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Kinetics of thermal degradation of PMMA-based dental resins scraps

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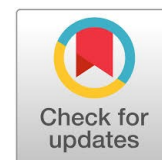
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ARTICLE INFORMATION

ABSTRACT

In this work, the cross-linked PPMA-based dental resins scraps were applied to pyrolysis to recover MMA (Methyl methacrylate). Thermal degradation of the cross-linked PPMA-based dental resins scraps was analyzed using TG/DTG to guide the operating condition. The reaction liquid products which were obtained at 30, 40, 50, 60, 70, 80, and 110 min, were physicochemically characterized for density, kinematic viscosity, and refractive index. The chemical composition of the reaction liquid products, obtained at 30, 40, 50, 60, 70, 80, and 110 min, was determined by GC-MS. The liquid phase yield was 55.50% (wt), while that of the gas phase was 31.69% (wt). The density, kinematic viscosity and refractive index of the reaction liquid products which were obtained at 30, 40, 50, 60, 70, 80, and 110 min, varied between 0.9227 and 0.9380 g/mL, 0.566 and 0.588 mm²/s, and 1.401 and 1.414, respectively. Moreover, it shows the percentage errors at the range of 0.74-2.36%, 7.40-10.86%, and 0.00-0.92%, respectively, as compared to the standard values for density, kinematic viscosity, and refractive index of pure MMA (Methyl metaclylate) at 20 °C. The GC-MS, identified in the reaction liquid products during pyrolysis, esters of carboxylic acids, alcohols, ketones, and aromatics, shows concentrations of MMA (Methyl metaclylate) between 88.003 and 98.975% (Area). The concentrations of MMA (Methyl metaclylate) in the liquid phase, between 30 and 80 min, reach purities above 98% (Area), decreasing drastically with increasing the reaction time after 100 min. Thus, it will be possible to depolymerize the cross-linked PPMA-based dental resins scraps by pyrolysis in order to recover MMA (Methyl methaclylate).

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Graphical Abstract
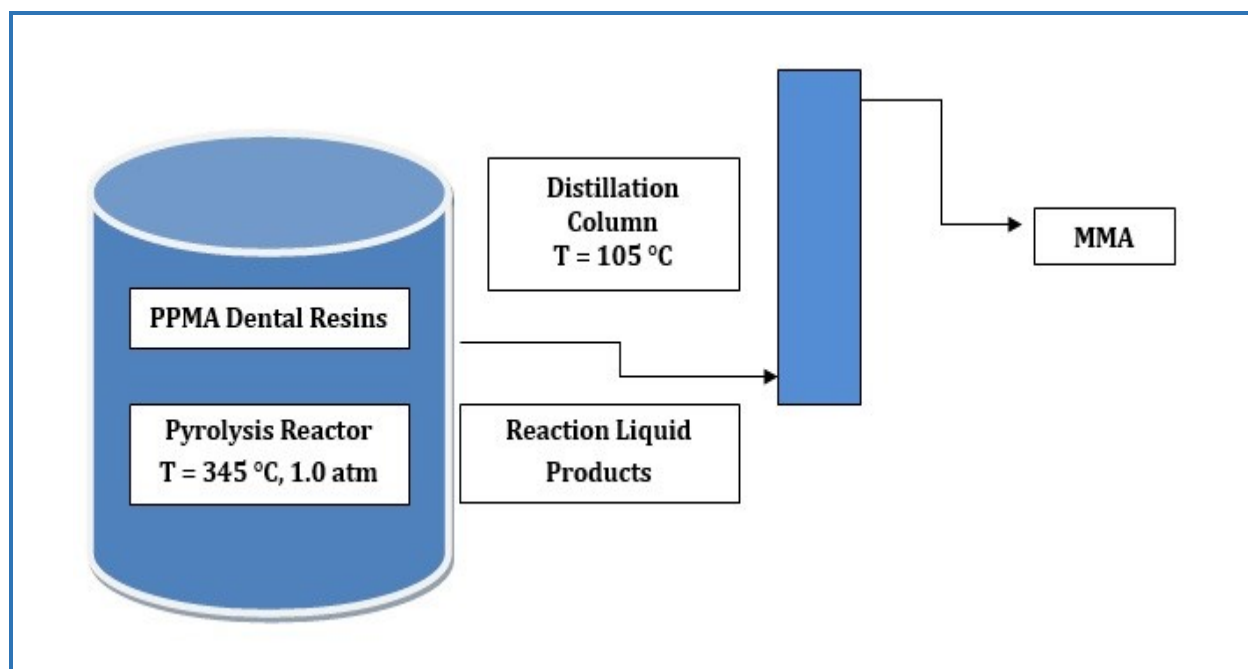
Introduction

Polymethyl methacrylate (PMMA) is an acrylic polymer (Ester of acrylic acid) with superior properties and/or characteristics; including, high ultraviolet (UV) resistance, high light transmission, opticall transparency, good stability, high gloss and hardness (Greatest surface hardness among all the thermoplastics), good abrasion resistance, good rigidity, low-medium density (1.17-1.20 g/cm^3) [1], being one of the most important industrial polymeric materials, and also being widely used in the automobile, construction, furniture, electronics, optical media, mobile communication, cosmetics, and medical/dentistry industries [1−4].

World production of PMMA is expected to reach 2.85 10^6 tons by 2020, growing at a compound annual growth rate of 6.1% from 2013 to 2020 [5]. Moreover, as an environmentally-friendly polymer, PMMA can be regarded as a recyclable material [5−8]. Over the years, plastics wastes were commonly dumped in a landfill or incinerated for energy recovery [8]. However, during the last decades, the global plastics production increased from 10^8 tons in 1989 to 335 10^6 tons in 2016 [9], resulting in increased waste streams [8, 9] and posing one of the greatest challenges for disposal and recycling of plastic wastes [8].

