

DETERMINATION OF DEGREE OF POLYMERIZATION BY LOW COST PHOTOMETRIC SYSTEM: APPLICATION OF UV LED AND PHOTODIODE

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Abstract: In function of the growth of application in which photopolymerization processes are concerned, as such UV print and rapid prototyping, techniques and equipments which collaborate to controlling, monitoring and characterizing the process are needed to be improved. In addition to that, it is highlighted the importance of identification of polymerization rate and conversion curve, whereas these provide the main responses for process control. Therefore, the main goal of this work is the evaluation of a measurement system dedicated to polymer conversion and which is compound by UV LED and photodiode. The material used in this study is methyl methacrylate which is initiated by 4% in wt of 2,2-Dimethoxy-2-phenylacetophenone, and for determining its degree of polymerization, it was used analytical, gravimetric methods in addition to photometric, which is the system proposed in this work. It was also compared the advantages and disadvantages of each of methods, as well verified accuracy of these. In conclusion, it was verified the feasibility of system, identifying that the difference between the results of both experimental methods in the initial stages of polymerization were in the tolerance of gravimetric method.

Key words: Photopolymerization, Photometry, Photodiode

1. INTRODUCTION

The photopolymerization is a process whose sort of application is tremendously growing around the world. Among these application, there are coating, inks, orthodontics application and additive manufacturing, which is also known as rapid prototyping (JASTY, 1999; ODIAN, 2004; VOLPATO, 2007; CUNICO, 2011).

One of the ways for characterizing this process is the determination of polymerization rate (R_p), consisting on analysis of variation of polymerized material as a function of time, as described in Eq. (1). Additionally, the photopolymerization has got a particular behaviour, being induced by light factors, as such light intensity. Therefore, Eq. (2) shows the relationship among the parameters that effect photopolymerization rate. Where k_p is constant of propagation, k_t is constant of termination, $[M]$ is molar concentration of monomer, $[A]$ is molar concentration of initiator, D is the height of layer, α is coefficient of absorption, I_o is luminous intensity, and ϕ is efficiency of absorption. In the case of non-punctual light source, ϕ is considered 1, while for a punctual light source as laser, it is considered 2 (MUKHERJEE, 1978; COYLE, 1986; MEZAKI e MA, 1997; MATYJASZEWSKI e DAVIS, 2002; RODRIGUES e NEUMANN, 2003; ODIAN, 2004).

$$R_p = \frac{-d[M]}{dt} \quad (1)$$

$$R_p = \frac{k_p}{\sqrt{k_t}} \cdot [M] \cdot \left(I_o \cdot \alpha \cdot \phi \cdot [A] \cdot e^{-\alpha[A]D} \right)^{1/2} \quad (2)$$

Among the techniques of measuring the polymerization rate, there are photometry, which is a method based on analysis of luminous intensity through material. This method is consistent whereas the photopolymerization rate is directly dependent on luminous intensity and absorption of initiator. Additionally, this technique has got purpose of monitoring the luminous intensity during the polymerization, being possible to determine conversion curve of material (MUKHERJEE, 1978; MATYJASZEWSKI e DAVIS, 2002; JUNIOR *et al.*, 2003; LEE *et al.*, 2003; MIYASAKA *et al.*, 2003; RODRIGUES e NEUMANN, 2003; ODIAN, 2004; SPERLING, 2006).

The main goal of this work is to determine and compare the conversion curve of photopolymeric material through three different methods, photometry, gravimetry and analytic. The photopolymeric material is compounded by methyl methacrylate initiated by 4% wt of 2,2-Dimethoxy-2-phenylacetophenone, while the photometric measurement system by UV LED and photodiode.

