23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

RHEOLOGICAL CHARACTERIZATION OF POLYMER BLENDS FOR MANUFACTURING OF DENTAL PROSTHESES

Daniel Osorio
Andrey Pérez
Mechanical Engineering Department
Universidad Nacional De Colombia Sede Medellín-Calle 59A No 63 - 20
dfosoriom@unal.edu.co
andfperezbri@unal.edu.co

Sandra Gaviria
New Stetic S.A- Cra 53 N° 50-09 (Guarne – Antioquia)
smgaviri@newstetic.com

Diana López
Mechanical Engineering Department
Tribology and Surfaces Group
Universidad Nacional De Colombia Sede Medellín-Calle 59A No 63 - 20
dmlopez3@unal.edu.co

Abstract. *In this study the rheological response of a polymer blend composed by polymethyl methacrylate- (PMMA) and monomer (MMA) used for manufacturing dental prosthesis was analyzed trying to simulate different processing conditions. Preliminary test were performed using the technique of concentric cylinders in a conventional viscometer with the aim of determining the effect of shear stress on the viscosity. After that, two types of oscillatory tests were performed using rotational rheometer with cooling / heating ETC System, fed by liquid nitrogen for temperature control. The first kind of oscillatory test (one stage) was carried out at 25ºC and -6ºC, trying to simulate the behavior of the blend under the mixing and storage stage. The second kind of oscillatory test (multistage) was developed following a sequence of temperatures: 20ºC,-10ºC,-4 ºC and 25ºC, trying to simulate the thermal path during the manufacture of the prostheses. It was found that changes in the viscosity and shear stress are functions of time of polymerization, and that the storage G'(ω) and loss modulus, G''(ω) can be good properties to characterize the different polymerization stages that passes the polymer blend during a production process of dental prostheses.*

Keywords: *Rheology, PMMA, polymer blends, dental prostheses.*

1. INTRODUCTION

Despite advances in oral health conducted in the last half century, there is still much work to do (NIH, 2000). The research about technological developments for the oral health industry focused to polymers blends for the manufacture of dental prostheses is still very limited to the traditional knowledge; just few reports are found about this topic in the technical literature, and some of them are very old. This landscape offers an opportunity for dental manufacturing industries, considering that the estimated investment for the dental industry inside the health budget of nations is not negligible (Christensen and Yancey, 2005). Authors as Kolmeder and Lion (2013) have carried out rheological characterization of PMMA cements, using configurations as concentric cylinders, cone-plate or parallel plates, however in those cases the polymerization reaction is very different from PMMA-MMA suggests that measuring rheological properties of highly viscous fluids is difficult and there are potential sources of error due to the fact that the tip of the cone is missing probably leads to lower shear rates in the middle of the configuration.

The manufacturing industry of dental prostheses from polymer blends requires a characterization that allows defining parameters to standardize processes and ensuring the quality and reliability of the production (Strassburger *et al*., 2006); thereby this paper aims to present a rheological characterization of a mixture PMMA – MMA that simulates some processing stages during the conformation of the prosthesis. For this purpose the procedure includes tests using concentric cylinders trying to assess the dependence of viscosity with the flow rate, temperature, and shear rate over time, and oscillatory parallel plate tests for evaluating the complex viscosity and parameters as storage G'(ω) and loss modulus, G''(ω), which are related to the shear stress by the Eq. (1), (Mezger, 2006)**:**

$$\sigma = G'\gamma_o \sin(\omega t) + G''\gamma_o \cos(\omega t) \quad (1)$$

Equation (1) has the advantage of having physical sense. Thereby the storage modulus G'(ω) is related to the response of σ in phase with γ and therefore this represents the part of the energy that is stored and can be retrieved. That is, it is a measure of elasticity. On the other hand, the loss modulus G''(ω) indicates the portion of σ out of phase in π / 2 radians with respect to γ and it is related to the dissipated energy. It is therefore a measure of the viscous nature of the material. In addition, the loss factor (or damping factor) it is given by the Eq. (2), this factor represents the ratio between the viscous and the elastic portion of the viscoelastic deformation behavior.

