

Thermoanalytical study of monomers: BisGMA, BisEMA, TEGDMA, UDMA and their mixture.

G. Bannach^{1,2}, C. C. S. Cavalheiro², L. Calixto², E. T. G. Cavalheiro²

¹Faculdade de Ciências – UNESP – Campus de Bauru, CEP 17033-360 Bauru, SP, Brasil.

²Instituto de Química de São Carlos – IQSC/USP, C.P. 780, CEP 13560-970, São Carlos, SP, Brazil.

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Abstract

Thermal behavior of BisGMA (bisphenylglycidyl dimethacrylate), TEGDMA (triethylene glycol dimethacrylate), BisEMA (ethoxylated bisphenol-A dimethacrylate), UDMA (Urethane dimethacrylate) monomers and one their mixtures was investigated by TG-DTA, DSC and coupled TG-FTIR. TG-DTA curves of monomers showed that the isolated compounds starts decomposition between 178-297 °C and mixture of fotocured monomers starts decomposition at 250°C. The TG-FTIR was used to characterize volatiles released during the thermal cure before thermal decomposition. The DSC curves showed the glass transition, melting point and crystallization temperatures of the samples.

Keywords: Polymers, Model Dental Resins, TGA

1. Introduction

Monomers with multiple functional groups have widely been used as crosslinking agents in methacrylate polymers resulting in materials used in several applications, including formulation of dental restorative resins, hydrogels for contact lenses, manufacture of laser video discs, the replication of optical discs [1].

Particularity BisGMA (bisphenylglycidyl dimethacrylate), TEGDMA (triethylene glycol dimethacrylate), BisEMA (ethoxylated bisphenol-A dimethacrylate) and UDMA (Urethane dimethacrylate) monomers (Figure 1) are extensively used as matrices in dental restorative materials, teeth bonding agents, and fissure sealing agents [2]. Polymerized light-cured composite dental resins require highly cross-linked three-dimensional network structures and photopolymerization of multifunctional monomers allows for the facile production of highly cross-linked polymer networks (thermoset polymers) that are useful in several applications. With that, photoinitiated polymerization of multifunctional monomers is fast allowing temporal and spatial control of the reaction.

These monomers exhibit many complex features including auto-acceleration and auto-deceleration, limiting double bond conversion and polymerization kinetics that are dependent on the rate of polymerization, and a reaction with diffusion-controlled termination mechanism. Most of this polymerization behavior can be attributed to the mobility of the reacting species in the system.

The degree of conversion on such monomers directly affects physical and mechanical properties of TEGDMA/BisGMA. This degree is also related to the rate at

which methacrylate C=C bonds are converted to aliphatic C-C bonds [1-6].

Foster and Walker first described UDMA (1,6-bis(methacrylyloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane) as a dental resin in 1974 and suggested it as an alternative to BisGMA [7]. Compared to last one UDMA monomer present some advantages such as a reduced viscosity, increased filler loading and higher toughness due to the flexibility of the urethane linkages. In addition polymers derived from UDMA monomer result in similar or slightly less water sorption than those prepared from Bis-GMA [8].

Thermal analysis techniques, as differential scanning calorimetry (DSC), thermogravimetry (TGA), or dynamical mechanical analysis (DMA), are suitable for examining the characteristics of polymers [9]. Investigating the thermal behavior can provide more specific information regarding internal structures of dental resins. Many factors affect the thermal degradation of polymers, including the molecular weight distribution, branching chains, cross-linked density, and end-groups. Copolymers exhibit more intricate thermal behavior than homo-polymers, because they are readily affected by the ratio of monomers or degree of conversion [10, 11].

In this work the thermal behavior of the BisGMA, TEGDMA, BisEMA and UDMA monomers and their mixture, were investigated using TG-DTA, DSC and coupled TG-FTIR, in order to evaluate the effect of the sample thickness and irradiation time in the curing of the monomers and their mixture as well as the volatiles liberated during the heating.