2. Material and Methods

2.1. Determination of conversion curve

In order to identify the relationship between luminous intensity and polymerization rate, it was initially determined the coefficient of absorption, which is an inherent property of initiator. This coefficient is a variable that is constant for a single light source, varying in accordance with absorbance of initiator, as show in Equation (3). This situation is possible as that absorbance varies as function of light wave length besides a light source has a fix range of light wave length, as shown in Figure 1. In other words, for each wave length, it is going to be attained a value of absorption (MUKHERJEE, 1978).

$$absorbance = 2.3 \cdot A \cdot \alpha \quad (3)$$

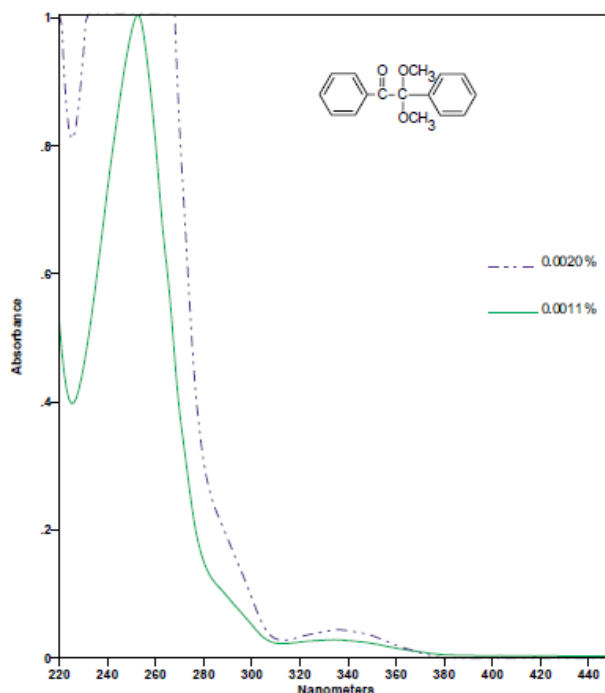


Figure 1 - Absorbance curve of initiator 2,2-Dimethoxy-2-phenylacetophenone (JASTY, 1999)

As consequence, applying Beer-Lambert Law, it is possible to identify the value of concentration of initiator through the difference of luminous intensity, as presented in Eq. (4) (MUKHERJEE, 1978; COYLE, 1986; MEZAKI e MA, 1997; MATYJASZEWSKI e DAVIS, 2002; RODRIGUES e NEUMANN, 2003; ODIAN, 2004).

$$A = -\frac{\log\left(\frac{I_i}{I_o}\right)}{D \cdot \alpha} \quad (4)$$

On that way, regarding the extinction of initiator along the time, it is possible to determine the conversion of monomer in polymer, as it is generally shown in Eq. (5) (MILLER, 2005).

$$conversion(\%) = \left(1 - \frac{I_i}{I_o}\right) \cdot 100 \quad (5)$$

2.2. Determination of photometric measurement system

As the measurement of variation of luminous intensity is the principle of photometry for determining conversion curve, it was necessary to define data acquisition and sensor, as well as measurement error.

With respect to sensors, there are two classes which are suitable to be applied in measurement of luminous intensity: photoconductive sensors and photoconjunctionive sensors. However, the most commons for UV light are the photoconjunctionive, as such photodiodes and phototransistors. In Figure 2, two typical modes of operation of photodiodes

are presented: photovoltaic in letter ‘a’ and reverse bias in ‘b’ (BOUCHARLAT e TRAHAND, 1998; WEBSTER, 1999).

On the other hand, it is possible to use a mode similar of photovoltaic, which is known as conductive mode. In this case, it is used inverse polarization of diode, providing better linearity and time of response than photovoltaic. In spite of such advantages, as well less thermal interferences than photovoltaic, this mode also provides higher dark current and noise (BOUCHARLAT e TRAHAND, 1998; WEBSTER, 1999).

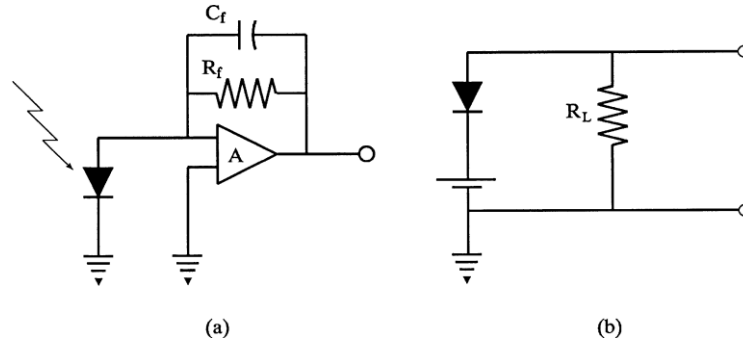


Figure 2 - Typical modes of operation of photodiodes: a) photovoltaic mode; b) reverse bias (BOUCHARLAT e TRAHAND, 1998; WEBSTER, 1999)

For this work, it was selected an integrated circuit (OPT101) that is compound by a photodiode and an operational amplifier. The mode of operation of this circuit is conductive, as it can be seen in Figure 3, where is also shown the curve of spectral response of integrated circuit. Through this figure, it is possible to identify a response between 0 and 0.1 V/ μ W for the studied range of light wave length, UVA (DATASHEET, 1994).