$$tan\,\delta = G''/G' \tag{2}$$

Ideal elastic behavior can be specified with δ=0, since G´ completely dominates G´´. On the contrary, ideal viscous behavior is characterized with δ=90, since G´´ completely dominates G´. Finally, the complex viscosity η∗ (Pa*s) is given by the Eq. (3), this viscosity represents the response of a sample under oscillatory shear stresses.

$$\eta^* = \tau(t)/\dot{\gamma}(t) \tag{3}$$

2. METHODOLOGY

2.1 Viscometry

The effect of shear stresses on the viscosity was analyzed using a rotational rheometry, using the technique of concentric cylinders in a conventional viscometer Brookfield LVDV-II+Pro, with TC-650 bath temperature control connected to a heating/cooling jacket SC4-8R(P). Samples composed by polymethyl methacrylate PMMA (powder) and monomer MMA (liquid) were prepared. The mixing was performed manually by means of crossed movements to obtain a homogeneous mixture. Two kinds of tests were performed; the first one at 5 °C and using a shear rate sweep from 0.5 to 4 s^{-1}, the second kind of test was carried out at -6°C and -10°C and constant shear rate of 0.05 s^{-1}.

2.2 Oscillatory tests

The oscillatory tests were performed in a rotational rheometer Bohlin C-VOR Instruments 200 with cooling / heating ETC fed by liquid nitrogen for temperature control (Fig. 1), using a parallel plate geometry with titanium plates of two different diameters: 15 mm and 25 mm. Samples composed by polymethyl methacrylate PMMA (powder) and monomer MMA (liquid) were obtained mixing with a propeller stirrer at a constant speed of 20 RPM. Two types of oscillatory tests were performed to study the behavior of the mixture: tests in a particular temperature of -6°C and 25°C during a period of approximately 4000 seconds (one stage), and continuous tests simulating the mixing process temperatures (multistage). The sequence for the multistage tests was: 1) Preparation: simulation conditions during preparation at 20°C, 2). Storage: post-mixing in which the storage of the polymer blend is made (sub-zero temperatures near -10°C and -4°C). 3) Extraction: final stage, in which the mixture is removed for molding at 25°C. The frequency and strain were kept constant for both types of tests (1Hz and 1% respectively). The storage G'(ω), loss modulus, G''(ω), the loss factor tanδ and complex viscosity η^* were analyzed in order to characterize the different polymerization stages that passes the polymer blend during a production process of dental prostheses.

Figure 1. Rotational rheometer Bohlin C-VOR with cooling / heating ETC fed by liquid nitrogen for temperature control

3. RESULTS AND DISCUSSION

Figure 2 shows the viscosity behavior as a function of the shear rate at 5°C. In this curve a shear-thinning behavior of the mixture is observed, this implies that the viscosity decreases with increasing the shear rate. It is important to point out that this behavior arises from the end of the mixing process to the beginning of the polymerization (Mezger, 2006). This result is consistent with the results found by other researchers of dental resins such as Mutlu *et al* ., (1990).