* Corresponding author: Tel.: +55 16-3373-8054

E-mail address: cavalheiro@iqsc.usp.br (E. T. G. Cavalheiro)

2. Experimental

2.1. Materials

The BisGMA, BisEMA, UDMA, TEGDMA dimethacrylate monomers of analytical grade from Aldrich were used as received. The resins were formulated using Camphorquinone (CQ, Aldrich) as photoinitiator, ethyl-4-dimethylaminobenzoate 99% (EDB, Aldrich) as coinitiator in the presence of butylated hydroxytoluene (BHT, Aldrich) to prevent polymerization at ambient light.

2.2. Preparation of copolymer sample

Copolymers were prepared by mixing 34.4% BisGMA, 28.6% BisEMA, 28.9% UDMA, 7.0% TEGDMA (wt. %), in the presence of 0.4% CQ, 0.5% EDB and 0.2% BHT (wt. %), resulting in a viscous liquid at room temperature. The mixture was mixed during 30 min in a Teflon mortar in a dark room, according to previously reported formulation. The mixture was stored in the dark inside a desiccator (over CaCl_2) until the photocuring.

For photocuring, Teflon® plate molds were prepared in which round grooves were excavated to be 10 mm diameter and 1 or 2 mm deep. Then the desired amount of monomers, or their mixture, was inserted into the groove and irradiated for 60, 120 or 240 s. The irradiation was carried out at 475 ± 15 nm range, with an ultra-blue IS LED (DMC Instruments, Brazil), keeping the light source 3 mm above the sample. The radiation/light at such wavelength range was also absorbed by CQ ($\lambda_{\text{max}} = 470$ nm, $\epsilon = 3.8 \cdot 10^4 \text{ cm}^2 \text{ mol}^{-1}$) [12].

2.3. TG-DTA and TG-FTIR Experiments

TG-DTA experiments were performed in a SDT-Q600 Simultaneous Thermogravimetric Analyzer (TA Instruments), using an alumina sample holder under air atmosphere at a flow rate of 100 mL min^{-1} in a temperature range from 25 to 800 °C. The sample mass was about 10 mg heated at a 20 °C min^{-1} heating rate.

Coupled TG-FTIR analysis was performed in a Nicolet iS10 spectrophotometer (Thermo Scientific) coupled to the gas exhaust of a simultaneous TGA-DTA 851 Mettler Toledo apparatus.

2.4. DSC experiments

DSC measurements were performed in a DSC-Q10 modulus (TA Instruments). The DSC curves were obtained under a dynamic nitrogen atmosphere (50 mL min^{-1}) with about 10 mg of a sample in the temperature range of -80 to 250 °C at a 20 °C min^{-1} heating rate. Accurately weighed samples (10 ± 0.5 mg) were placed in an aluminum open sample holder. The DSC instrument was calibrated for the temperature and enthalpy heat with $> 99.99\%$ indium metal. Samples had been submitted to heat-cool-heat cycles between -80 and 250 °C.

3. Results and Discussion

3.1. TG-DTA curves

The thermal behavior of BisGMA, BisEMA, UDMA, TEGDMA monomers and their mixture were evaluated using TG-DTA and DSC. The resulting TG-DTA curves of the monomers and for the non-polymerized mixture (Poly-NC) are presented in Fig. 1, while the details of the thermal events (mass losses, temperature intervals and maximum peak temperatures) are described in Table 1.

On heating all the monomers presented similar sequence of thermal event, of each one with their own particularities. In a general there is a small mass loss since the starting of the heating up to 200-240 °C depending on the sample. This mass loss is accompanied by an endothermic process in the DTA curve and was attributed to the loss of residual volatiles [13].

During this first slight mass loss there are evidences of thermal curing process in the BisGMA and BisEMA, represented by exotherms in the DTA curves. The UDMA and TGDMA on their turn exhibited discrete exothermic peaks of curing in the DTA. The temperatures of these events are presented in Table 1.

Finally all the monomers presented decomposition in two (BisGMA and BisEMA) or three (UDMA and TGDMA) steps, depending on the sample. The DTA curves revealed that these decomposition processes can be relatively simple as in BisGMA or complex with many overlapping steps as in TEGDMA, in which several exo and endothermic events appears overlapped.

