiation sites upon exposure to light, an inhomogeneous polymerization ensues. Microgel regions, which are more highly crosslinked than the rest of the polymer, are created at these initiation sites. Due to microgel formation, unreacted monomer pools and highly crosslinked polymer regions coexist within the same material. In addition, when multifunctional monomers are polymerized, a pendant double bond can react intramolecularly with the radical in its propagating chain to form a loop in a primary cyclization reaction [33,34]. Primary cyclization reactions are generally undesirable, since they do not contribute to overall crosslinking density, but does promote network heterogeneity, incomplete conversion and reduced mechanical strength [35]. Pendant double bonds are created by the consumption of monomer and react away, either by crosslinking or cyclization reactions. Monomer chain stiffness has been proved to play a dominant role in cyclization reactions [33]. As both Bis-GMA and Bis-EMA resins contain the kinked and rigid bis-phenol A core structure, it is expected that this connecting-group rigidity is primarily responsible for a reduction in the amount of cyclization reactions occurring in these resins. Bis-GMA is not flexible enough to react intramolecularly with the radical on the same propagating chain, until several repeat units have been added. Thus it forms an excellent monomer for dental applications because it provides more crosslinking than a similar more flexible monomer [35]. In contrast, TEGDMA and UDMA due to their non-aromatic nuclei are more flexible monomers and therefore their pendants can cycle more readily after they are created. In fact, TEGDMA pendants undergo cyclization reactions almost three times more than Bis-GMA pendants [33]. A schematic representation of the primary cyclization reaction in TEGDMA resin, occurring during polymerization appears in Scheme 2. Therefore, the degradation of Bis-GMA and Bis-EMA resins at higher temperatures is attributed to the existence of only a small number of cycles (meaning inhomogeneities) in the polymer network. In contrast, the existence of a large number of cycles in the TEGDMA and in UDMA resins leads to defect points in the network, which could more easily be degraded. A schematic representation of network with high or low degree of cyclization appears in Scheme 3. Furthermore, compared with the 2-hydroxy-propyl groups of Bis-GMA, the longer and more flexible ethoxylated linkages in Bis-EMA and



Scheme 2. Primary cyclization reaction occurring during polymerization of TEGDMA.



Scheme 3. Polymer network with high (a) and low (b) degree of cyclization.

the lack of hydrogen bonding allow a greater degree of mobility and as a result a degradation in lower temperatures. The highly homogeneous network formed in Bis-GMA and Bis-EMA resins is also mainly responsible for the appearance of only one degradation temperature in these resins. In contrast, the appearance of two degradation steps in the resins formed from TEGDMA and UDMA is attributed to inhomogeneities in the network structure mainly due to the formation of primary cycles during polymerization. The first degradation step, at low temperatures, corresponds to bond breaking near the cycling points, while the second to the main network.

The final point to be discussed is the greater thermal stability observed in the UDMA resin compared to TEGDMA resin. To understand this phenomenon the chemical structure of the resins is examined next. In both these resins, aromatic nuclei are absent, although two major differences exist. The first is connected with the appearance of hydrogen bonding interactions in the UDMA resin due to the existence of the N–H groups. Hydrogen bonding generally leads to a viscosity increase that results in enhanced polymerization kinetics. The existence of hydrogen bonding leads to a need of extra energy for the network to degrade. The second reason has to do again with the defects formed in the network structure due to the cyclization reactions. In general cyclization is more likely when the crosslinker size is smaller [36]. Pendant double bonds in a higher molecular weight crosslinker are more dilute therefore they do not react (with the same degree of probability as in the case of a lower molecular weight crosslinker) with the active centre that consumed the first double bond. The molecular mass of UDMA is 470, while that of TEGDMA only 286. Therefore, the larger size of UDMA leads to less probability of cyclization and therefore to lower inhomogeneites in the netwotk structure compared to TEGDMA.