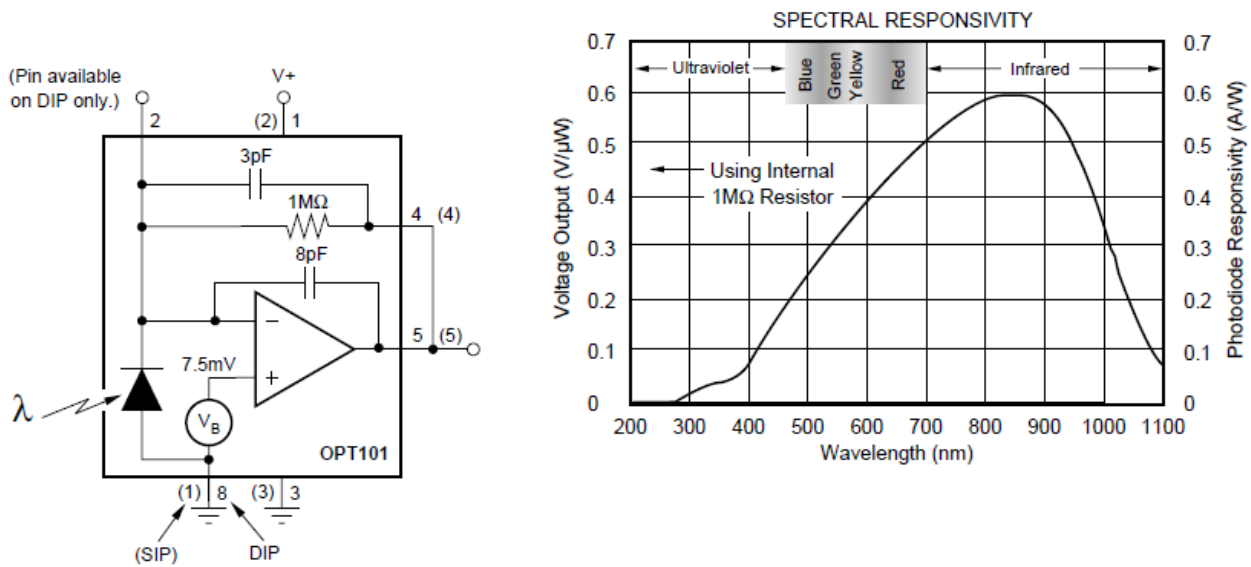


Figure 3 – Scheme of electronic circuit and curve of spectral response of OPT101(DATASHEET, 1994)

The light source which was used is a 5 mm UV LED, providing light wave length of 400nm into an angle of 15°. The power of this LED is 0.12mW when feed in a maximum tension of 5V and current of 20mA. In addition to that, the spectral distribution as a function of light wave length can be seen in Figure 4 (DATASHEET, V. O., 2009).

With reference to data acquisition system, it was used an oscilloscope DS0201, which is supplied by Seeds Studio Works. The specification of this oscilloscope includes the maximum sample rate of 1MS/s, the resolution of 12 bits and memory of 4096 samples in a single channel. By the end, the horizontal resolution is 1 μ s/div, while the vertical sensibility 10mV/div (DATASHEET, S. S. W., 2009).

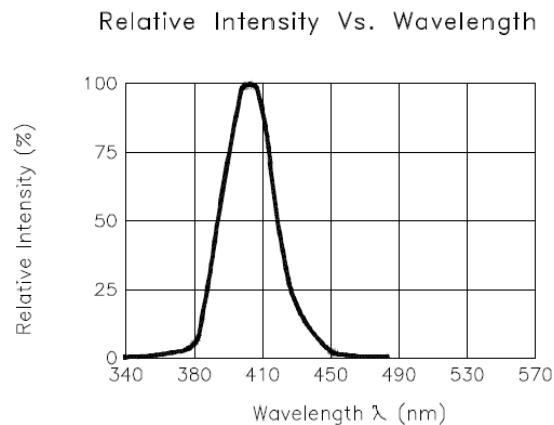


Figure 4 - Spectral distribution of UV LED (DATASHEET, V. O., 2009)

About the mould wherein was applied the material, it was made of glass with 99% of transparency and whose shape is presented in Figure 5. This figure also shows a simplified scheme of measurement system, where the frame was wood made, completely closed and black painted, in order to minimize any noise in photodetector.