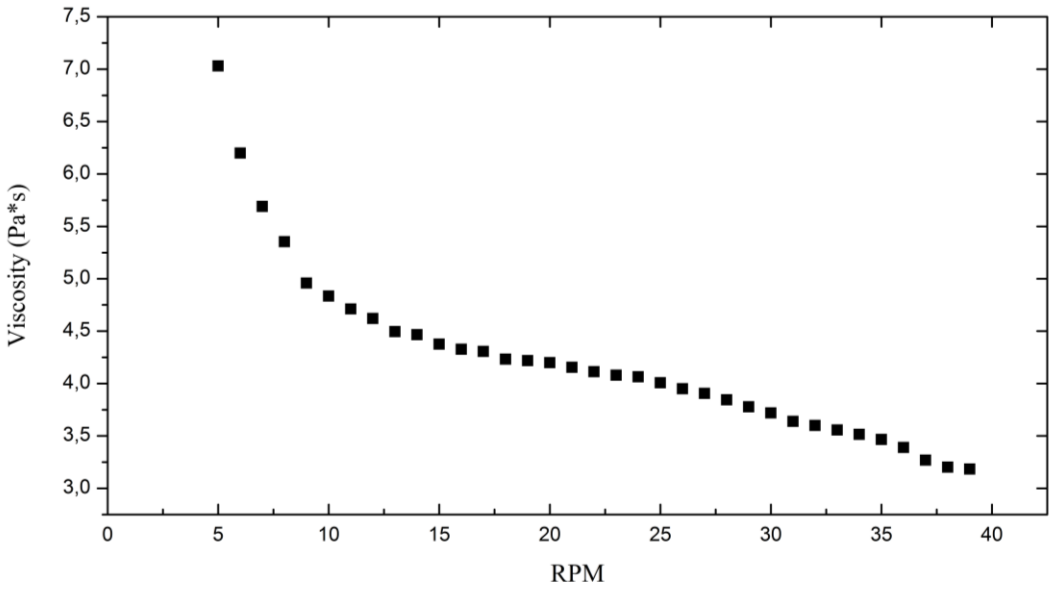

Figure 2. Effect of the shear rate on viscosity at 5 °C and shear rate sweep from 0.5 to 4 s^{-1}

Figure 3 shows the effect of time on the viscosity behavior of the sample at two different temperatures (-6 and -10°C) and constant shear rate (0.05 s^{-1}). The results show an exponential growth of the viscosity over time. When polymerization starts, there is an apparent rheopectic behavior, since viscosity increases over time irreversibly (Maestro, 2003). Likewise, it is shown the strong effect of temperature on the polymerization time; when the temperature decreases in only 4°C, the polymerization reaction is meaningfully delayed, this is observed in the final viscosity value at each temperature: 263.94 Pa*.s at -6°C and 98.37 Pa*s at -6°C. This is an important result for this research because it supports the selection of parameters for the storage and handling of such mixtures.

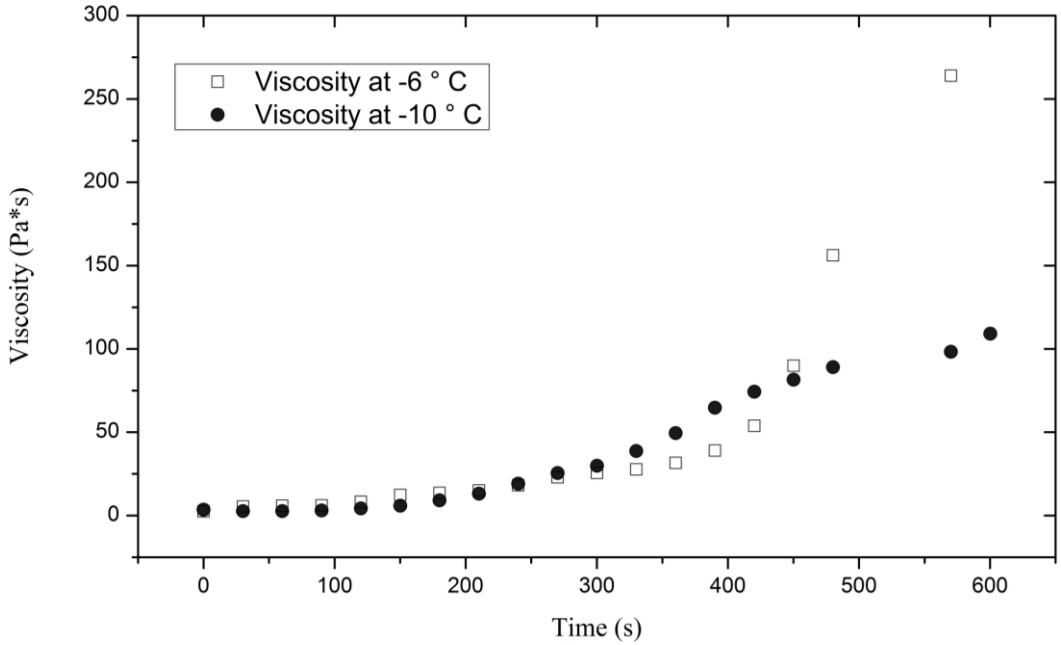

Figure 3. Diagram of viscosity versus time at -6 and -10°C. Shear rate: 0.05 s^{-1}