4.3. *Isoconversional kinetic analysis*

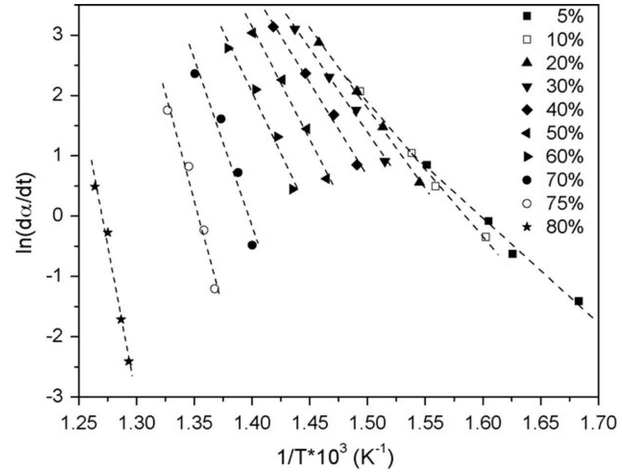


Fig. 6. Typical plot of ln(dα/dt) vs. 1/T according to Eq. (4) of the differential isoconversional method of Friedman, for the Bis-GMA resin at different extents of degradation.

An isoconversional kinetic analysis of the data reported previously is presented in this section and the activation energies, E_α, as a function of the extent of degradation, α, are calculated. Analysis of the E_α dependences proves generally to be very helpful in exploring the effect of the structure of the polymeric material on its degradation kinetics. Typical plots of ln(dα/dt) versus 1/T according to Eq. (4) of the differential isoconversional method of Friedman, for the Bis-GMA resin and at different extents of degradation, appear in Fig. 6. As it can be seen a good linearity was observed in almost all sets of experimental data. From the slope of these curves the effective activation energy is calculated and plotted as a function of the extent of degradation in Fig. 7. Use of the integral isoconversional method of FWO permits the calculation of the corresponding activation energy by plotting ln(β) versus 1/T. Such plots for Bis-GMA appear in Fig. 8. From the slope of these lines the activation energies estimated at different conversions are plotted also in Fig. 7. Activation energies were also estimated using the CR method and plotted in Fig. 7. From the data plotted in Fig. 7 it is clear that all three methods predict the same trend of dependence of the activation energy on the extent of degradation. In addition, results form the methods of FWO almost are identical with those estimated using the CR method. Therefore, the latter method was not employed in further calculations. The steady difference appeared between the differential and the integral calculation method can be explained by the systematic error due to integration. The differential method of Friedman employs instantaneous rate values and therefore is sensitive to experimental noise, while in the

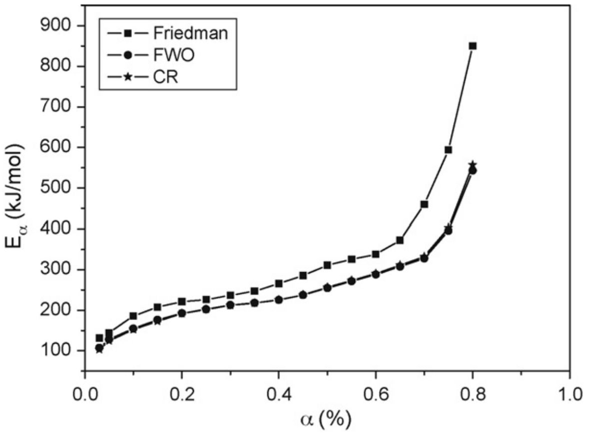


Fig. 7. Effective activation energy as a function of the extent of degradation for the Bis-GMA resin estimated using different methods.