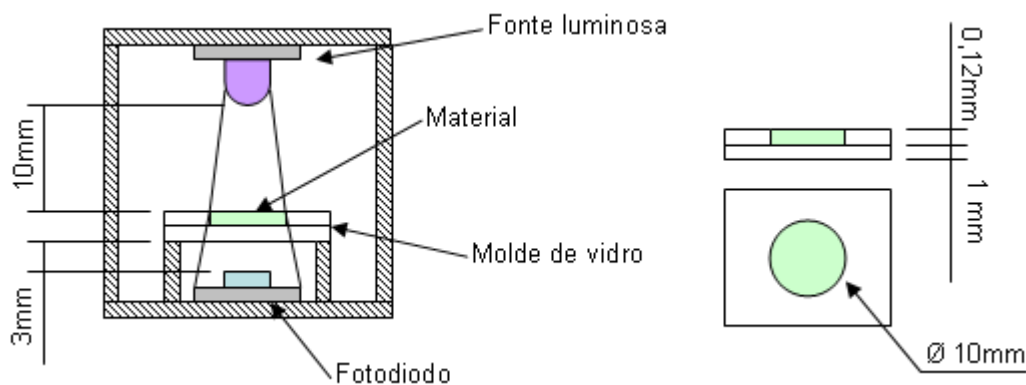


Figure 5 - Scheme of measurement system layout and shape of glass mould

2.3. Gravimetry

Another method for determining polymerization rate is Gravimetry, which consist in the analysis of mass of solution along the polymerization. The technique involves precipitating of the polymerized material by addition of a non-solvent, following by drying and weighting. In other words, the polymer is precipitated by non-solvent while the monomer is dissolved. After precipitation, the solution is filtered and dried while the polymer is retained by filter (RODRIGUES e NEUMANN, 2003; ODIAN, 2004; SPERLING, 2006).

In that study, the measurement of converted material was made by a digital balance which provided accuracy of 0.01g. As consequence of that, it was possible to identify a variation of 8.5% of conversion.

2.4. Experimental part

With purpose of calibrate the system, it was analytically selected a formulation of material which allow us to determinate the conversion curve by gravimetry. This formulation, which is compounded by 96% in wt of methyl methacrylate and 4% of 2,2-Dimethoxy-2-phenylacetophenone, provide a conversion of 80% of monomer in polymer in 70 seconds. Other values concerned in polymerization process and that were used in analytical determination can be seen in Table 1.

For the determination of conversion curve by gravimetry, it was measured 15 samples of material which were divided in 5 intervals of 10 seconds. The non-solvent that was applied for this procedure was isopropyl alcohol, while the time for drying the solution after filtering was 3 hours. In conclusion, the samples were weighted, allowing to identify the curve of conversion of material.

Table 1 - Values of constants of study

Constants	Values
*Kp/Kt ^{0.5}	7,14
M(wt %)	96
M (mol/l)	9,38873352
A(wt %)	4
A(mol/l)	0,146703082
D (cm)	0,012

Finally, it was compared all of three methods of determination of conversion, verifying divergences of results.

3. Results and discussions

Initially, it was analytically determined the curve of conversion in order to include the possibility of used gravimetric method. The results of conversion of monomer in polymer [P] and the extinction of monomer [M] can be seen in Figure 6. In this case, the monomer was 80% polymerized in 70 seconds.

