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Use of DSC in degree of conversion of dimethacrylate polymers: easier and faster than MIR technique

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Abstract
This work aims to determine the degree of conversion of polymers obtained using diurethane dimethacrylate (UDMA) monomer by two different techniques: differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (MIR). The measurements were made in triplicate on both equipment, which resulted in average values for MIR $79.52 \pm 3.57\%$ (camphorquinone photoinitiator) and $78.15 \pm 1.86\%$ (fluorescein photoinitiator) and for DSC 80.85 ± 1.06 and $78.27 \pm 1.71\%$. The DSC technique showed higher accuracy and lesser standard deviation. Furthermore, this technique is easier and faster than the MIR, and in situ polymerization is not necessary on the DSC equipment.

Keywords Photopolymerization · DSC · MIR · Degree of conversion · Techniques comparison · Dimethacrylate

Introduction

Dimethacrylate monomers are widely used in photopolymerization to produce a high quantity of different materials such as composites, biomaterials, optical materials, and coatings [1–6]. To synthesize these materials, the use of an initiator is necessary, which means a chromophore molecule that is excited by light to generate radicals that initiate the polymerization reaction. A variety of molecules can be used as photoinitiator, such as camphorquinone [7, 8], fluorescein [9], curcumin [10, 11], riboflavin [12, 13], and benzophenone-naphthalimide [14]. Currently, many articles describe the use of Mid-Infrared Spectroscopy (MIR) as a technique to calculate the conversion degree of dimethacrylate monomers [15–17]. Other works describe photo-DSC for this purpose [18, 19], which calculates the energy in photopolymerization process. However, both these techniques require in situ polymerization (on the equipment). Hence, a sensitive technique, which does not require the in situ formation of the polymer, is needed. One alternative is the use of standard DSC, which only requires a previously polymerized sample; moreover, standard DSC is faster and less laborious than MIR analysis. DSC is widely used in thermal characterization of polymers, providing important thermal information such as glass transitions, temperature, enthalpy of fusion, etc. [20–22]; thus, its use to determine the total degree of conversion is additional information. DSC uses the difference of standard enthalpy of bond cleavage (C=C) and the curve energy (calculated), making it possible to calculate the monomers that remain in the polymers and, consequently, its total degree of conversion.

This work shows the use of standard DSC (not mentioned in the literature before) as an alternative to MIR in the calculation of degree of conversion for dimethacrylate monomers by photopolymerization, the both results techniques were compared by *F* test, a statistic tool.

Materials and methods

Preparation of the monomeric mixtures and photopolymerization

To prepare the monomeric mixtures, Urethane Dimethacrylate (UDMA) (Aldrich) was added to six individual plastic containers, each with 0.01 mol of the monomer. Two different photoinitiating solutions were prepared by dissolving the photoinitiators (chromophore

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molecule that is excited by light) camphorquinone (CQ) and fluorescein (FL) and ethyl-*p*-dimethylaminobenzoate (coinitiator, molecule that promotes radical formation) in 10 mL of acetone at a concentration of 20 mmols of each reagent and added to the reaction mixture (UDMA) at the proportion of 20% (mol).

The final mixtures containing monomers (UDMA) and initiator system (camphorquinone or fluorescein both with coinitiator) were photopolymerized at room temperature using the light emission equipment D-2000 (DMC Ltd., São Carlos, SP, Brazil), which uses LED to emit blue light (1 W cm^{-2}) in the range 430–490 nm, as specified by the manufacturer. The mixtures were placed in a Teflon mold with 1.5 mm in depth and 3.0 mm in diameter and were polymerized for 450 s in triplicate.

Degree of conversion

Differential scanning calorimetry (DSC)

DSC curves for each polymer were obtained with a Mettler-Toledo DSC1 Star^{e} system. Approximately 13 mg of sample were placed in a 40 μL closed aluminum crucible with perforated lid. The heating rate was 10 °C min^{-1}, and the flow rate was 50 mL min^{-1}. Dry air atmosphere was used and the temperature ranged from 150.0 to 220.0 °C. The thermal events observed in the DSC curves were used to calculate the degree of conversion (DC). The C=C bond requires 60 kJ mol^{-1} to cleave the π ligation, which is considered the standard enthalpy of polymerization (ΔH_{pol}) [23–26]. The energy obtained in polymerization peak in DSC curves of polymers refers to residual monomer in polymers previously photopolymerized (E_p). It is possible to obtain the DC (%) from DSC curves using Eq. 1.

$$\mathrm{DC}\ (\%) = \left[1 - \left(\frac{E_p \cdot \mathrm{MM}}{\Delta H_{pol} \cdot m_a}\right)\right] \times 100 \qquad (1)$$

Equation 1: formula to calculate the degree of conversion (DC) percentage using the DSC.