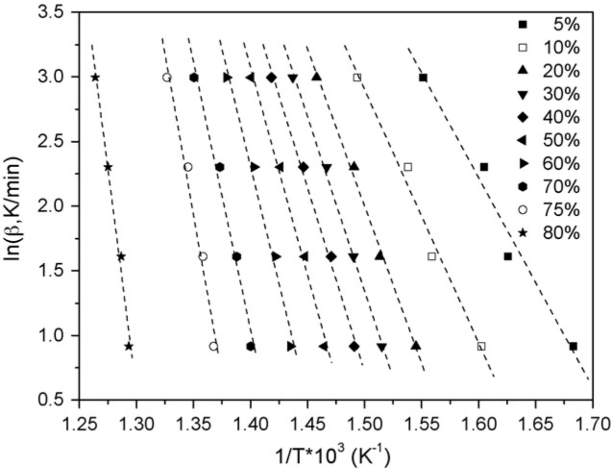


Fig. 8. Typical plot of ln(β) vs. 1/T according to Eq. (6) of the integral isoconversional method of Flynn, Wall and Ozawa, for the Bis-GMA resin at different extents of degradation.

FWO method the equation used is derived assuming constant activation energy, introducing thus a systematic error in the estimation of E in the case that E varies with α [3]. Furthermore, from the results shown in Fig. 7, it is clear that degradation is characterized by steadily increasing activation energy. E_α starts from initial low values of about 130 kJ/mol at $\alpha = 0.03$ and increase to a maximum of almost 850 kJ/mol (according to the Friedman method) at $\alpha = 0.80$. As it is well-known thermal degradation starts rather easily, because of the weak link sites inherent with the polymer chain [6]. The initial lower value of the activation energy is most likely associated with the initiation process that occurs at these weak links. As these weak links are consumed, the limiting step of degradation shifts towards the degradation initiated by random scission, which typically has greater activation energy [1]. The very high values of E_α calculated at large extends of degradation explain the large amount of solid residue remained (almost 17%). An increase of E_α with α has been also reported in literature for other types of polymers [1,3,4,6].

Results on the E_α versus α, dependence for the Bis-EMA resin appear in Fig. 9. Almost the same trend with that observed for Bis-GMA resin was calculated. Data from the two methods investigated coincide in the intervals 5–10% and 60–70% degradation, whereas again data from the Friedman method are higher than those from the FWO method. As it was reported previously for Bis-GMA resin, initial low values for E_α were estimated increasing steadily. However, the lack of hydrogen bonding in Bis-EMA resin, results in more easily breaking network and as a result lower activation energies were estimated throughout the whole extent of degradation. These values start at approximately 100 kJ/mol for $\alpha = 0.05$ and reach a maximum value of 370 kJ/mol (according to the Friedman method) at $\alpha = 0.85$. The much lower maximum value of E_α estimated for the Bis-EMA resin compared to the corresponding for the Bis-GMA, explains the much lower amount of solid residue (approximately 5%, Table 1) measured in this resin.

In contrast to Bis-GMA and Bis-EMA resins, a more complex E_α on α dependence was calculated for TEGDMA resin (Fig. 10). It involves an initial value of about 130 kJ/mol at $\alpha = 0.05$, slightly decreasing up to 110 kJ/mol at $\alpha = 0.40$. A rapid increase follows and a peak appears at $\alpha = 0.65$ with a maximum $E_\alpha = 200$ kJ/mol. Afterwards the E_α values reach a minimum at $\alpha = 0.75$, followed by a second increase up to the maximum value of approximately 210 kJ/mol (according to the Friedman method). Again, results from the two methods slightly differ at most data while they coincide in a few. The appearance of inhomogeneities in the network of this resin, as it was reported previously, is probably responsible for the particular shape of the activation energy. The initial estimated value of E_α is about the same with that observed in Bis-GMA resin while slightly higher than that of Bis-EMA. In order to explain this behavior an additional plot of the DTGA values versus α is presented in Fig. 11. As it was reported previously degradation of TEGDMA resins starts at weak links (defects) in the resin network which have been attributed to cycles incorporated in the network. Therefore the first initial low E_α values reflect breakage of these parts and a maximum in DTGA appears at $\alpha = 0.40$ where the minimum in E_α has been observed. The end of the first degradation stage is characterized by a decrease in the values of DTGA (approximately at 63–69% degradation, Fig. 11) and a peak in the E_α