In Figure 4 the simulation of the mixing stage is presented. The figure shows the curves for the storage modulus G ', the loss modulus G ", the complex viscosity and the tangent δ, obtained at 25°C, 1 Hz, strain of 0.01 and temperature control with nitrogen. At the beginning of hardening or curing of the polymer, G ', G " and η* show minimal values while δ shows a maximum value. This point corresponds to a time of approximately 102 s, which marks the beginning of the stringy stage. Then the values of G', G" and η* begin to increase and tanδ decrease by the polymerization reaction and hardening. It is observed that G' remains above G", indicating that the elastic response is who imposes the behavior of the sample (Mezger, 2010). This is observed up to 660 s when these curves have an intercept, which can be associated with the end of the stringy response of the sample and the beginning of the plastic stage. Tab. 1 lists the stages of polymerization and their range of estimated times for the studied mixture reported from the experience and the qualitative appreciation of technicians that shapes the pieces. The time obtained by this intercept of the curves is in agreement with the times reported by technicians. The same is observed with a new intercept around 1610 s, which marks the end of the plastic stage and the start of the final hardening stage.

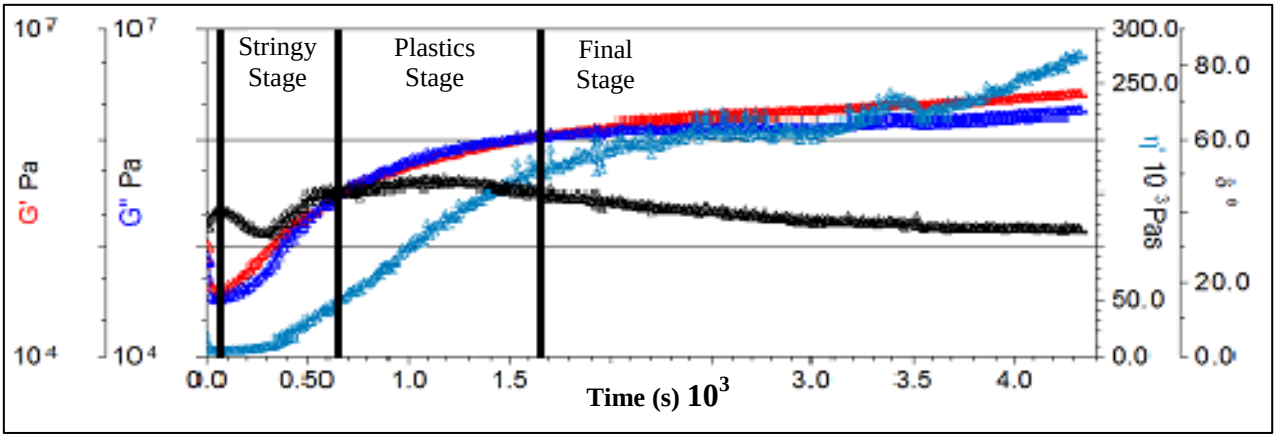

Figure 4. Oscillatory test simulating the post stage mixing stage, frequency of 1Hz, 1% strain, a temperature of 25 ° C during 4330s

Table 1.Stages and times that passes the mixture until the final stage of polymerization (obtained from experience).