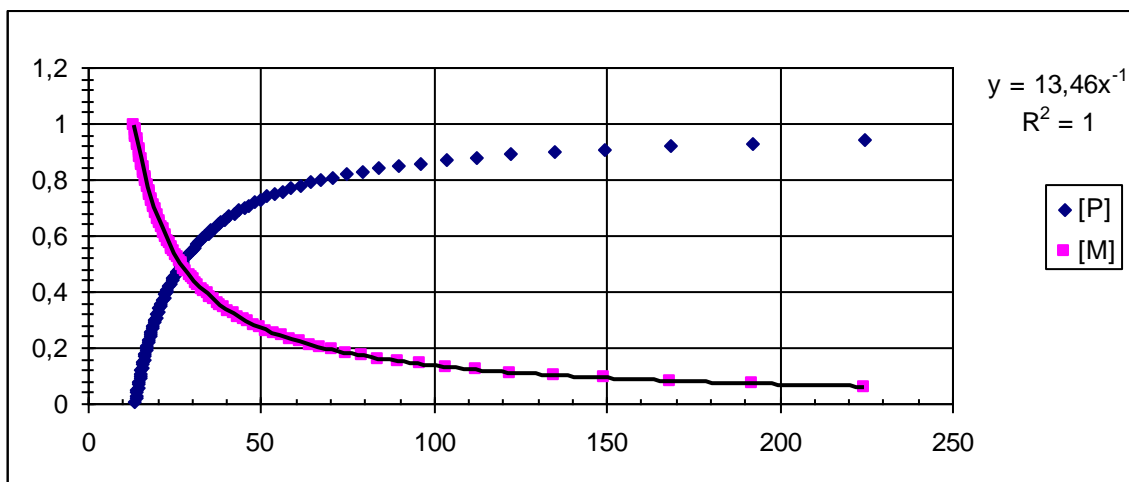


Figure 6 - Conversion curve determined by analytical method

On the other hand, the results of gravimetry were shown in Table 2, where “weight 0” represents the initial weight and “weight 1” the weight after precipitation, filtering and drying. In that, it was also possible to identify the conversion of polymer and equivalent extinction of monomer.

Table 2 - Relation of gravimetric results

tare	weight 0	weight 1	time	P (%)	M (%)
38,14	38,27	38,19	10	38,46%	61,54%
38,02	38,14	38,08	20	50,00%	50,00%
38,02	38,12	38,08	30	60,00%	40,00%
38,03	38,13	38,1	40	70,00%	30,00%
38,02	38,11	38,09	50	77,78%	22,22%

In Figure 7, it is allowed to see a divergence between the values of conversion during the begin of polymerization, even though the values converged along the polymerization. This difference might be related to process of filtering and drying of gravimetric process, whereas the time of drying might not have been enough to evaporate the non-solvent and monomer. It would also explain the convergence of values in higher degrees of polymerization, where the amount of monomer was reduced, leading to a lower value of measurement error.

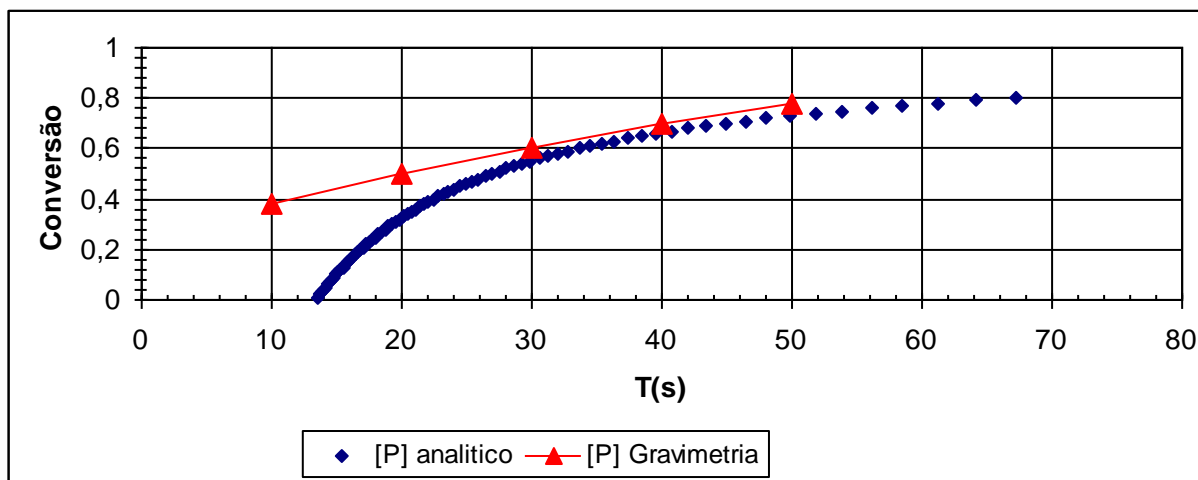


Figure 7 - Comparison of conversion curve of analytical and gravimetric methods

For determination of conversion curve through photometric method, it was monitoring the variation of tension in output of system along the time. This acquisition of values can be regarded in Figure 8, considering vertical resolution of 0.5V/div and 10s/div. The total variation of tension that could be found is 0.5V (3.8 to 3.8V), being the stabilization of signal found at 60 seconds. Being an exponential curve, this sort of behaviour is a typical characteristic of photopolymerization systems.

