Kinetic Study on the Thermal Degradation of UDMA-BisGMA Copolymers

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Dimethacrylate-based resins cured using a photoinitiator system are widely used as matrices in dental restorative composites. In this work, the thermal degradation of copolymers based on urethane dimethacrylate (UDMA) and bis-phenol A glycidyl dimethacrylate (BisGMA) were investigated by thermogravimetric analysis. Different weight ratios (100/0, 70/30, 50/50, 30/70 and 0/100) between the UDMA and BisGMA comonomers were employed. The camphorquinone – ethyl-4-dimethylaminobenzoate photoinitiator system was used. The degradation of copolymers occurs in three steps, contrarily to two steps for UDMA homopolymer and a single step for BisGMA homopolymer. Activation energies of the degradation processes were calculated using differential and integral isoconversional methods. The influence of copolymers composition on the activation energy as a function of the degradation conversion degree was studied.

Keywords: thermal degradation, dimethacrylate copolymers, UDMA/BisGMA

Dental composite materials based on methacrylate and dimethacrylate resins were introduced on the market in the 60’s for the restoration of anterior teeth. The first used dimethacrylate monomer was 2,2-bis[p-(2'-hydroxy-3'-methacryloxy propoxy) phenylene] propane (usually known as Bisphenol A glycidyl dimethacrylate - BisGMA) previously synthesized by Bowen in 1956 [1]. Even today, BisGMA remains the most used monomer and it can be found in most of commercial dental composites having some advantages: high molecular weight, low polymerization shrinkage, good mechanical properties and rapid hardening [2]. All these benefits of BisGMA resin are partially cancelled by its high viscosity ($\eta \approx 600-1000$ Pa·s at $23^\circ$C), due to intermolecular hydrogen bonds, high molecular weight and the presence of two aromatic rings within the molecule. Therefore, BisGMA requires dilution with low-viscosity dimethacrylate comonomers, especially in the case of inorganic fillers incorporation. Triethylene glycol dimethacrylate (TEGDMA, $\eta = 0.05$ Pa·s at $23^\circ$C) and ethoxylated bisphenol-A dimethacrylate (BisEMA, $\eta = 3$ Pa·s at $23^\circ$C) are two examples of such reactive comonomers [3-6].

Another monomer widely used in dental materials is 1,6-bis[methacryloyloxy-2-ethoxycarbonylamo]-2,4,4-trimethylhexane (usually referred as urethane dimethacrylate - UDMA). This monomer presents a lower viscosity ($\eta \approx 23$ Pa·s at $23^\circ$C) [7] and a more flexible structure as compared to BisGMA at a similar molecular weight (MW$_{\text{UDMA}} = 470$ g/mol versus MW$_{\text{BisGMA}} = 512$ g/mol). UDMA can be used alone as polymeric matrix in dental materials or together with BisGMA (in this case UDMA playing the role of diluter) or TEGDMA [8-10].

The polymerization of these dimethacrylate monomers occurs at the C=C double bonds, resulting homo- or copolymers with a highly cross-linked structure. The reaction may be conducted at ambient temperature (by using a photoinitiation system or a redox initiation system) or at higher temperature (heat polymerization) [11-13]. Photopolymerization at ambient temperature is a convenient method for dental materials preparation. The main disadvantage is that the conversion of double bonds is not complete, due to a lower mobility and diffusivity of free radicals after the formation of glassy resin. The unreacted double bonds may be found in free monomer or as pendant groups in the polymer network and can cause irritation in oral mucosa and promote allergic reactions. The conversion degree of resins directly affects the final material [14-16].

