

EFFECT OF THE REACTION CONDITIONS OVER THE YIELD AND PROPERTIES OF METHYLCELLULOSE OBTAINED FROM PINUS RADIATA KRAFT BLEACHED CELLULOSE

C. TAPIA^{1*}, J. SAPAG-HAGAR¹, C.T. ANDRADE²,
J. HASSÓN¹, F. VALENZUELA¹, C. BASUALTO¹

¹Laboratorio de Operaciones Unitarias, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago1, Chile

²Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525. 21945-970 Rio de Janeiro, RJ, Brazil

RESUMEN

Celulosa blanqueada kraft proveniente de *Pinus radiata* fue sometida a reacciones de metilación en medio heterogéneo. Después de la activación con solución de NaOH al 29% p/p, las reacciones de metilación se realizaron tanto con sulfato de dimetilo (SDM) como con yoduro de metilo (YM). Fueron estudiados el efecto de la razón de prensado, tiempo de reacción y tipo de agente metilante. Los mejores rendimientos se obtuvieron con sulfato de dimetilo y no se encontró un efecto significativo de la relación de prensado y tiempo de reacción sobre el rendimiento. La metilcelulosa (MC) de mayor grado de sustitución se extrajo con agua y la de menor grado de sustitución con hidróxido de sodio al 8%. Algunas de las MCs obtenidas fueron caracterizadas de acuerdo a su peso molecular viscosimétrico, comportamiento térmico, grado de sustitución y comportamiento de sus soluciones bajo condiciones de cizalla en estado estacionario. La MC extraída con agua y obtenida bajo ciertas condiciones de reacción mostró similar comportamiento que la MC comercial.

PALABRAS CLAVE: Metilcelulosa, Reacciones de Celulosa, Propiedades de Solución, Termogravimetría, Morfología.

ABSTRACT

Kraft bleached cellulose from *Pinus radiata* was submitted to methylation reactions in heterogeneous media. After activation with 29% (w/w) NaOH solution, methylation reactions were carried out both with dimethyl sulfate (DMS) and methyl iodide (MI). The effects of the pressing ratio, reaction time and type of methylation agent were studied. The better yields were obtained with dimethylsulphate and the pressing ratio and reaction time were not significant over the yield. Methylcellulose (MC) of high degree of substitution was extracted with water and the MC of low degree of substitution was extracted with 8%w/w NaOH. Some of the MCs obtained were characterized by viscosity average molecular weight, thermal behavior, degree of substitution, steady shear solution behavior. The MC water extracted obtained under certain reaction conditions showed similar behavior that commercial MC.

KEYWORDS: Methylcellulose, Cellulose reactions, Solution properties, Thermogravimetry, Morphology.

Author to whom correspondence should be sent: C. Tapia E-mail: ctapia@uchile.cl

INTRODUCTION

Cellulose is the most abundant polysaccharide, widely distributed in higher plants and to a lesser degree in other living organisms, such as algae, fungi and bacteria. Cellulose occurs naturally as highly ordered, insoluble microfibrils, as two distinct polymorphic forms, namely cellulose I and II. Cellulose I is the most commonly found polymorph and is characterized by the parallel arrangement of polymer chains (1,2).

Besides being a renewable resource, cellulose presents versatile chemical properties, which have attracted the attention of several research groups. Many of these studies have been devoted to the synthesis of hydrophobically modified products.

Cellulose ethers are widely used in the pharmaceutical and food industries as film coatings, stabilizing, thickening, binding and emulsifying agents. Their properties are determined by the substitution pattern and their molecular weight (3). The cellulose source and the type of physical and chemical treatments imparted to cellulose are important factors that influence the products properties. Due to the natural insolubility of cellulose in the majority of organic and inorganic solvents, heterogeneous processes are often used to carry out chemical modifications (4,5).