As consequence of that, defining a scale directly related to extinction of monomer in accordance with gravimetric calibration, we have been able to find extreme values of polymerization degree, as such 0 V to 0% and 0.5V to 80%. Therefore, it was possible to determine the curve of conversion by photometry method.

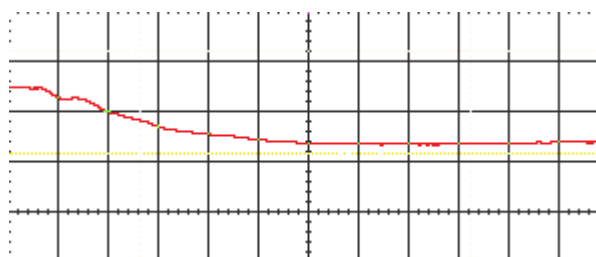


Figure 8 - monitoring of tension of photometric measurement system

In Figure 9, it is shown the curve of conversion obtained by photometry, as well it is possible to see a comparison of analytical, gravimetric and photometric methods.

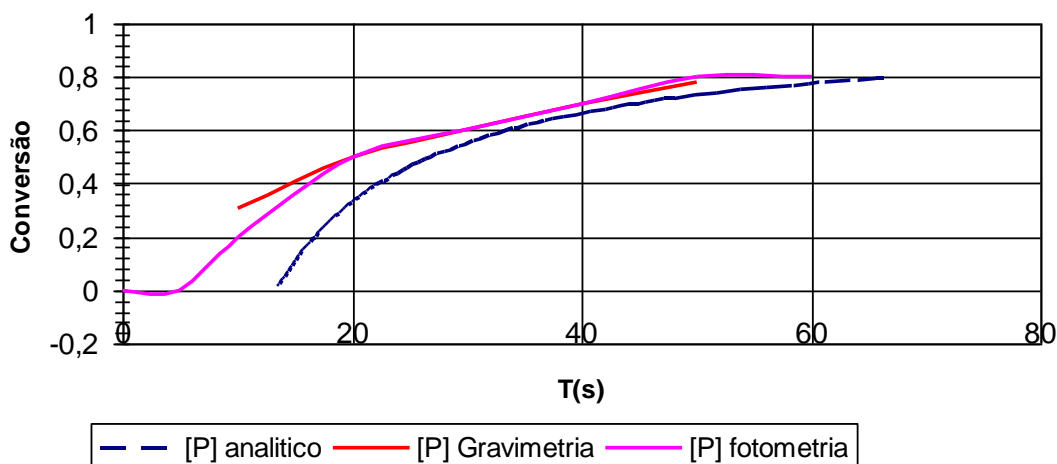


Figure 9- comparison of conversion curve of gravimetric, analytical and photometric methods

Despite the divergence of values in initial stage of polymerization, It was possible to see the convergence of this values along the polymerization. Other point to be highlighted is that although both of experimental methods obtained different values from analytical method, the difference between each other was into the range of error provided by

balance (8.5% of conversion). Therefore, the divergence between analytical and experimental methods might be explained by impurities of monomer, whereas it was not previously distilled.

Above all, it is important to be highlighted that the convergence of curves that were obtained experimentally validates the system of photometry for the proposed application. In addition to that, it can be seen that the total time of photometric procedures took about 60 seconds in contrast with gravimetric, which took about 4 hours to be concluded. That emphasizes the agility and capability of photometric system.

4. Conclusion

In this work, it was possible to determinate a low cost measurement system for process of photopolymerization which was compounded by photodiode and UV LED. Additionally, this system was calibrated through two particular methods of determination of conversion curve, analytical and gravimetric methods.