Most polymers can be pyrolyzed into hydrocarbons (Olefins, aromatic and aliphatic compounds) [6]. By the pyrolysis of polymethyl methacrylate and polystyrene, the main reaction liquid products are their precursor monomers methyl methacrylate (MMA) and styrene [6−8]. In this scenery,

pyrolysis, which can be regarded as one of the most promising processes to convert organic polymers of high molecular weight (Macromolecules) into smaller fragments [7], has proven to be an alternative for depolymerization of polymethyl methacrylate (PMMA) into methyl methacrylate (MMA) [6–8], as the literature reports several studies on the subject [6–8, 10–35]. By pyrolysis of PMMA, the reaction products include a gas (non-condensable), a liquid (condensable), and a solid phase [6–8, 10–17, 34, 35], and, in this regard, even a H_2O phase has been reported [7, 11, 35] probably due to dehydration reactions [18].

The reaction liquid products have been mainly composed of MMA [6–8, 11–17, 34, 35], as well as small concentrations of methyl esters of carboxylic acids [7, 11–17, 35], ethyl and butyl esters of carboxylic acids [14, 15], hydrocarbons [7, 11–16, 35], alcohols [7, 8, 11, 12, 35], diesters of carboxylic acids [17], phthalates [34], ketones [35], and carboxylic acids, among other chemical functions [7, 11–16].

Most studies on the pyrolysis of PMMA have been focused on the reaction mechanism and reaction kinetics by thermo-gravimetric [19–24, 26–28], thermo-gravimetric fourier transform infrared spectroscopy [25, 26], differential scanning calorimetry [28], thermal analysis fourier transform infrared spectroscopy [29], pyrolysis mass spectrometry [30, 31], flash pyrolysis/analytical pyrolysis [16], as well as those focusing on PPMA depolymerization in fluidized bed reactors [6–8, 11–13, 32, 35], fixed bed reactors [14, 34], conical spouted bed reactors [15], and stirred tank batch reactors [16, 17].

The thermal degradation experiments can be carried out in micro scale [16, 19–32], bench scale [12, 14, 17], laboratory [8, 11, 13, 15–17, 34, 35], and only a few in pilot and/or technical scale [7, 11]. Besides, the mode of operation of PPMA thermal degradation [6–8, 11–17, 32, 34, 35] and other factors that affect the chemical composition and yield of reaction liquid products are the characteristics of raw material (pure, filled, and scrap PPMA), reaction temperature, residence time, reaction time, gas flow rate, and the process scale [7, 8, 11, 17, 35].

The advantages of thermal degradation of PPMA by pyrolysis include the reduction in the volume of the produced gases (Non-condensable) [6], the possibility to use low quality PPMA-based materials [6–8, 11, 16, 17, 35], and the fact that reaction liquid products are composed mainly of MMA [6–8, 11, 13-17, 34, 35]. In addition, the reaction liquid products can be easily purified by distillation to produce high concentrated and/or pure MMA [6, 7, 17].

The drawbacks of thermal degradation of PPMA by pyrolysis remain on the fact that PPMA has poor thermal conductivity, degradation of polymeric macromolecules requires considerable amounts of energy, and the residence time of monomer vapors in the reactor must be minimized in order to reduce the formation of degradation products [6, 7]. In addition, if high yields are desired,

one needs to operate the reactor as a gas-solid fluidized bed, and the operation of gas-solid fluidized reactors with high solid and gas flow rates is complex [35].

In this context, significant studies have tried to analyze the influence of process parameters on thermal degradation of PPMA by pyrolysis in order to maximize both the liquid reaction products and the concentration of MMA within the liquid phase [7, 8, 11, 17, 35]. The liquid reaction products with relative high concentrations of MMA can be submitted to filtration, as well as decantation, if a H_2O phase is present [7–11], followed by distillation to obtain pure MMA [17].

Despite some studies focusing the process analysis of PPMA thermal degradation in laboratory [8, 11–13, 15–17, 35], and pilot or technical scale [7–11], no study has yet investigated the kinetic of PPMA depolymerization in pilot scale, particularly the MMA concentration profile and the cumulative mass of reaction liquid products as a function of reaction time.

This work aims at evaluating the kinetics of thermal degradation of the cross-linked PPMA-based dental resins scraps by pyrolysis at 345 °C, 1.0 atmosphere, in pilot scale reactor of 143 L. The kinetics has been systematically investigated during the course of pyrolysis to evaluate/analyze the effect of reaction time on the cumulative mass and MMA (Methyl methacrylate) concentration within the reaction liquid products. The liquid phase was submitted to the fractional distillation in a laboratory scale column (Vigreux) at 105 °C in order to obtain fractions not only with high concentration of MMA, but also with similar physicochemical properties (Density, kinematic viscosity, and refraction index) of pure MMA.

Experimental

Materials and methods

The cross-linked PPMA-based dental resin scraps, as illustrated in Figure 1, were gently provided by Dentsply Indústria e Comércio Ltda (Petrópolis, Rio de Janeiro, Brazil). The PPMA-based dental resin scraps contain 1.0% (wt) inert color spreaders (TiO$_2$) and 5.0% (wt) of the cross-linking agent EGDMA (Ethylene glycol dimethacrylate) [17].