The non-photocured mixture presented four mass loss steps (Fig. 1.e). The first one appeared between 20-264 °C and is associated with the endothermic process with peak at 76 °C in the DTA curve. When the sample was heated in a heating plate it was possible to see bubbles at the same time that a smell of solvent is noted, and at the same time the sample became rigid. This confirms the observations described above, concerning the loss of volatiles and thermal curing of the resin. In the case of this mixture these events are represented by the exotherm near 200 °C which should be the resulting of the sum of all the heats involved in both the volatilization of the residual solvents (endothermic) and the curing process (exothermic).

The second mass loss (206-287 °C) seems to be related with the first decomposition step of the non-photocured mixture with strong contribution from BisEMA, UDMA and TEGDMA, according to the TG curves of the monomers discussed above.

The third mass loss seems to be associated to the decomposition of the BisGMA once it is coincident with the temperature intervals of the TG curve of this monomer (Fig 1.a) and the amount of mass lost here is consistent with the larger amount of this monomer in the mixture.

The 2nd, 3rd and 4th events observed in the TG curves are represented by the respective exothermic events and peak in the DTA curve (details in Table 1).

Finally the last step in the TG curve is related with the oxidation of the carbonaceous residue, represented the exothermic event in the DTA.

The TG-DTA curves of the mixture of monomers photocured with the thickness of 1 or 2 mm and exposition time of 60, 120 and 240 s (respectively called Poly 1-60, Poly 1-120, Poly 1-240, Poly 2-60, Poly 2-120, Poly 2-240), are represented in Fig. 2, while the details of the thermal events (mass losses, temperature intervals and peak temperatures) are also described in Table 1.

These samples presented generally four mass loss steps between 20-610 °C, associated with exothermic and endothermic peaks in the DTA as described below. The same loss of residual solvents from the monomers is observed in all the samples since the photocuring do not involves heating.

Evidences of exothermic curing can be observed in the DTA curves. These processes could be related with the non-cured fraction of the polymeric samples during the exposition to light, as previously described [13]. However the DTA is not sensitive enough to clearly show these events (See DSC data below).

The 2nd and 3rd TG events are related with the decomposition of the polymeric material and are represented by overlapping exothermic and endothermic processes in the DTA curves (Fig. 2).

Finally the burning of the carbonaceous material is observed accompanied by exothermic peaks in the DTA.

The data in Table 1 suggest that changing the sample width from 1 to 2 mm as well as the exposition time from 60-240 s do not affect remarkably the sample stability or the thermal decomposition profile.

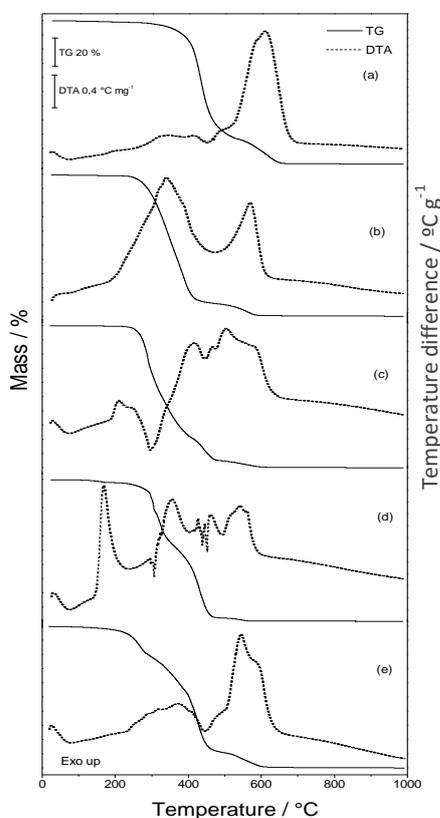


Figure 1. TG-DTA curves: (a) BisGMA; (b) BisEMA; (c) UDMA; (d) TEGDMA; (e) Poly-NC.