MM is the molar mass of monomer, and m_a is the sample mass used in DSC analysis.

Two previous works described the use of DSC to calculate the degree of conversion of methacrylate monomers [27, 28]; however, these works just consider the polymerization by temperature using thermoinitiator (benzoyl peroxide and 2,2′-azobizisobutyronitrile), not comparing techniques or mentioning photopolymerization.

Middle infrared spectroscopy (MIR)

To calculate the degree of conversion for each polymer, a spectrophotometer from Bruker, model Vertex 70, was used. The equipment operated in the range 4000–400 cm^{-1}. Monomeric mixtures were placed over the diamond crystal and polymerized, while the transmittance (*T%*) of each sample was collected. Data collection occurred every 10 s, and 45 measurements were made for all samples (in triplicate). Equation 2 is used to quantify the degree of conversion for each sample [8, 9, 11].

$$\mathrm{DC}\ (\%) = \left[1 - \frac{T_{t=x}(\mathrm{C=C})}{T_{t=0}(\mathrm{C=C})}\right] \times (-1000) \qquad (2)$$

Equation 2: formula to calculate the degree of conversion (DC) percentage using the transmittance of double carbon bonds (C=C) present in the monomer.

Transmittance of the C=C bond is seen near the 1640 cm^{-1} wavenumber. At the initial time ($t = 0$), a minimum transmittance is observed at this wave number, as polymerization has not yet begun. At any other future time ($t = x$), the transmittance increases, as polymerization takes place and double bonds are cleaved. With this input of data and applying Eq. 2, graphs for degree of conversion over time were plotted.

Statistical analysis

The results obtained from both techniques were analyzed by *F* test, following the steps described by the Ref. [29].

Results and discussion

Degree of conversion

Middle infrared spectroscopy (MIR)

The MIR measurements depicted a band near 1640 cm^{-1}, evincing the C=C double bond present in the dimethacrylate molecules. As expected, the intensity of this band decreased considerably for the polymers, because this process involved the cleavage of the π bond. Hence, it was possible to calculate the conversion degree of each monomer using Eq. 1. Figure 1 shows the degree of conversion for all samples (UDMA with CQ and FL) studied, at different times during polymerization.

Therefore, for the UDMA with CQ and FL photoinitiators, the degree of conversion for the three samples had an average of 79.52 ± 3.57% for the CQ system and a conversion average of 78.15 ± 1.86% for the FL system.

Differential scanning calorimetry (DSC)

The DSC curves in Fig. 2 illustrate that all systems exhibited similar thermal behavior: an exothermic peak (187.5 °C) associated to polymerization of residual

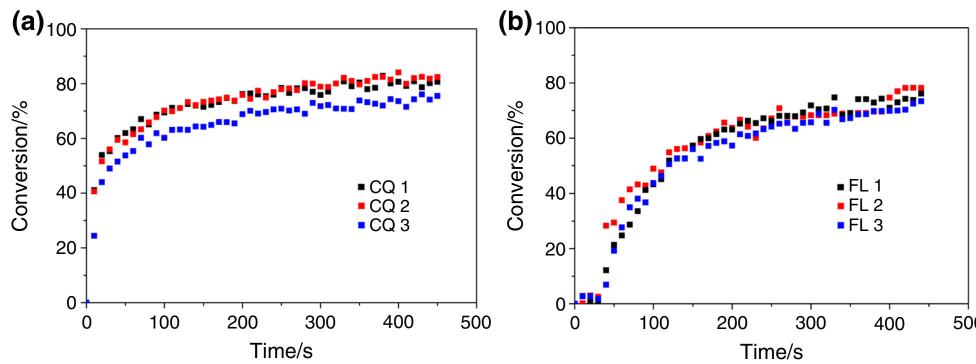

Fig. 1 Degree of conversion curves for UDMA with CQ (**a**) and UDMA with FL (**b**)