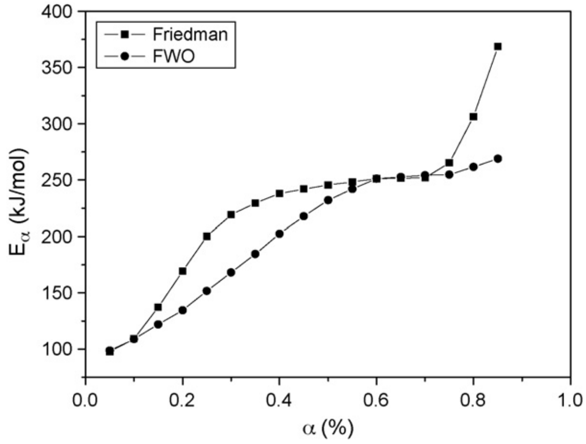


Fig. 9. Effective activation energy as a function of the extent of degradation for the Bis-EMA resin estimated using different methods.

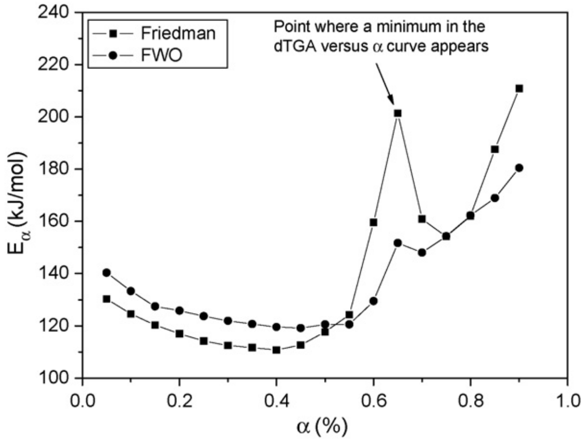


Fig. 10. Effective activation energy as a function of the extent of degradation for the TEGDMA resin estimated using different methods.

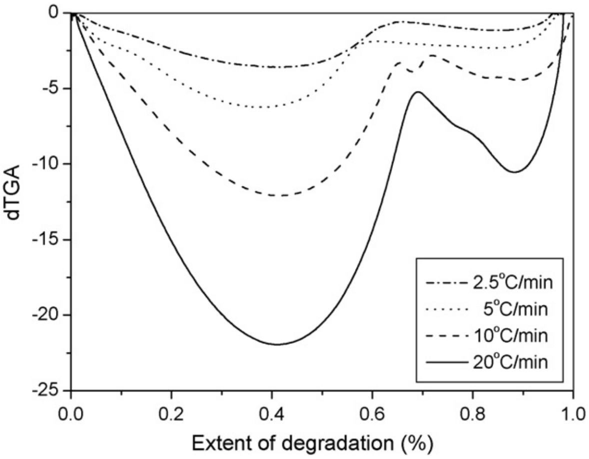


Fig. 11. Differential TGA curves versus the extent of degradation for the TEGDMA resin at different heating rates.

at the same extent of degradation. Therefore, the degradation where the bond breaking changes from one mechanism to the other denotes the local peak in the estimated activation energy values. The rather low maximum E_α value leads to a low amount of solid residue (approximately 2%, Table 1).