The traditional procedure for the obtainment of methylcellulose (MC) is based on the Williamson etherification reaction using alkyl halide, generally methylchloride, which react with alkaline cellulose (6). The technical problems associated with this procedure are: i) The difficulty to get a uniform substitution since the reaction is heterogeneous. ii) Low yield reaction because side reactions between water and etherification agent (7) Unfortunately the homogeneous procedure for the obtainment of MC from KBC showed low mass yield and low percentage of methoxylation, mainly by a low NaOH solubility in the solvent mixture DMAc/LiCl which produce a poor cellulose activation, compared with the heterogeneous procedure (8).

The studied procedure uses dimethylsulphate instead of the methylchloride used at industrial level by two important reasons: a) Chile has clear advantages for the production of dimethylsulphate since it is obtained from methanol and sulfuric acid, both produced plenty in the country; b) the reaction with dimethylsulphate is carried out at normal pressure and low temperature (30°C) which allows a suitable handling at the laboratory of such a dangerous reagent. By the other hand the reaction with methylchloride must be carried out under gaseous phase at high temperature and pressure which brings about a high risk for its achievement at the laboratory.

Since the initial molecular weight of the pinus cellulose used is low in comparison with that of cotton cellulose and considering that this molecular weight falls largely by the alkaline treatment used for the cellulose activation, it is known that the cellulose ethers obtained will be of low viscosity. These derivatives have important application as covering films. The purpose of this work was to evaluate the effect of the reaction conditions over the yield and properties of the MC obtained. For this the properties of the obtained product is compared with those of a commercial MC of low viscosity.

EXPERIMENTAL

Materials

The samples of kraft bleached cellulose (KBC) from *Pinus radiata* were supplied by Compañía Manufacturera de Papeles y Cartones (CMPC), Puente Alto, Chile. The KBC had the following composition according to the supplier: α -cellulose=86.2%, β -cellulose= 7.4%, γ -cellulose=6.4%. The sample was dried, milled in a hammer mill (Diaf A/S 21F), provided with a stainless steel screen of 1.6 mm diameter, and in a knife mill (Siemens MC-2310, model KM13). The milled sample was submitted to the ASTM-E11 method and the average particle size was determined as 335 μ m. A sample of methylcellulose (25 mPas) from Sigma (St. Louis, USA) was used as a standard. All other reagents were of commercial grade.

Methods

Preparation of alkal cellulose

KBC (15 g) was suspended in 300 ml of 29% (w/w) NaOH and stirred at 20°C for 1 h. The paste was centrifuged at different rates for different periods of time, depending on the pressing ratio required. The pressing ratio is given by the weight (g) of alkali cellulose divided by the KBC weight (g). The viscosimetric average molecular weight (M_v) of KBC was around 460,000 and the treatment with 29% w/w NaOH solution for 1 hour reduce the (M_v) to around 100,000 (9).

Methylation reaction

The alkal cellulose obtained was dispersed in 100 ml isopropyl alcohol in a glass reactor immersed in a thermoregulated bath at 30 ± 1°C. An excess of the methylation agent (9:1 mol of anhydrous glucose) was added slowly. Dimethyl sulphate (DMS) or methyl iodide (MI) were used as methylation agents. After a certain reaction period, the resulting product was filtered and washed three times with methyl alcohol, and suspended in hot water. Once the product was swelled and completely dispersed, cold water was added and the mixture was stirred for 30 min. This suspension was vacuum filtered or centrifuged at 18,000 rpm for 60 minutes, depending on the viscosity. The solution obtained was placed into a dialysis tubing and immersed in 900 ml water. Dialysis was carried out with stirring for 90 h. After dialysis, excess water was eliminated under vacuum at 65°C, and the final product was obtained as a film. This product was called methylcellulose (MC) water extracted. Fibers that were not dissolved in water were neutralized with NaOH solution and suspended in a 8 % NaOH solution. This suspension was submitted to at the same treatment describe above except that dialysis step was for 150 h. This product was called methylcellulose (MC) alkali extracted.