Thermogravimetric (TG) analysis of the cross-linked PPMA-based dental resin scraps

The weight loss of the cross-linked PPMA-based dental resins scraps was measured by TG/DTG using a thermal analyzer (Shimadzu, Japan, Model: DTG 60-H), in which the following operating conditions were used: the sample (5.575 mg) was placed inside a platinum crucible in the balance mechanism, the temperature was selected in the range 25 °C-600 °C, heating rate of 10 °C/min, and under N_2 atmosphere with a volumetric flow rate of 50 mL/min.
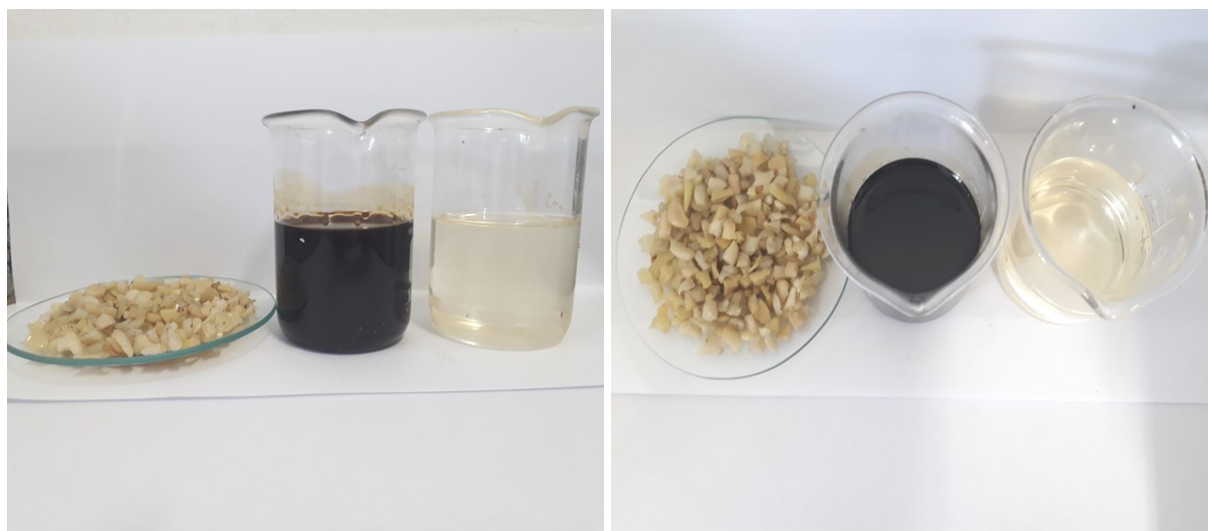
*(Becker: 250 mL, d=70 mm, h=95 mm; DIN: 12331, ISO: 3819)

Figure 1. Cross-linked PPMA-based dental resins scraps, liquid reaction products (Dark Liquid) obtained after pyrolysis at 345 °C, 1.0 atmosphere, and 70 min, and MMA (colorless liquid) obtained by fractional distillation of liquid reaction products

Pyrolysis, experimental apparatus and procedures

The experimental apparatus, a 143 L reactor (Thermal catalytic cracking unit), used for the pyrolysis of the cross-linked PPMA-based dental resins scraps, is illustrated in Figure 2. The apparatus which has been described in details [37–39] operates in batch mode at 345 °C and 1.0 atmosphere, under air atmosphere, using pieces of the cross-linked PPMA-based dental resins scraps as raw material. The average mass M_M of particle aggregate was 100.00±47.70 mg, while the average transversal $\emptyset_{M,T}$ and longitudinal $\emptyset_{M,L}$ diameters were 5.94±1.49 and 8.69±1.83 mm, respectively. The collected condensable gases were weighed every 10 and/or 30 min, and, then, the cumulative mass of reaction liquid products computed. Afterwards, samples were filtered and physicochemically characterized for density, kinematic viscosity, and refractive index.

Figure 2. Experimental apparatus (thermal catalytic cracking unit) for the pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, in pilot scale

Fractional distillation of liquid phase reaction products: experimental apparatus and procedures

The fractional distillation of reaction liquid products was performed using an experimental apparatus like that described in the literature [37]. The distillation apparatus, described in details [37−39], has an electrical heating blanket of 480 W (Fisaton, Model: 202E, Class: 300), and thermostatically controlls a 500 mL round bottom, and two neck flasks with outer joints. The side joint was used to insert a long thin thermocouple of a digital thermometer, the center joint, and connected to a distillation column (Vigreux) of 30 cm. The center top outer joint was connected to the bottom inner joint of a Liebig glass-borosilicate condenser. The Liebig glass-borosilicate condenser was connected to a 250 mL glass separator funnel by the top outer joint. The distillation was carried out at 105 °C ($T_{Boiling,MMA}$=101 °C). The mass of distillates was weighed and physicochemically characterized for density, kinematic viscosity, and refractive index.

Physicochemical analysis of distillation fractions

The distillation fractions, obtained according to the boiling temperature range of methyl methacrylate (MMA), were physicochemically characterized for density (ASTM D4052) at 25 °C, kinematic viscosity (ASTM D445/D446) at 40 °C, and refractive index (AOCS Cc 7-25), as described in the literature [37−39].