Thermogravimetric analysis (TGA) is an experimental method which gives information about the polymer degradation. The thermal degradation of polymers is affected by many factors, such as molecular weight, molecular weight distribution, chain branching, cross-linking density and conversion degree. The thermal degradation process of copolymers is more complex than the degradation of homopolymers and it strongly depends on the comonomers ratio. The study of polymer degradation becomes even more difficult when the comonomers form a three dimensional network and not a linear macro-molecular chain, as in the case of dimethacrylate resin. Thus, there are few articles in literature that study the thermal degradation of dimetacrylate networks: BisGMA, UDMA, TEGDMA, BisEMA homopolymers [17], BisGMA-TEGDMA copolymers [18-21], UDMA-TEGDMA and UDMA-BisEMA copolymers [22]. Only one of these papers attempts to explain the chemistry of degradation process by identification of products resulting from pyrolysis of BisGMA-TEGDMA copolymers using thermogravimetric-gas chromatography mass spectrometry [20]. Apart from a simple TGA scan, experimental data allow some computational kinetic analysis using isoconversional methods, in order to determine the activation energy of the degradation process [17,21,22]. The main advantage of isoconversional methods is that they allow the computation of the activation energy for each given composition independent of the reaction model.

In this work, the thermal degradation kinetics of different composition copolymers based on UDMA and BisGMA were investigated by thermogravimetric analysis. The variation of activation energies as a function of degradation process conversion was calculated using isoconversional methods.

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Experimental part

Five polymer samples were prepared using BisGMA and UDMA monomers: 2 homopolymers and 3 copolymers with 30/70, 50/50 and 70/30 weight ratios. To make the resins light-curing, a photo-initiator system with camphorquinone (CQ, 0.2 wt. %) and ethyl-4-((N,N'-dimethylamino)benzoate (4EDMAB, 0.8 wt. %) was used. All the chemicals (scheme 1) were supplied by Sigma-Aldrich Chemicals and used as received without any further purification.

For all samples, 2 g of monomers and calculated quantities of CQ and 4EDMAB were mixed at 35°C until the photoinitiators were dissolved in monomers. Bar samples with 40×10×2 mm size were obtained in Teflon molds covered by two glass plates (2 mm thickness). The irradiation was achieved through the glass plates using a blue LED device (radiation wavelength 460-480 nm, light intensity 700 mW/cm²) for 60 s on each side.

Thermogravimetric measurements of each sample were performed at four different heating rates (2, 5, 10, 20°C/min), in nitrogen atmosphere (balance flow 10 mL/min, oven flow 90 mL/min), from ambient temperature up to 600°C, using a TGA Q500 equipment (TA Instruments). The samples weight was 2.2 ± 0.1 mg.

Isoconversional methods

The kinetics of reactions in solids (including polymer degradation) is usually described by eq. (1):

\[
\frac{da}{dt} = k(T)f(\alpha)
\]  

(1)

where:

- \( \alpha \) = the conversion degree
- \( t \) = time
- \( \frac{da}{dt} \) = the reaction rate
- \( f(\alpha) \) = the reaction model
- \( k(T) \) = temperature-dependent rate constant

In the case of thermogravimetric analysis, the conversion degree \( \alpha \) can be determined from TGA data as a fraction of the mass loss or from DTG (derivative thermogravimetric) data as a fraction of the area under the DTG curve. Using an Arrhenius-type expression to describe the temperature dependence of \( k(T) \), the eq. (1) yields:

\[
\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]  

(2)

where:

- \( A \) = the preexponential factor
- \( E \) = the activation energy
- \( R \) = the gas constant.

By logarithmation of eq. (2), than differentiation versus \( T^{-1} \), the eq. (3) is obtained:

\[
\frac{d\ln(da/dt)}{dT^{-1}} = -\frac{E}{R}
\]  

(3)

Equation (3) shows that the reaction rate is a function only of the temperature at a specific conversion degree (the subscript \( \alpha \) denotes values at this definite conversion \( \alpha \)). Thus, isocconversional methods need multiple experimental data sets at different heating rates in order to calculate the activation energy \( E_{\alpha} \) for each particular \( \alpha \).

Using eq. (2), Friedman [23] suggested an expression (eq. 4) that allows the computation of the activation energy (known as differential isocconversional method of Friedman - FR).

\[
\ln\left(\frac{da}{dt}\right)_{\alpha i} = \ln(A_\alpha f(\alpha)) - \frac{E_{\alpha}}{RT_{\alpha i}}
\]  

(4)

where the subscript \( i \) denotes the ordinal number of the experiment conducted with different heating rate (\( \beta \)). The activation energy can be evaluated from the plot \( \ln(da/dt)_{\alpha i} \) vs. \( 1/T_{\alpha i} \) at constant conversion degree \( \alpha \), for the \( i \) heating rate. In the case of noisy experimental data, the FR method leads to unstable activation energy values due to numerical differentiation of the experimental data. This problem could be avoided by using integral isocconversional methods [24].