Stage	Time (min)
Stringy	6 – 13
Plastics	19 – 34
Final	25 - 48

Figure 5 shows the curves obtained for the mixture at a temperature of -6°C, this figure shows the simulation of the post-mixed storage stage. In these curves, the complex viscosity, G 'and G“ have a maximum at the beginning and after that, they achieve a more stable behavior, which allows to deduce that the polymerization slows down. Comparing the values of complex viscosity in Fig. 4 and Fig. 5, it is noted that while at 25°C there is a continuous change by two orders of magnitude (from 10^3 to 10^5 Pa * s), at -6 ° C, a relatively stable viscosity for about $7x10^3$ Pa*s remains nearly for an hour of test. Similarly, Fig. 5 shows that G ' remains above G" during the complete test, indicating that the material tends to behave as a semi-solid one showing again the elastic behavior.

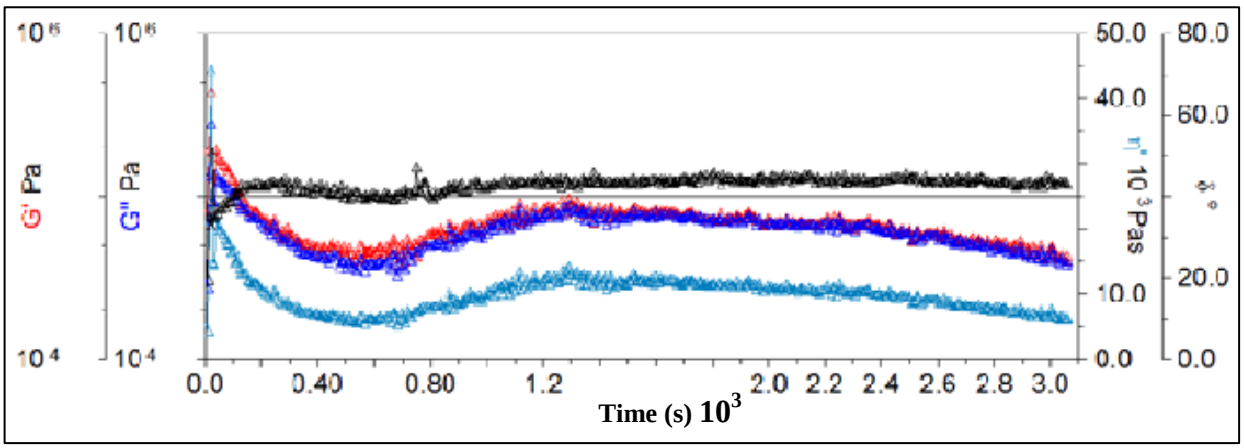

Figure 5. Oscillatory test simulating the post stage mixing stage, frequency of 1Hz, 1% strain, a temperature of -6 ° C during 4330s

Figure 6 shows the curves obtained for a simulation of the whole process until the pre-molding stage. The first stage is between 0 and 2500 s at 25°C, this phase shows again that G ' remains above G'', indicating that the material tends to behave as a semi-solid one, the second stage is between 2500s and 3500s at -10°C, this phase shows a constant behavior, and the same goes for times between 3500s and 4800s at -4°C, this indicates that the sub-zero temperatures delay the curing time and make the polymer blend retain their properties for longer time. In the final stage of the curve, the temperature is increased, showing a similar behavior that the start of the test, which means that the semi-solid behavior is recovered even having crossed a low temperature zone in the earlier stages.