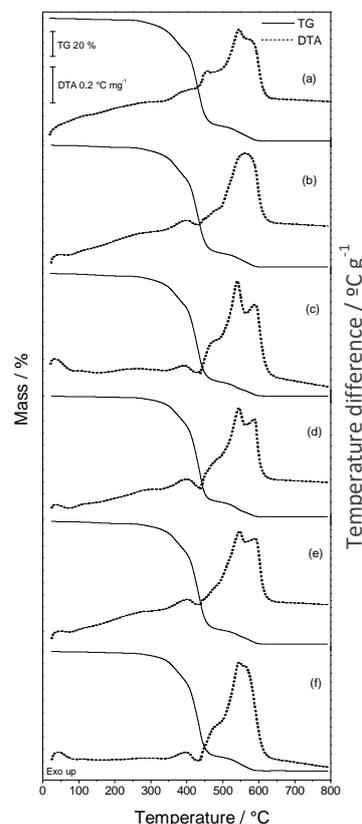


Figure 2. TG-DTA curves: (a) Poly 1-60; (b) Poly 1-120; (c) Poly 1-240; (d) Poly 2-60; (e) Poly 2-120; (f) Poly 2-240.

Table 1. Thermoanalytical data^a

Compound		Steps			
		First	Second	Third	Fourth
BisGMA	θ °C	20-297	297-520	520-687	-
	Loss (%)	1.9	79.6	18.5	-
	Peak (°C)	72 (endo)	270-443 (exoterm)	609 (exo)	-
BisEMA	θ °C	20-236	236-440	440-687	-
	Loss (%)	1.2	89.0	9.8	-
	Peak (°C)	72 (endo)	338 (exo)	568 (exo)	-
UDMA	θ °C	20-222	222-407	407-482	482-623
	Loss (%)	0.4	78.6	16.0	5.0
	Peak (°C)	71 (endo)	295 (endo)	415, 465 (exo)	502 (exo)
TEGDMA	θ °C	24-178	178-347	347-481	481-600
	Loss (%)	2.0	41.7	54.0	2.3
	Peak (°C)	71 (endo)	304 (endo)	437 (endo)	539 (exo)
Poly-NC	θ °C	20-206	206-287	287-480	480-624
	Loss (%)	2.9	15.9	65.8	11.1
	Peak (°C)	76 (endo)	206-287 (exo)	287-442 (exoterm)	542 (exo)
Poly 1-60	θ °C	20-250	250-396	396-488	488-610
	Loss (%)	1.7	25.3	60.5	12.5
	Peak (°C)	-	340-422 (exo)	453 (exo)	543 (exo)
Poly 1-120	θ °C	20-250	250-396	396-488	488-610
	Loss (%)	2.0	24.9	61.4	11.7
	Peak (°C)	-	340-422 (exo)	-	562 (exo)
Poly 1-240	θ °C	20-250	250-396	396-488	488-611
	Loss (%)	2.1	24.5	61.5	11.9
	Peak (°C)	-	344-416 (exo)	-	539, 587 (exo)
Poly 2-60	θ °C	20-257	257-396	396-480	480-611
	Loss (%)	1.7	22.8	63.1	12.4
	Peak (°C)	-	341-427 (exo)	-	542, 585 (exo)
Poly 2-120	θ °C	20-258	258-396	396-480	480-611
	Loss (%)	2.0	22.6	63.0	12.4
	Peak (°C)	-	341-425 (exo)	-	545, 589 (exo)
Poly 2-240	θ °C	20-258	258-396	396-480	480-611
	Loss (%)	1.7	22.8	63.4	12.1
	Peak (°C)	-	352-421 (exo)	-	544 (exo)

^a exo = exothermic; endo = endothermic

3.2. DSC curves

The DSC curves of the monomers BisGMA, BisEMA, UDMA, TEGDMA and that for their mixture with 1 mm thick photocured during 60s (Poly 1-60) are presented in Fig. 3. The curves of the mixture photocured under different conditions (Poly 1-120, Poly 1-240, Poly 2-60, Poly 2-120, Poly 2-240) are not presented since they are very similar to that for Poly 1-60.