GC-MS of reaction liquid products

The separation and identification of all the chemical compounds, present in the liquid phase, were performed by CG-MS using a gas chromatograph (Agilent Technologies, USA, Model: CG-7890B), coupled to MS-5977A mass spectrometer, a SLBTM-5 ms (30 m × 0.25 mm × 0.25 mm) fused silica capillary column. The temperature conditions used in the CG-MS were: injector temperature: 290 °C; split: 1:20, detector temperature: 320 °C and quadrupole: 150 °C; injection volume: 1.0 μL; oven: 70 °C, 1 min; 10 °C/min, 280 °C; 13 min. The intensity, retention time and compound identification were recorded for each peak analyzed according to the NIST (Standard Reference Database 1 A, V 14) mass spectra library. The identification is made based on the similarity of the peak mass spectrum obtained with the spectra within the library database, and those available in the software. The concentrations, expressed in area (area%), of all the chemical compounds identified in each sample were computed and the chemical composition of each experiment was determined.

Material balance by pyrolysis of the cross-linked PPMA-based dental resins scraps

Application of mass conservation principle in the form of an overall steady state mass balance within the stirred tank reactor, operating in batch mode, closed thermodynamic system, yields the following equations.

$$\sum_i M_{i,In} = \sum_j M_{j,Out} \tag{4}$$

$$M_{Reactor} = M_{Feed} \tag{5}$$

$$M_{Reactor} = M_{SP} + M_{LP} + M_{Gas} \tag{6}$$

Where $M_{i,In}$ is the mass of i-th stream entering the reactor, $M_{j,Out}$ is the mass of j-th stream leaving the reactor, $M_{Feed} = M_{PPMA}$ is the mass of the cross-linked PPMA-based dental resins scraps, M_{SP} is the mass of solid phase (coke), M_{LP} is the mass of reaction liquid products, M_{Gas} is the mass of gas. The process performance was evaluated by computing the yields of liquid and solid reaction products defined by Eqs. (7) and (8), and the yield of gas by difference, using Eq. (9).

$$Y_{LP}[\%] = \frac{M_{LP}}{M_{PPMA}} \times 100 \tag{7}$$

$$Y_{SP}[\%] = \frac{M_{SP}}{M_{PPMA}} \times 100 \tag{8}$$

$$Y_{Gas}[\%] = 100 - (Y_{LP} + Y_{SP}) \tag{9}$$

Results and Discussion

Thermogravimetric (TG/DTG) analysis of the cross-linked PPMA-based dental resin scraps

In order to analyze the thermal decomposition behavior and/or characteristics of the cross-linked PPMA-based dental resin scraps, the TG/DTG technique was applied, in order to better guide the experimental conditions. Figure 3 shows the thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis of the cross-linked PPMA-based dental resin scraps. As one observes, the cross-linked PPMA-based dental resin scraps are thermally stable between 25 °C and 200 °C. The thermal degradation of cross-linked PPMA-based dental resin scraps started around 200 °C, losing approximately 5.0% (wt) mass at 300 °C, 40.0% (wt) mass at 350 °C, 90.0% (wt) mass at 405 °C, 95.0% (wt) mass at 420 °C, and 100.0% (wt) mass at 420 °C, showing a thermal degradation behavior similar to that reported by *Braido* et al. [17] for parings PPMA. The presence of 1.0% (wt) inert color spreaders (TiO₂) and 5.0% (wt) of the cross-linking agent ethylene glycol dimethacrylate [17] is probably responsible for the absence of 02 (two) reaction stages, as observed by

homopolymer PMMA thermal degradation [17–19]. As reported elsewhere [19–21], by thermal degradation of PMMA under oxygen containing atmosphere (O_2, Air), a complex oxidation process takes place [19]. In addition, thermal degradation of PPMA under oxygen-containing atmosphere (O_2, Air) causes an increase on the PMMA thermal stability by increasing it from 50 °C to 70 °C, the temperature for initiation of mass loss [19–21]. However, above 230 °C, gas-phase oxygen containing atmosphere (O_2, Air) destabilizes the PPMA, causing an acceleration of the thermal degradation process [19–21]. *Hirata* et al. [19] and *Peterson* et al. [21] reported that by thermal degradation of virgin PPMA under oxygen containing atmosphere (O_2, Air) a mass loss of approximately 90.0% (wt) occurs at 350 °C, while, at 400 °C, PPMA has been completely decomposed. Due to the fact that the experimental apparatus described in section 2.3.1 operates under air atmosphere, the pyrolysis temperature was set at 345 °C in order to minimize the energy consumption of LPG.
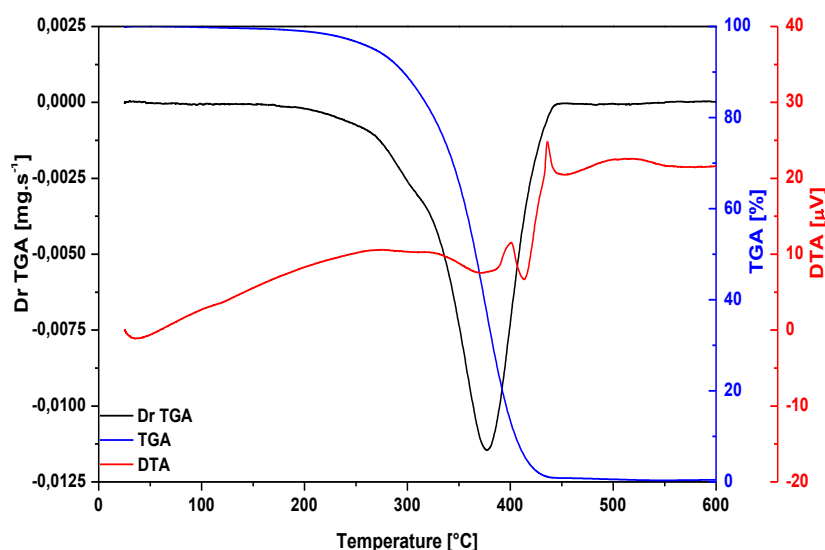