Determination of the degree of substitution

The method described by Hodges (10) was used to determine the degree of substitution. By this method, MC is reacted with hydrogen iodide and the resulting methyl iodide product is quantified by gas chromatography.

Capillary viscometry

Viscosity average molecular weights of MC were determined by capillary viscometry in water at 25°C, using the method described by Neely (11).

Preparation of solutions

Aqueous solutions of MC were prepared by stirring the samples in water, and filtering the solution through membranes of 1.2 µm pore diameter. The final polymer concentrations were determined as total solids dried at 90 - 100°C until constant weight.

Rheological measurements

A Contraves Low Shear 40 rheometer, fitted with concentric cylinders geometry (MS-DIN 412), was used to analyse MC solutions prepared approximately at 20 g/l under steady shear at 20°C. Steady shear measurements were carried out over the shear rate range of 10⁻¹ to 10² s⁻¹.

Thermogravimetric analysis (TGA)

MC samples were submitted to TGA using a Perkin Elmer 7 system.

Scanning electron microscopy (SEM)

Films were examined on a JEOL scanning electron microscope, model JSM-25-SII at 30 kV, after deposition of a thin film of gold.

RESULTS AND DISCUSSION

Figure 1 shows the effect of the pressing ratio used for the preparation of alkal cellulose using DMS as methylation agent and reaction time of 22 h. As it is shown, there was no significant difference in the MC yield obtained.

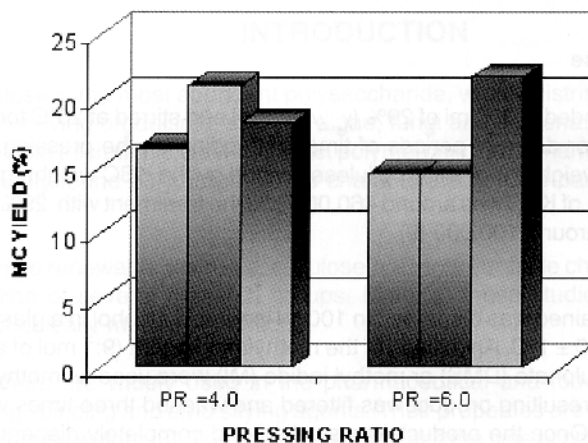


Fig. 1. Effect of pressing ratio over MC yield

The reaction time and speed of addition of etheryficant agent is related with the kinetics of main and lateral reactions (12). If it is assume that the order of main reaction, between alkalicellulose and etheryficant agent, is lower than the order of lateral reactions, between etheryficant agent and NaOH or water, then a slow rate of etheryficant addition and long reaction time would be recommended. Besides, at higher temperature the kinetics of principal and lateral reactions would be increased as well as the kinetics of alkalicellulose oxidative degradation. But, if the reaction is diffusion controlled, the effect of increasing the temperature over the yield product would not be very significant. The effect of the reaction time over the MC yield was evaluated (see Figure 2). There was not observed significant effect of the reaction time even if the reaction time was duplicated. Then the reaction could be diffusion controlled.

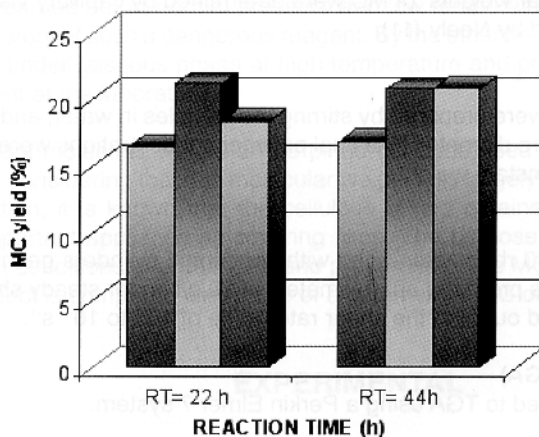


Fig. 2. Effect of reaction time over MC yield

High methylation agent/cellulose ratios are usually used in heterogenous reactions of cellulose. This is concerned with possible side reactions of the reagent with residual water from the alkalicellulose intermediate. DMS and MI were used as methylation reagents. When the methylation reaction were carried out with MI, at the same pressing ratio (4.0) and time of reaction (22 h), a small yield of MC was obtained (see Figure 3). This result may be attributed to the difficulty of mixing the reagent mixture due to the high density of methyl iodide.