The BisGMA monomer was submitted to cool-heat-cool-heat cycles in the temperature range from -80 to 270 °C, resulting in the curves in Fig. 3.a. During the first cooling from room temperature to -80 °C any thermal event was observed. When the sample was heated from -80 to 270 °C, a glass transition appeared at -7.4 °C (mid-point), followed by a broad exothermic process between 150-215 °C, attributed to the thermal curing event. During the second cooling cycle the DSC curve presented a glass transition at 200.2 °C (mid-point). The presence of two glass transitions suggests that the heat curing process is not complete and correspond to the polymerized and non-polymerized fractions of the sample, which is consistent with the time scale of the experiment in which there is not enough time at the curing temperature to allow a complete cure process to occur.

Unfortunately the second glass transition could not be observed near to 0 °C, since, according to the manufacturer information, the equipment is not able to keep the cooling rate below this temperature, but it is possible to observe a base line change from 10 to -7 °C. During the second heating cycle it was possible to observe two glass transitions at 6.7 and 208 °C (mid-point). The absence of the broad endothermic process from 50 to 150 °C in the second heat cycle corroborates to the idea of releasing of the volatiles in this temperature range during the first heating.

The BisEMA monomer was submitted to heat-cool-heat cycles from -80 to 220 °C. During the first cooling from room temperature to -80 °C the monomer presented a crystallization peak at -44.2 °C ($\Delta H_{crys} = 9.4 \text{ J g}^{-1}$) with evidences of a glass transition at c.a. -56 °C. The precise determination of its temperature was not possible due to effect of the crystallization peak as well as to the non-linearity in the cooling rate in this region.

During the first heating cycle the sample presented a glass transition at -57.4°C (mid-point), followed by a cold crystallization peak at -39.0 °C ($\Delta H_{crys} = 30.8 \text{ J g}^{-1}$) and melting at 12.0 °C ($\Delta H_{fus} = 72.6 \text{ J g}^{-1}$). From 25 to 150 °C appeared a broad endothermic process related to the loss of the residual solvent. In the second cooling ramp only the crystallization peak is observed at -39 °C ($\Delta H_{crys} = 40.2 \text{ J g}^{-1}$), but the process is more effective, probably due to the elimination of the residual solvent. As a consequence of this more effective crystallization, the glass transition was not clearly observed as well as the cold crystallization peak during the second heating cycle. However the melting appeared with peak at 15.0 °C ($\Delta H_{fus} = 76.5 \text{ J g}^{-1}$), the small changes in the melting point peak were attributed the purity of the sample after solvent elimination. The evidences of thermal curing observed in the

DTA appeared above the temperatures used in the DSC experiment.

The UDMA was submitted to the same heat-cool-heat cycles. During the cooling from room temperature to -80 °C any thermal event was observed. In the first heating cycle a glass transition was observed at -1.0 °C (mid-point), followed by the release of residual solvents from 33-111 °C and a second order transition at 172 °C. The second cooling cycle presented a glass transition at 34 °C (mid-point). The last heating cycle presented a not well-defined glass transition *c.a.* 0 °C, without evidences of volatiles and the second order transition at 149 °C (mid-point). This second order transition precedes an endothermic event related to a mass loss in the TG curve (Fig. 1.c). The heating curing of the monomer is not reached at the temperature in which the DSC curve was interrupted here.

The TGDMA was also submitted to heat-cool-heat cycles. During the cooling from room temperature to -80 °C, the glass transition was not evident due to the non-linearity in the cooling rate in this region. The first heating cycle showed a well defined glass transition at -32,3 °C (mid-point), followed by an exothermic peak at 190 °C, due to the thermal curing event in agreement with the DTA curve (Fig. 1.d). During the cooling there was any clear thermal event, except the glass transition non-defined as discussed above. The second heating showed the glass transition at -29.7 °C (mid-point), but any curing was noticed in this cycle suggesting that a high cure extension during the first heating.

The mixture of monomers with 1 mm thickness and cured during 60 s resulted in the DSC curve presented in Fig. 3.e. In the first heating cycle the glass transition is masked by the volatilization of the residual solvents from the monomers. During the next cooling and heating it was possible to detect the glass transitions as summarized in Table 2 for all the samples.

The similarity in the DSC profiles of the polymers obtained with different widths and irradiation times used in the present work, suggests that these parameters do not affect the resulting materials.