Figure 3. Thermo-gravimetric (TG/DTG) analysis of the cross-linked PPMA-based dental resins scraps in the temperature range of 25-600 °C, heating rate of 10 °C/min, N_2 atmosphere, volumetric flow rate of 50 mL/min

Pyrolysis of the cross-linked PPMA-based dental resins scraps

Process conditions, material balances, and yields of reaction products by pyrolysis of the cross-linked PPMA-based dental resins scraps

The process conditions, material balances, yields of reaction products (Solid, liquid, and gas), after the pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, and the reaction times of 125 minutes, using a pilot scale stirred tank reactor of 143 L, are illustrated in Table 1. The experimental data show the liquid phase yield of 55.50% (wt), solid phase yield of 11.67% (wt), and

gas yield of 31.69% (wt). The liquid phase yield is lower, but close to those reported by *Szabo* et al. (65.0%) [16] and *Braido* et al. (66.30%) [17], who used the same raw material (Cross-linked PPMA-based dental resins scraps) and an apparatus like that described in the sections 2.3.1 [17], smaller than those reported by *Kaminsky* (96.60%) [6], *Kaminsky* and *Frank* (92.13%) [7], *Kang* et al. (96.80 and 98.40%) [13], and *Popescu* et al. (90.0%) [34], and higher than those reported by *Kaminsky* et al. (24.825%) [8], *Kaminsky* and *Eger* (27.87-28.07%) [11], and *Grause* et al. (18.0-31.0%) [35], for the thermal degradation of filled PPMA and PPMA wastes [6–8, 11–13, 16, 17, 34, 35]. The liquid phase yield is lower than those reported in the literature [6, 7, 13], probably due not only to the mode of operation [6, 7], but also to the smaller particle sizes $\emptyset_{Particle}$ used on the thermal degradation processes [7, 11–13, 35]. Since PPMA has a poor thermal conductivity [6], the larger the particle size $\emptyset_{Particle}$, the worse the heat transfer, and the lower the conversion of PPMA into MMA, and hence the liquid phase yield.

Physicochemical analysis of distillation fractions

Table 2 presents the physicochemical characterization of distillation fractions after distillation at 105 °C, and of the reaction liquid products obtained during the thermal degradation of cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 min. The density of distillation fractions, measured at 30 °C, varied between 0.9227 and 0.9380 g/cm³, showing deviations between 0.74 and 2.36%, as compared to the density of pure MMA at 20 °C. The densities are lower as compared to that reported by *Szabo* et al. [16], of 0.945 g/cm³. The kinematic viscosity, measured at 40 °C, varied between 0.566 and 0.588 mm²/s, showing deviations between 7.40 and 10.86%, as compared to the kinematic viscosity of pure MMA at 20 °C. The kinematic viscosities which are lower than that reported by *Szabo* et al. [16] are of 1.90 mm²/s, as measured at 40 °C for PPMA-ABS thermal degradation. Finally, the refractive index, measured at 30 °C, varied between 1.401 and 1.414 [-], showing the deviations between 0.00 and 0.92%, as compared to the refractive index of pure MMA at 20 °C. The results, presented in Table 2, show lower values for the densities and kinematic viscosities, as compared to those of pure MMA at 20 °C and illustrated in Table 2. In this sense, it is so due to the fact that the physicochemical properties were measured at 30 and 40 °C, respectively, and the kinematic viscosity of MMA decreased with temperature [16].

Kinetics of PPMA thermal degradation

The cumulative mass of reaction liquid products obtained by thermal degradation of the cross-linked PPMA-based dental resins scraps at 345 °C, reaction times of 125 min, using a pilot scale stirred tank reactor of 143 L, is illustrated in Figure 4. The cumulative mass of reaction liquid

products shows the first-order kinetic behavior, that is, the cumulative mass of reaction liquid products grows exponentially with a root mean square error of 0.99, showing a maximum between 90-100 minutes. The exponential first-order-grow function validates the assumption of the first-order kinetics, in according to the kinetic of PPMA depolymerization reaction reported by *Smolders* and *Baeyens* [12] and *Lopez* et al. [15], respectively. In fact, until now, no study, reported in the literature, has reported the kinetic of cumulative mass during thermal degradation process of PPMA by pyrolysis in pilot scale.

Table 1. Process parameters and overall steady state material balance by thermal degradation of the cross-linked PPMA-based dental resins scraps at 345 °C and 1.0 atmosphere

Process Parameters	T [°C] 345
Mass of Dental Resins [kg]	14.60
Mass of LPG [kg]	7.00
Thermal Cracking Time [min]	125
Mechanical Stirrer Speed [rpm]	0
Initial Temperature of Liquid Condensation [°C]	68
Initial Temperature of Gas Production [°C]	85
Final Cracking Temperature [°C]	345
Mass of Solids [kg]	1.87
Mass of Liquids [kg]	8.10
Mass of Gas [kg]	4.63
Yield of Liquids [kg]	55.50
Yield of Solids [kg]	12.81
Yield of Gas [kg]	31.69

Table 2. Physicochemical characterization of distillation fractions after distillation at 105 °C, of reaction liquid products obtained during the thermal degradation of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 min

Physicochemical Properties	Cracking Temperature [°C] 345							
	Time [min]							
	30	40	50	60	70	80	110	Ref.
ρ [g/mL], 30 °C	0.9312	0.9299	0.9320	0.9380	0.9227	0.9240	0.926	0.945 (20 °C)