Finally, the estimated activation energy versus the extent of degradation value obtained using both the Friedman method and the FWO for UDMA appears in Fig. 12. Results from the two methods are similar in most of the extent of degradation. Activation energy initially starts at nearly a constant value between 100 and 110 kJ/mol until $\alpha = 0.50$, whereas afterwards a peak appears at $\alpha = 0.55$ and $E_\alpha = 280$ kJ/mol. Again these results denote two degradation mechanisms. The first exhibiting the plateau in the E_α values, corresponds to the breakage of weak links (like primary cycles, or hydrogen bonds), while the second with the high enough values of E_α corresponds to degradation of the main network bonds. It is for this reason that the estimated maximum value of E_α is close to the values observed for Bis-EMA (where in the degradation range from 0.40 to 0.7 a constant value equal to 250 kJ/mol, was calculated). The final very low E_α values (approximately 220 kJ/mol) are responsible for the lowest

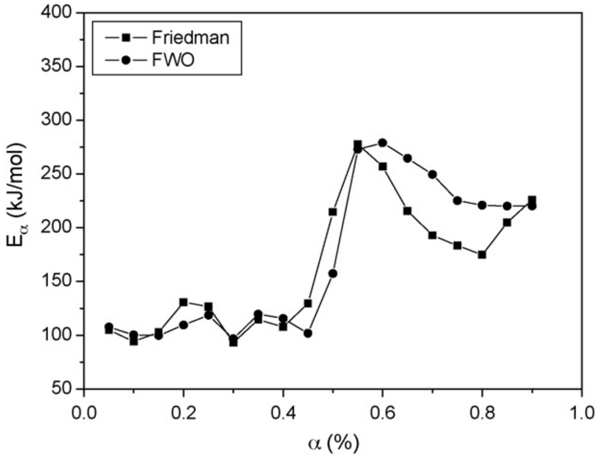


Fig. 12. Effective activation energy as a function of the extent of degradation for the UDMA resin estimated using different methods.

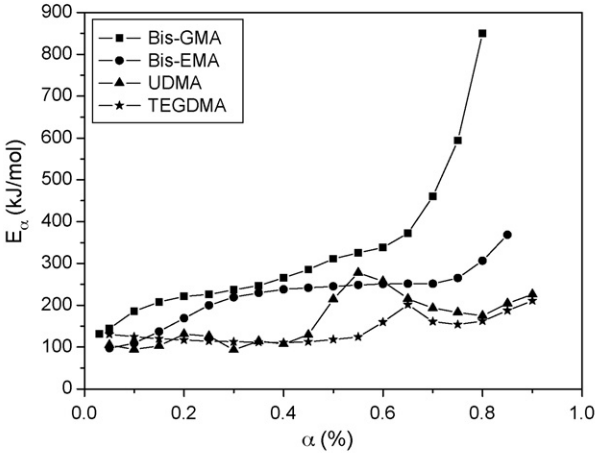


Fig. 13. Effect of the chemical structure of the resin on the activation energy as a function of the extent of degradation estimated using the method of Friedman.

amount of solid residue (ca. 1.5%, Table 1) measured in this resin.

A comparative plot of the activation energy as a function of the extent of degradation using the method of Friedman for all polymers studied is illustrated in Fig. 13.

5. Conclusions

The thermal degradation mechanism of four dimethacrylate-based resins used in dental applications was examined. The study was completed by thermogravimetric measurements together with an isoconversional kinetic analysis using a differential and an integral method. Differences in the chemical structure of the resins formed influence much the degradation behaviour of the resins. Thus, Bis-GMA and Bis-EMA because of their rigid aromatic nuclei form a more rigid network decomposing at higher temperatures compared to that from TEGDMA and UDMA. In advance, the strong hydrogen bonding ability of Bis-GMA is considered responsible for its slightly higher thermal stability compared to Bis-EMA. The absence of defects in the network structure of Bis-GMA and Bis-EMA leads to one-step degradation mechanism. In contrast the appearance of two degradation steps in the resins formed from TEGDMA and UDMA is attributed to inhomogeneities in the network structure mainly due to the formation of primary cycles during polymerization. Finally, the higher thermal stability of UDMA compared to TEGDMA is attributed to the existence of hydrogen bonds from the N–H groups in the UDMA resin as well as to its lower primary cycling probability. These results were verified from isoconversional kinetic analysis and estimation of the activation energy as a function of the extent of degradation.

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