The DSC results agreed with the TG-DTA curves, in which it was possible to observe the release of residual solvents, since they only could be observed in the first cycle but not in the second one.

It is also important to note that the full curing is reached only after heating of the monomers mixture, being important information since, when used in dentistry these resins remain uncured into the patient's teeth.

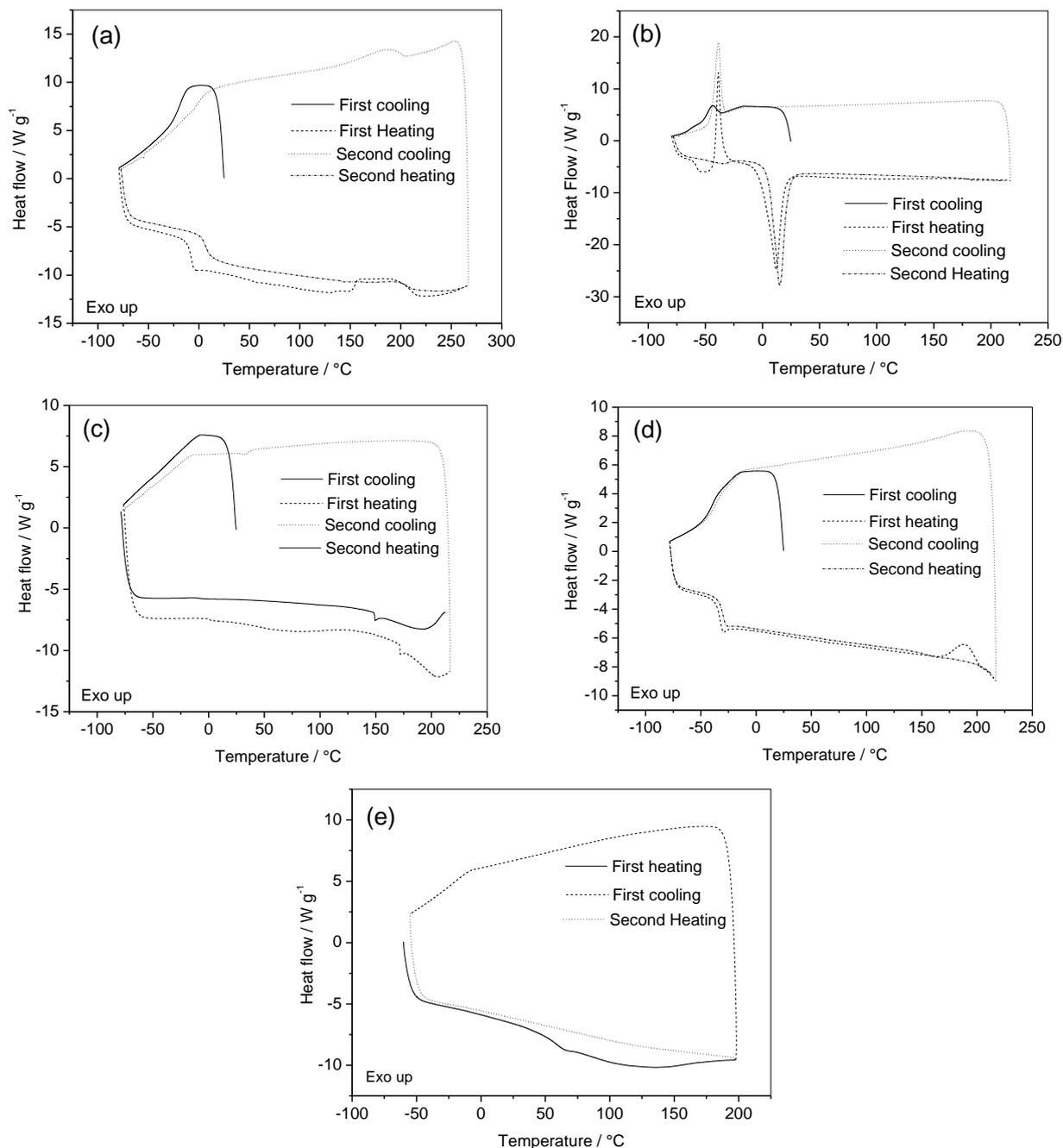


Figure 3. DSC curves: (a) BisGEMA; (b) BisEMA; (c) UDMA; (d) TEGDMA; (e) poly 1mm 60s