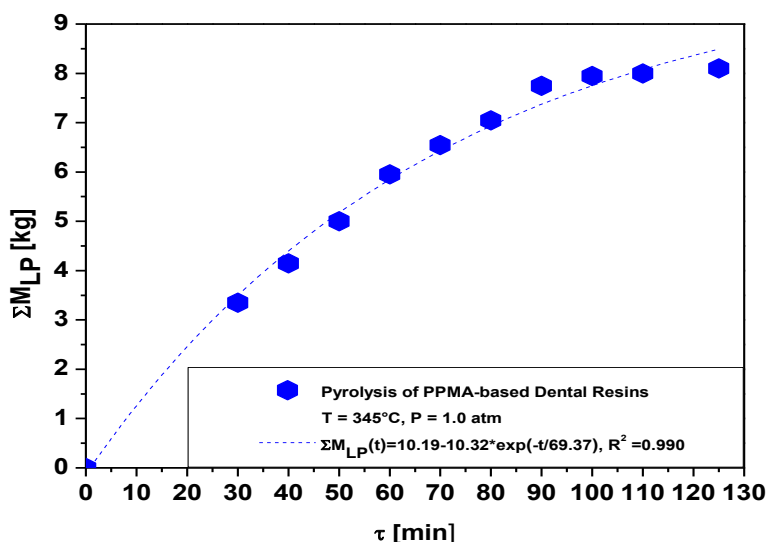|								
Refractive Index [-], 30 °C	1.404	1.411	1.401	1.409	1.414	1.405	1.401	1.414-1.416 (20 °C)
μ [cSt], 40 °C	0.574	0.569	0.588	0.576	0.568	0.570	0.566	0.635 cSt (20 °C)

Figure 4. Cumulative mass of reaction liquid products obtained by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C and 1.0 atmosphere

According to Table 3, MMA concentrations up to 98.97% (area) could be achieved in the liquid phase at 345 °C, 1.0 atmosphere, and 30 min, higher than those reported by *Kaminsky* and *Frank* (97.20%) [6], *Kaminsky* and *Frank* (90.99%) [7], *Kaminsky* et al. (18.10%) [8], *Kaminsky* and *Eger* (86.60-90.50%) [11], *Kang* et al. (95.65-97.29%) [13], *Szabo* et al. (21.50%) [16], *Braido* et al. (82.20-95.40%) [17], and *Grause* et al. (53.0-69.0%) [35]. In addition, the only side products identified by GC-MS in the liquid-reaction products which were obtained by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, and 80 min, were methyl isobutyrate and ethylene glycol dimethacrylate, referring to the fact that no side reactions have taken place as compared to several side products reaction reported in the literature [7, 8, 11, 13–17, 34, 35], and corroborating to assert that thermal degradation of PPMA should be carried at the reaction times up to and/or around 80 min. This probably refers to the fact that high residence times, as well as high operating temperatures of monomer vapors inside the reactor contribute to the formation of degradation products [6, 7].

Table 3. Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS of liquid reaction products obtained by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, and 110 min

τ [min]	Class of chemical compounds	RT [min]	CAS	ω_i (area%)
30	Esters of carboxylic acids			
	Methyl isobutyrate	3.319	547-63-7	1.025
	Methyl methacrylate	3.676	80-62-6	98.975
	Σ (area%) =			100.000
40	Esters of carboxylic acids			
	Methyl isobutyrate	3.322	547-63-7	1.224
	Methyl methacrylate	3.669	80-62-6	98.776
	Σ (area%) =			100.000
50	Esters of carboxylic acids			
	Methyl isobutyrate	3.321	547-63-7	1.254
	Methyl methacrylate	3.670	80-62-6	97.148
	Ethylene glycol dimethacrylate	14.004	97-90-5	1.598
	Σ (area%) =			100.000
60	Esters of carboxylic acids			
	Methyl isobutyrate	3.320	547-63-7	1.430
	Methyl methacrylate	3.668	80-62-6	98.570
	Σ (area%) =			100.000
70	Esters of carboxylic acids			
	Methyl isobutyrate	3.320	547-63-7	1.762
	Methyl methacrylate	3.678	80-62-6	98.238
	Σ (area%) =			100.000
80	Esters of carboxylic acids			
	Methyl isobutyrate	3.318	547-63-7	2.242
	Methyl methacrylate	3.668	80-62-6	97.758
	Σ (area%) =			100.000
110	Esters of carboxylic acids			
	Methyl isobutyrate	3.314	547-63-7	3.562
	Methyl methacrylate	3.664	80-62-6	88.003

Butanoic acid, 2-methyl-, methyl ester	4.717	868-57-5	1.827
Σ (area%) =			93.392
Aromatics			
Toluene	4.560	108-88-3	2.320
Σ (area%) =			2.320
Alcohols			
Mesitol	12.458	527-60-6	2.179
Σ (area%) =			2.179
Ketones			
Platambin-1,6-dione	18.495	58556-83-5	2.109
Σ (area%) =			2.109

Chemical analysis of liquid reaction products

Kinetic of composition profile of MMA in the liquid reaction products

Table 3 illustrates the classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS of the liquid-reaction products obtained by pyrolysis of cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30, 40, 50, 60, 70, 80, 110 min. The chemical compositions represented in Table 3, were plotted in Figure 5 in order to analyze the influence of reaction time on the concentration of MMA within the liquid-reaction products. By analyzing the concentration profile of MMA in the liquid reaction products with reaction times, one observes that high concentrations of MMA are achieved at the beginning of monomer vapors condensation around 30 min, decreasing with reaction time in a smooth fashion up to 80 min, whereas a drastic decrease on the concentration of MMA occurs between 80 and 130 min, corroborating to assert that reaction time should not exceed the 80-90 min.