Using a constant heating rate \( \beta = dT/dt \), eq. (2) can be written:

\[
\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]  

and by integration:

\[
g(\alpha) = \int \frac{da}{\beta f(\alpha)} = \int \frac{A \exp\left(-\frac{E}{RT}\right)}{\beta} dx
\]  

(6)

Since the right side integral of eq. (6) does not exhibit an analytical solution, the equation can be rewritten as:

\[
g(\alpha) = \frac{AE}{\beta R} \left[\exp(-x) - \exp(-x_{\alpha})\right] = \frac{AE}{\beta R} p(x)
\]  

(7)

where \( x = E/RT \). Even if the integral in eq. (7) can not be analytically solved, the function \( p(x) \) can be estimated using many approximations.

In [25, 26] is used the approximation \( p(x) = e^{-x}/x^2 \) and is obtained eq. (8) (KAS method):

\[
\ln\left(\frac{\beta_1}{\beta_{\alpha i}}\right) = \ln\left(\frac{AR}{E_{\alpha}}\right) - \ln[g(\alpha)] = \ln\left(\frac{E_{\alpha}}{E_{\alpha i}}\right) = \text{const.} - \frac{E_{\alpha}}{R} \frac{1}{T_{\alpha i}}
\]  

(8)

In [27-29] is used approximation \( \ln p(x) = -5.3305-1.052 x \) and is obtained eq. (9) (OFW method):

\[
\ln(\beta_1) = \text{const.} - 1.502 \frac{E_{\alpha}}{R} \frac{1}{T_{\alpha i}}
\]  

(9)

In both KAS and OFW methods, the activation energy is determined from the plot of left side of eqs. (8) and (9).
versus $1/T_{\alpha}$ at constant conversion degree $\alpha$, for the $i$ heating rate.

Opposite to these methods which use approximation, Vyazovkin [30, 31] increases the precision of integral methods using numerical integration. This method (known as non-linear isoconversional method - NLN) takes into account a possible variation of the activation energy. Recently, was proposed a rapid iterative method obtaining similar results as Vyazovkin NLN method [32].

In this work, only FR, KAS and OPW methods were used.

### Results and discussions

#### Thermal decomposition study

Figures 1 and 2 comparatively show the TGA and DTG curves for the 5 UDMA/BisGMA copolymers with different monomer ratios, at 10 °C/min heating rate. In order to use isoconversional methods to calculate activation energy of the degradation process, four thermogravimetric measurements at different heating rates (2, 5, 10, 20 °C/min) were performed for each copolymer sample. Due to space limitation, the TGA/DTG curves for all heating rates are showed only for the UDMA/BisGMA : 50/50 copolymer.
The degradation of the unreacted monomers or the amount is insignificant, so their degradation starts at higher temperature. Both starting degradation temperature and maximum degradation temperature of unreacted monomers are higher when BisGMA content increases, due to the higher thermal stability of BisGMA. In the second interval, only the samples with UDMA content show thermal degradation. For the same heating rate, the maximum degradation temperature is independent of the UDMA content, but the value of the peak in DTG curve is higher when UDMA content increases. The degradation process of the main copolymer network occurs at higher temperature and the peaks in DTG curve are higher than those of the degradation process situated at lower temperatures. The maximum degradation temperature varies approximatively linear with the monomer content, between the maximum degradation temperatures of UDMA and BisGMA homopolymers.

The temperature of the degradation process end increases with the BisGMA content. Even though the maximum degradation temperature for the last degradation stage of UDMA homopolymer is higher than that of BisGMA homopolymer, the last one exhibit a large degradation peak on DTG curve.

The residual mass (at 600°C) of the samples increases with BisGMA content, due to the higher carbon residue mass of BisGMA. Moreover, for the samples with high BisGMA content a dependence of the residual mass on the heating rate can be observed, higher heating rate leading to lower solid residue.