Table 2. DSC glass transition data

Compound	Glass transition DSC curves. (°C)				
	Heating 1	Cooling 1	Heating 2	Cooling 2	Heating 3
Poly 1-60	-	98.5	102.0	98.5	102.0
Poly 1-120	-	97.6	106.0	97.6	106.0
Poly 1-240	-	98.0	92.0	98.0	92.0
Poly 2-60	-	98.0	99.0	99.0	99.0
Poly 2-120	-	99.0	100.0	101.0	100.0
Poly 2-240	-	105.0	101.0	105.0	101.0

3.3. TG-FTIR

Once the TEGDMA was the monomer that present the lowest thermal stability and higher amount of volatiles released according to the TG-DTA curves it was chosen to be investigated by TG-FTIR analysis in order to characterize the volatiles evolved from the sample in the 20-250 °C temperature range. The photocured Poly 1-60 mixture of monomers was also analyzed under these conditions by the technique.

The Gram-Schmidt plots obtained for the TGDMA and the mixture are presented in Figs. 4a-b. At the maximum concentration of volatiles released, around 250 °C, it were collected the FTIR spectra of the gaseous phase. The analysis of this spectrum is presented in Fig. 5, from which

it is possible to deduce that 2-hydroxymethylmetacrylate, is being released from the sample.

The volatile released from the TEGDMA monomer was also analyzed by TG-FTIR. The FTIR spectrum of these volatiles compared to that released by the photocured mixture is presented in Fig. 6, from which is easy to observe that they are very similar. This allows one to conclude that the TEGDMA is the main responsible for the volatiles evolved from the polymer.

Gases evolved at higher temperatures were not analyzed once during the decomposition of the polymeric matrix the FTIR cell became saturated of gases resulting in a non-resolved continuum spectrum.

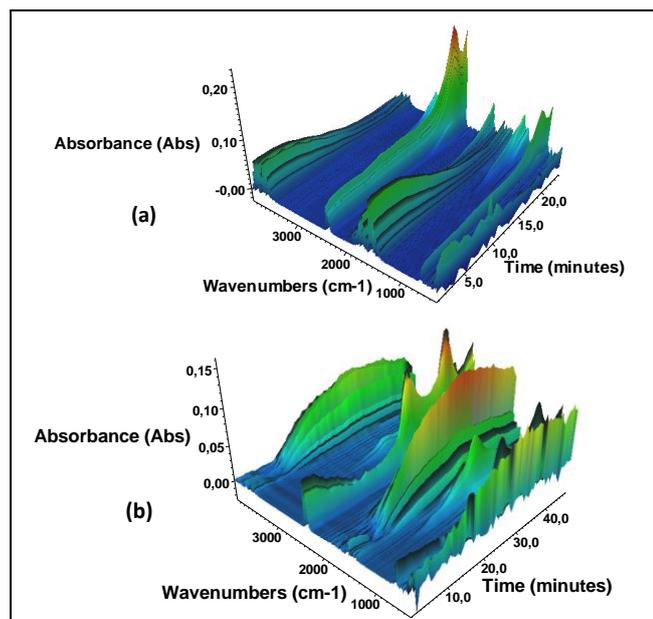


Figure 4. TGA-FTIR infrared spectra Grand-Schmitt plots (a) Poly 1-60 mixture of monomers range of the 20-250 °C. (b) TEGDMA range of the 20-250 °C.