Figure 6 illustrates the GC-MS of reaction liquid products after pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30 min. As described in Table 3, only 02 (Two) chemical compounds were identified, MMA (Methyl methacrylate) with a concentration of 98.975% (Area) and methyl isobutyrate with a concentration of 1.025% (Area), showing that pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30 min, produced MMA of high purity, and hence, great amounts of the cross-linked PPMA-based dental resins scraps could be recovered.
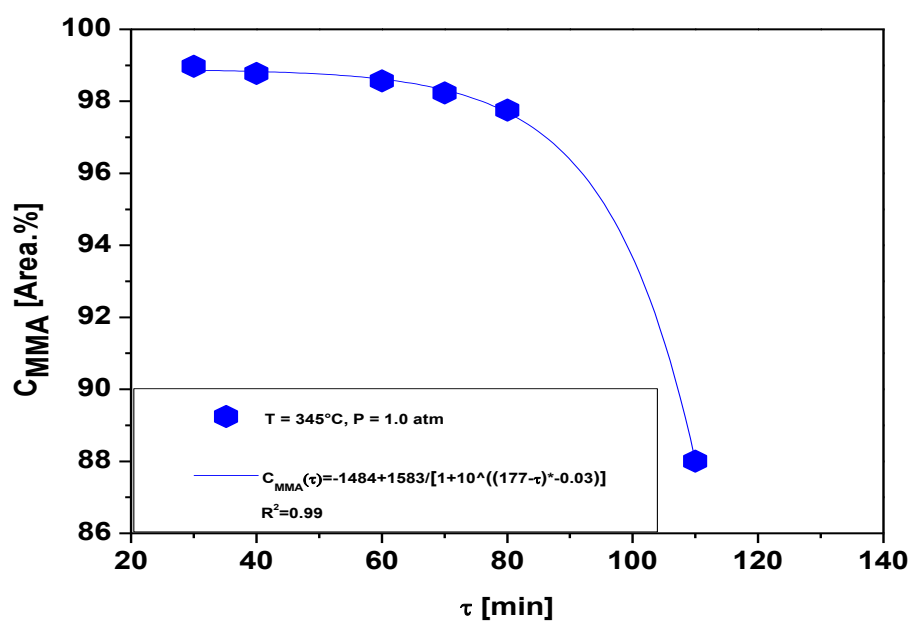
Figure 5. Concentration profile of methyl methacrylate (MMA) by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 30, 40, 50, 60, 70, 80, 110 min, and 1.0 atmosphere
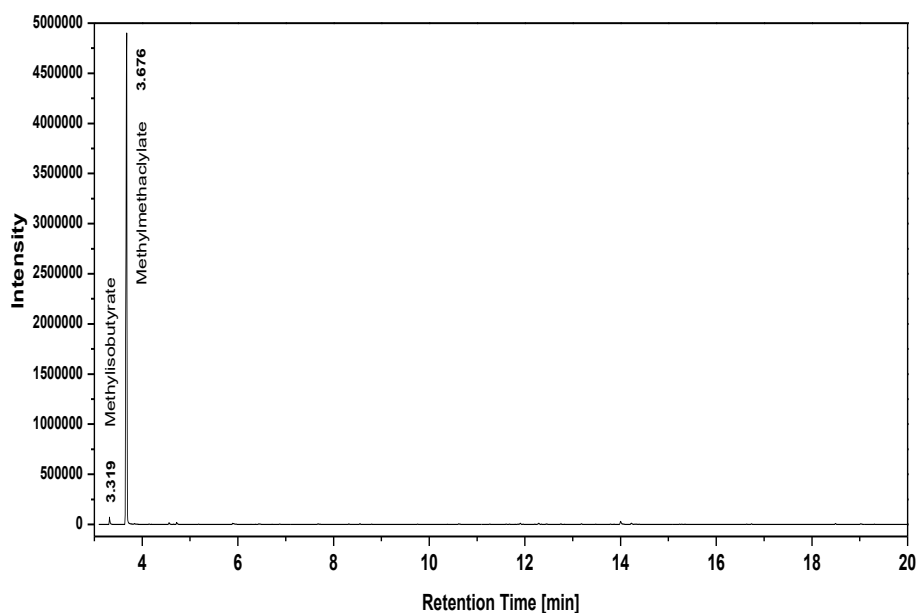

Figure 6. GC-MS of reaction liquid products after pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, and 30 min

Influence of reaction time on reaction side products (methyl isobutyrate)

The concentration profile of methyl iso-butyrate, a side reaction product, as a function of reaction time by pyrolysis of cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, 30, 40,