**Isoconversional decomposition kinetics**

The previously presented thermogravimetric data were further used to compute the activation energy $E_a$ as a function of the conversion degree of the degradation process, $\alpha$. In this respect, the differential (FR) and integral (KAS and OFW) isoconversional methods were used.

The extent of degradation $\alpha$ was calculated from DTG data as fraction of the area under the DTG curve. The typical plots for isoconversional methods consist in linear representations of $\ln(d\alpha/dt)$ vs. $1/T$ (FR method, eq. 4), $\ln(\beta/T^2)$ vs. $1/T$ (KAS method, eq. 8) and $\ln(\beta)$ vs. $1/T$ (OFW method, eq. 9) at different extent of degradation $\alpha$. The activation energy $E_a$ for each $\alpha$ is determined from the

![Fig. 4. Plot of ln(dα/dt) vs. 1/T according to FR method, at different extents of degradation for UDMA/BisGMA : 70/30 sample](http://www.revmaterialeplastice.ro)
slope of these lines. Good linearity of points was observed for all the samples and methods, with a better superposition of lines in the case of higher conversion degrees ($\alpha > 0.4$) (examples in fig. 4-6, one figure for each method for different copolymer samples).

$E_\alpha$ values obtained by FR differential method (example in figure 7 for UDMA/BisGMA : 70/30 copolymer). Moreover, this last method seems to be more sensitive to experimental noise [24]. In these conditions, only the values obtained from the OFW method were used for the comparative study of the influence of copolymers composition on the activation energy as a function of the degradation conversion (fig. 8).

For UDMA homopolymer, the activation energy $E_\alpha$ shows two zones with near constant value (fig. 8): the first one at 165-170 kJ/mol (up to a conversion degree of 40 %) and the second one at 275 kJ/mol (for conversion degree higher than 60%). These two values correspond to the two degradation processes observed in DTG curves. At a conversion degree of 50 % the curve shows a maximum for $E_\alpha$ corresponding to the minimum value between the DTG peaks.

The activation energy $E_\alpha$ of BisGMA homopolymer continuously increases with the degradation extent, from 95 kJ/mol at $\alpha = 5$ % to 250 kJ/mol at $\alpha = 80$ %. Then the activation energy strongly increases, due to the large amount of the remained solid residue [17].

The UDMA/BisGMA 50/50 and 30/70 copolymers show higher activation energies at lower conversions, due to the degradation of the unreacted monomers (first degradation step, at 230-280 °C, fig. 2). Higher peaks in $E_\alpha$ vs. $\alpha$ curves can be observed at conversion $\alpha = 15-17$ %, this maximum corresponding to the minimum between the first and second degradation process in DTG curves. This degradation process does not occur in the case of homopolymers and is insignificant in the case of UDMA/BisGMA 70/30 copolymer, where the conversion of monomer units or pendant double bonds is higher due to the higher mobility of UDMA chain. Due to the smaller number of unreacted double bonds for this copolymer, the activation energy for the second process of degradation is not affected by the first one and it is approximately constant (160 kJ/mol), similar to UDMA (for $\alpha$ between 20 and 40%). For a conversion degree higher than 60%, the activation energy becomes similar to those of BisGMA homopolymer. For all copolymers, the $E_\alpha$ values for the third degradation process are situated between those of homopolymers (250 kJ/mol at $\alpha = 80$ %).

Conclusions

The thermal degradation of UDMA/BisGMA copolymers with different monomer ratios was investigated by thermogravimetric analysis. The UDMA/BisGMA copolymers show a decomposition in three stages, different...
from the homopolymers which degrade in a single phase (BisGMA homopolymer) or in two stages (UDMA homopolymer). The first degradation process is assigned to the evaporation and scission of the nonreacted monomer units and radical trapped in the copolymer structure. The second degradation is assigned to the destruction of the small cycles intramolecularly formed into the polymer network, and the third one is attributed to the main network degradation. The activation energies of copolymers degradation process were calculated using isoconversional methods. The UDMA/BisGMA 50/50 and 30/70 copolymers show higher values of activation energy at lower conversions, due to the degradation of an important quantity of unreacted monomers. The values of activation energy for the second degradation step are influenced in this case by the presence of unreacted monomers.

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