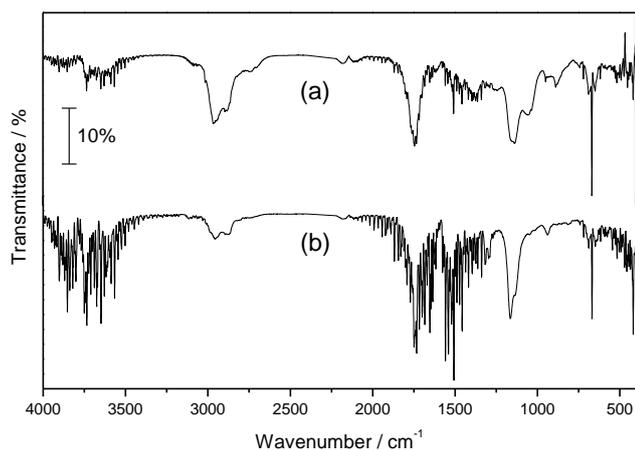


Figure 6. TGA-FTIR infrared spectra of: (a) Poly 1-60 mixture of monomers; (b) TEGDMA collected up to 250 °C, in gas phase, from the Grand-Schmitt plot.

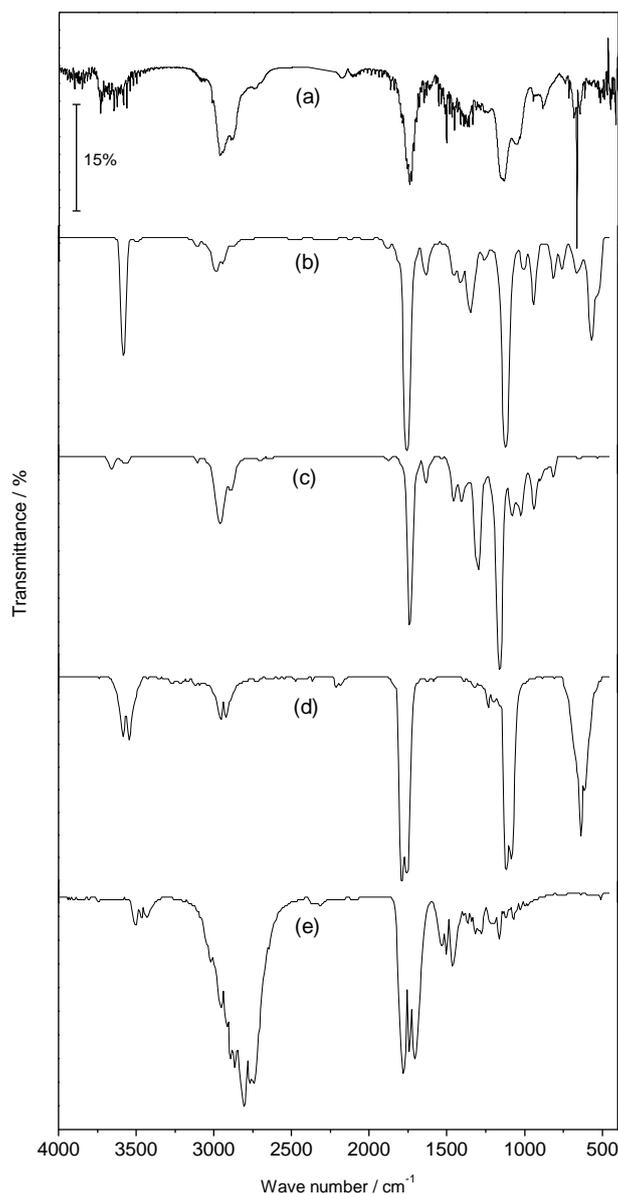


Figure 5. TGA-FTIR infrared spectra of: (a) Poly 1-60 mixture of monomers; (b) methacrylic acid; (c) 2-hydroxymethylmetacrylate; (d) formic acid; (e) formaldehyde collected up to 250 °C, in gas phase, from the Grand-Schmitt plot.

4. Conclusion

From results obtained it was possible to deduce that the monomers release volatiles residues before thermal curing. Under the parameters investigated, that reproduces practical conditions of use, the sample thickness and the irradiation time did not influenced the thermal properties of the resulting polymer.

The main volatiles released during heating of the monomers are methacrylic acid, 2-hydroxymethylmetacrylate, formic acid and formaldehyde, or their mixtures.

The cure of the polymer is incomplete after irradiation of the mixture of monomers, being completed only after heating.

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