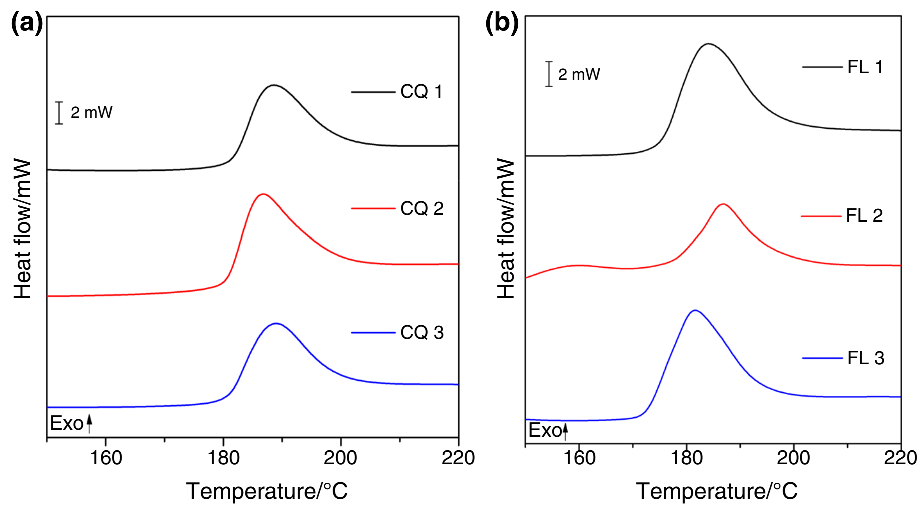

Fig. 2 DSC curves for UDMA with CQ (**a**) and UDMA with FL (**b**)

monomers in photopolymerization. The area integration was made according to Fig. 3, and just the middle peak was considered in E_p (Eq. 2). The curve area (marked in blue in Fig. 3) is determined by two points, the first one is the onset (the point that reaction initiate) and endset that was considered the final curve point. The endeset is necessary, due to was not possible determine with accuracy

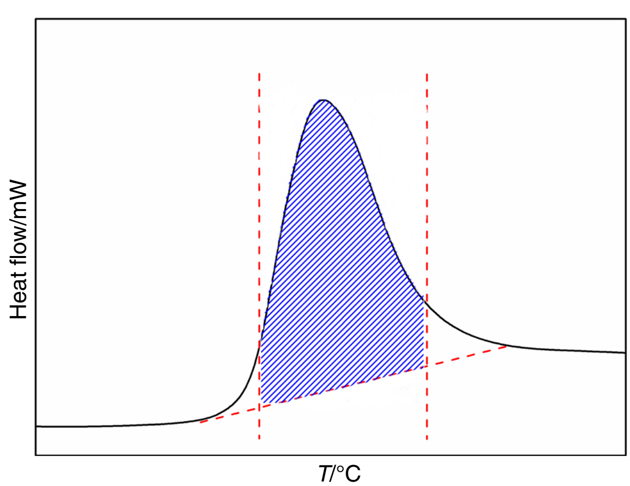

Fig. 3 Representative DSC curve for E_p calculation

the end of the reaction, this end process could occur in any point after the maximum peak, this fact is observed in all thermal process in thermal analysis such as polymerization, degradation, phase transition etc.

Finally, the results of DSC measurement showed an average value similar to MIR: 80.85 ± 1.06% (CQ) and 78.27 ± 1.71% (FL); thus, the standard deviation value in DSC is less than MIR values, which indicates more accurate analyses. This could be because the MIR does not have a sample control such as mass or thickness. The degree of conversion values obtained for each sample for each technique is exhibited in Table 1.

Statistical analysis

The F test was used to compare the variance values, assuming the confidence interval equal to 95%. All values of F were lower than $F_{critical}$, demonstrating that the values of both techniques did not distinguish themselves [29]. These results indicate that DSC could be use in determination of the degree of conversion. The statistical data are shown in Table 2.

Table 1 Values of degree of conversion, average and standard deviation obtained for each sample using DSC and MIR

Photoinitiator	Equipment	DC/%	Average/%	SD
CQ	DSC	81.49	80.85	1.06
		79.63		
		81.44		
	MIR	80.65	79.52	3.57
		82.39		
		75.52		
FL	DSC	77.06	78.27	1.71
		80.24		
		77.53		
	MIR	76.12	75.90	2.41
		78.20		
		73.39		

DC degree of conversion, *SD* standard deviation

Table 2 Values of F and $F_{critical}$ obtained by the F test

Initiator	CQ	FL
F	11.4	1.9
$F_{critical}$	19.0	19.0

Conclusions

The average values for degree of conversion obtained by DSC and MIR were very similar, and the F test showed that the variance values did not differ. Hence, these results prove that DSC could be an alternative of MIR technique in degree of conversion for dimethacrylate monomers.

The principal advantage of DSC is its accuracy, higher than MIR, as observed in standard deviation values (in both photoinitiator); another advantage that in situ polymerization is not necessary.

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