It was also possible to identify divergences between analytical and experimental methods at the initial stages of polymerization in function of impurities of monomer. On the other hand, the divergence between photometric and gravimetric methods at the initial stages of polymerization was found acceptable, as the difference between these values remain into error margin.

With reference to the advantages of photometric method, it was important to highlight the short period of time spent on this procedures, as well as the higher volume of samples per second. It can be clearly seen when the difference of time between both of experimental methods is analyzed, being 60 seconds of photometry against 4 hours of gravimetry. Another situation that was also regarded is the number of samples per second for generating the conversion curve, in the case of this study, gravimetric method considered a curve with 5 point while photometric, 4096.

In conclusion, this work allows us to identify the possibility of applying this sort of low cost measurement system for determination of photopolymerization rate.

5. References

BOUCHARLAT, G. e J. TRAHAND. Détecteurs ultraviolet, visible et proche infrarouge= Ultraviolet, visible and near-infrared sensors. **Techniques de l'ingénieur. Electronique**, v.6, n.E4065, p.E4065. 1998.

COYLE, J. D. **Introduction to Organic Photochemistry**: John Wiley & Sons Ltd. 1986. 190 p.

CUNICO, M. M. W. M. Development of New Rapid Prototyping Process. **Rapid Prototyping Journal**, v.17, n.2, p.6-6. 2011.

DATASHEET, S. S. W. DSO Nano Manual. 2009. Disponível em: <<http://www.seeedstudio.com/depot/images/product/dsomanual.pdf>>. Acesso em: 01 de dezembro de 2010.

DATASHEET, T. OPT-101 Monolithic Photodiode and Single-Supply Transimpedance Amplifier. **Online Document**. 1994.

DATASHEET, V. O. UV LED LAMP - VAOL-5EUV0T4. 2009. Disponível em: <<http://vcclite.com/wp-content/files/VAOL-5EUV0T4-LED-5mm-UV.pdf>>. Acesso em: 01 de dezembro de 2010.

JASTY, S. Aldrich Polymer Products Application and Reference Information. Sigma-Aldrich. 1999. Disponível em: <www.sigmaaldrich.com/aldrich/brochure/al_pp_applications.pdf>. Acesso em: 10 jul. 2008.

JUNIOR, A. P. D. C., V. D. P. P. D. CUNHA, *et al.* Modelo de Calibração da Concentração de Metilmetacrilato em Solução Aquosa Utilizando Espectroscopia de Absorção no Ultravioleta. **Química Nova**, v.26, n.6, p.4. 2003.

LEE, T. Y., T. M. ROPER, *et al.* The kinetics of vinyl acrylate photopolymerization. **Polymer**, v.44, p.7. 2003.

MATYJASZEWSKI, K. e T. P. DAVIS, Eds. **Handbook of Radical Polymerization**: John Wiley and Sons, Inc., Hoboken., p.935 ed. 2002.

MEZAKI, R. e G.-H. MA. **Rate Equations of Polymerization Reactions**: ChemTec Publishing. 1997. 334 p.

MILLER, C. Perspectives in Chemistry: Searching for the Cure. RADTECH. 2005. Disponível em: <http://radtech.org/members/member_documents/Perspectives%20in%20Chemistry%20-%20Searching%20for%20the%20Cure.pdf>. Acesso em: 01 de dezembro de 2010.

MIYASAKA, H., S. R. KHAN, *et al.* Photoinduced electron transfer dynamics in aromatic vinyl polymers and related systems: time-resolved detection of primary events. **Journal of Photochemistry and Photobiology C: Photochemistry Reviews**, v.4, p.20. 2003.

MUKHERJEE, K. K. R. **Fundamentals of photochemistry** Wiley. 1978. 347 p.

ODIAN, G. **Principles of Polymerization**: John Wiley & Sons, Inc. 2004. 840 p.

RODRIGUES, M. R. e G. M. NEUMANN. Fotopolimerização: Princípios e Métodos. . **Polímeros: Ciência e Tecnologia**, v.13, p.10. 2003.

SPERLING, L. H. **Introduction to Physical Polymer Science**: John Wiley & Sons, Inc. 2006. 866 p.

VOLPATO, N., Ed. **Prototipagem rápida: tecnologias e aplicações**: Edgard Blücher ed. 2007.

WEBSTER, J. **The measurement, instrumentation, and sensors handbook**: Springer. 1999