50, 60, 70, 80, and 110 min is shown in Figure 7. It can be observed that concentration of methyl iso-butyrate increases with the reaction time in a sigmoid fashion, reaching around 3.75% (area) at 110 min. This is probably due to high residence times and the operating temperatures of monomer vapors inside the reactor, thus, contributing to the formation of degradation products [6, 7]. In fact, others side reaction products; including, esters of carboxylic acids (1.827%), aromatics (2.320%), alcohols (2.179%), and ketones (2.109) have been identified by CG-MS, totalizing 11.997% (area). The formation of side-reaction products by thermal degradation of virgin PPMA filled PPMA as the waste PPMA has been extensively reported in the literature [7, 8, 11, 13-17, 34, 35].
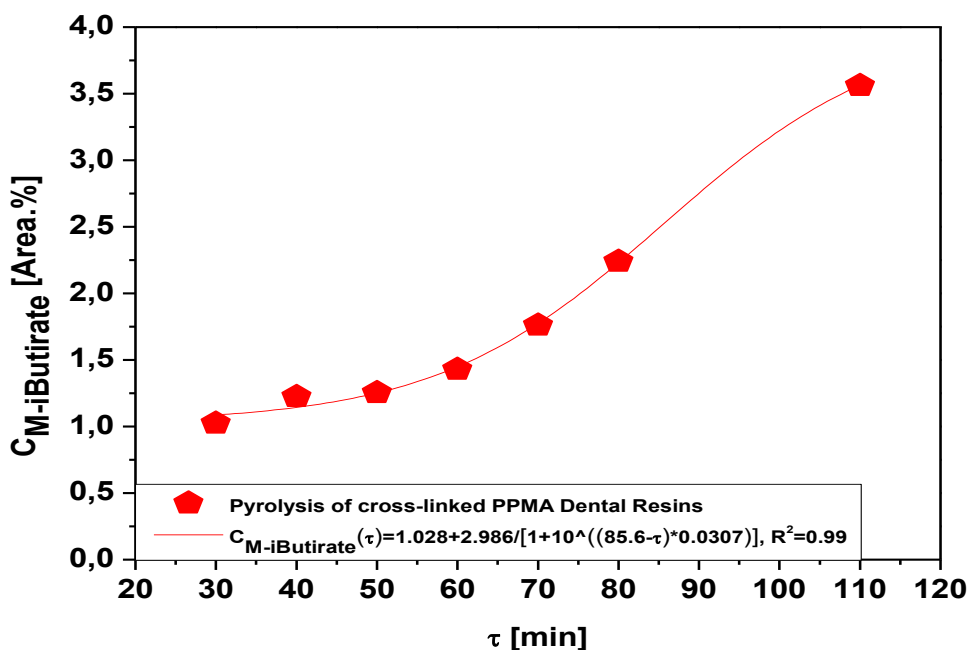

Figure 7. Concentration profile of methyl iso-butyrate, a side reaction product, by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, 30, 40, 50, 60, 70, 80, and 110 min

Conclusions

TG and DTG analyses showed that cross-linked PPMA-based dental resin scraps were thermally stable between 25 °C and 200 °C. Thermal degradation of the cross-linked PPMA-based dental resin scraps started at around 200 °C, losing approximately 5.0% (wt) mass at 300 °C, 40.0% (wt) mass at 350 °C, 90.0% (wt) mass at 405 °C, 95.0% (wt) mass at 420 °C, and 100.0% (wt) mass at 420 °C, showing a thermal degradation behavior similar to that reported by *Braido* et al. [17] for the PPMA parings. Due to the fact that the experimental apparatus operates under air atmosphere, the pyrolysis temperature was set at 345 °C in order to minimize the energy consumption of LPG.

The experimental data show the liquid phase yield of 55.50% (wt), solid phase yield of 11.67% (wt) and gas yield of 31.69% (wt). The liquid phase yield is lower, but close to those reported by *Braido* et al. (66.30%) [17], who used the same raw material (cross-linked PPMA-based dental resins scraps) and an apparatus similar to that described in section 2.3.1 [17], smaller than those reported by *Kaminsky* (96.60%) [6], *Kaminsky* and *Frank* (92.13%) [7], *Kang* et al. (96.80 and 98.40%) [13], and *Popescu* et al. (90.0%) [34], and higher than those reported by *Kaminsky* et al. (24.825%) [8], *Kaminsky* and *Eger* (27.87-28.07%) [11], and *Grause* et al. (18.0-31.0%) [35], for the thermal degradation of filled PPMA and PPMA wastes [6–8, 11, 13–16, 17, 34, 35].

The cumulative mass of reaction liquid products shows the first-order kinetic behavior, that is, it grows exponentially with a root mean square error of 0.99, showing a maximum between 90-100 min. The exponential first-order-grow function validates the assumption of a first-order kinetics in accordance to the kinetic of PPMA depolymerization reaction reported by *Smolders* and *Baeyens* [12] and *Lopez* et al. [15].

The density of distillation fractions, measured at 30 °C, varied between 0.9227 and 0.9380 g/cm^3, with deviations between 0.74 and 2.36%, as compared to the density of pure MMA at 20 °C. The kinematic viscosity, measured at 40 °C, varied between 0.566 and 0.588 mm^2/s, with deviations between 7.40 and 10.86%, as compared to the kinematic viscosity of pure MMA at 20 °C. Finally, the refractive index, measured at 30 °C, varied between 1.401 and 1.414 [-], with deviations between 0.00 and 0.92%, as compared to the refractive index of pure MMA at 20 °C, showing that the pure MMA was obtained after distillation.

By analyzing the concentration profile of MMA in the liquid reaction products with reaction times, one observes that high concentrations of MMA are obtained at the beginning of monomer vapors condensation at around 30 min, decreasing with the reaction time in a smooth fashion up to 80 min, whereas a drastic decrease in the concentration of MMA occurs between 80 and 110 min referring to the fact that the reaction time should not exceed 80-90 min. The concentration profile of methyl iso-butyrate, a side reaction product, as a function of reaction time by pyrolysis of the cross-linked PPMA-based dental resins scraps at 345 °C, 1.0 atmosphere, 30, 40, 50, 60, 70, 80, and 110 min, increases with the reaction time in a sigmoid fashion, reaching around 3.75% (Area) at 110 min.

Disclosure statement

No potential conflict of interest was reported by the authors.

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