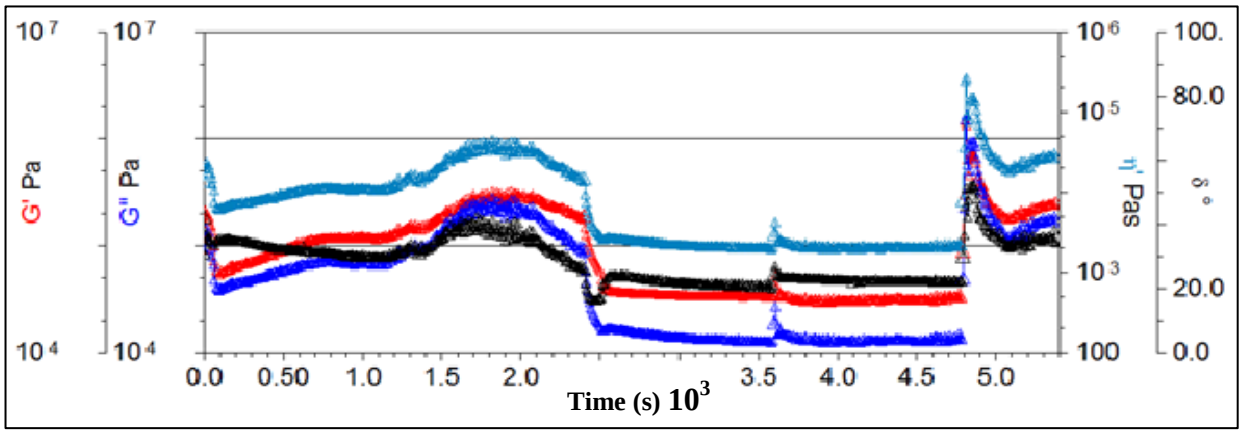

Figure 6. oscillatory test simulating the process until the pre-molding, frequency of 1Hz, 1% to sequence deformation temperature of 20 °C, -10°C, -4 °C and 25 ° C

4. CONCLUSIONS

The polymer blend has a shear-thinning behavior when subjected to low shear rates, this occurs from the end of the mixing process until the start of polymerization.

Experimentally it was found that the behavior of viscosity over time is exponential; this is due to the response of the mixture that undergoes polymerization, also a rheopectic behavior is confirmed, since viscosity increases over time irreversibly.

The storage G'(ω) and loss modulus, G''(ω) characterize the behavior of the polymer blend at different stages, it was found that the semi-solid behavior predominates, and this is maintained even after passing through by low temperatures at earlier stages.

It is evident that the temperature has a direct influence on the values of apparent and complex viscosity, delaying the polymerization process at low values.

The reaction times for different stages of processing obtained through the rheological characterization were confirmed by the times previously considered by the technicians, indicating that the developed experimental procedure can be used as a tool for simulation of transformations in the samples during the shaping process.

This research could be expanded for future work in analyzing the effect of different pigments used for dentures coloring. Modify the storage times of the precursors is also a field to explore.

5. REFERENCES

Christensen, G.J. and Yancey, W., 2005 "Dental laboratory technology in crisis: the challenges facing the industry". *JADA*, Vol. 136, p. 783-786.

Kolmeder, S., and A. Lion., 2013 "Characterisation and modelling rheological properties of acrylic bone cement during application". *Mechanics Research Communications*, Vol. 48, p. 93-99.

Maestro Garriga, A.,2003. *Reología de espesantes celulósicos para pinturas al agua: Modelización y mecanismo de espesamiento*. Ph.D. thesis, University of Barcelona, Barcelona.

Mezger, Thomas G., 2006. *The Rheology Handbook*,. Vincentz Network, Hannover, 2nd edition.

Mutlu, G., Huggett, R., Harrison, A., Goodwin, J. W. and Hughes R. W., 1994 "Factors that affect the rheologic properties of acrylic resin denture base materials". *The journal of prosthetic dentistry*, Vol. 71(2), p. 91-108.

NIH, 2000. "La Salud Oral en los Estados Unidos: Informe del Cirujano General-- Resumen Ejecutivo" National Institute of Dental and Craniofacial Research. 21 june. 2015 <http://www.nidcr.nih.gov/DataStatistics/SurgeonGeneral/Report/ExecSummSpanish.htm>

Strassburger, C., Kerschbaum, T., Heydecke G., 2006 "Influence of implant and conventional prostheses on satisfaction and quality of life: A literature review. Part 2: Qualitative analysis and evaluation of the studies". *The international Journal of Prosthodontics*, Vol. 19, p. 783-786.

6. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.