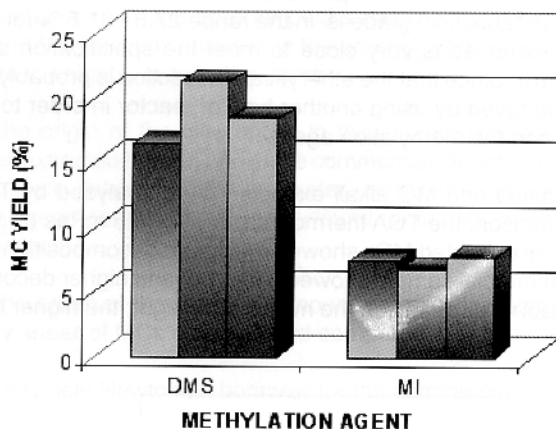


Fig. 3. Effect of methylation agent over MC yield

Greminger et al (13) pointed out that MC with low degree of substitution are soluble in strong alkalis (8% NaOH solution) and as the degree of substitution is increased MC become soluble in weaker alkali (2% NaOH solution) and then in water. Thus, high substituted MC would be extracted from the reaction mixture after swelling in hot water and dissolution in cold water, and low substituted MC would be extracted in 8% w/w NaOH solution. It is observed in Figure 4 that the MC yield obtained when the product is extracted with 8% w/w NaOH solution is approximately the double than that obtained when the product is extracted with water. That means that the main percentage of product obtained had lower substitution degree.

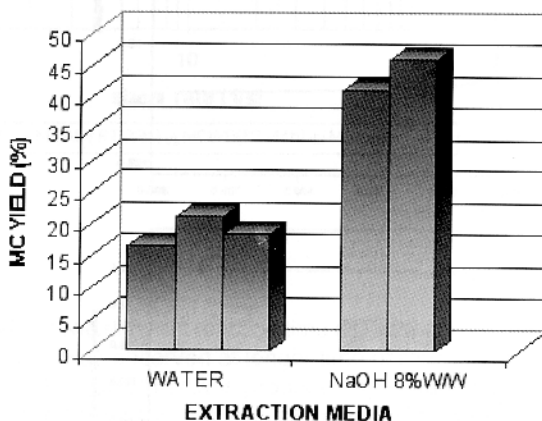


Fig. 4. Effect of the extraction media over MC yield

The degree of substitution (DS), expressed as percentage of methoxy groups, of MC water extracted was $27.2 \pm 0.2\%$ ($n=6$), significant higher compared to MC alkali extracted which was $22.3 \pm 0.1\%$ ($n=6$). The specification for MC pharmaceutical grade is in the range 27.5 - 31.5 % for all viscosity grades (14). Then the DS of MC water extracted is very close to meet the specification and the DS of MC alkali extracted was not too far from it. Since that the etheryfication reaction is probably diffusion controlled then the DS obtained could be improved by using another type of reactor in order to provide a better contact between the alkalicellulose and the methylation agent.

Both MC water extracted and MC alkali extracted were analyzed by TGA, and the results are shown in Figure 5. For comparison, the TGA thermogram of a MC 25 mPas (Sigma) commercial sample was included. Water and alkali extracted MCs showed maximum decomposition temperatures at 311 and 307°C, respectively. The commercial sample showed a sharper and higher decomposition temperature at 322°C. Cellulose thermal stability depends on the molecular weight; the higher the molecular weight, the

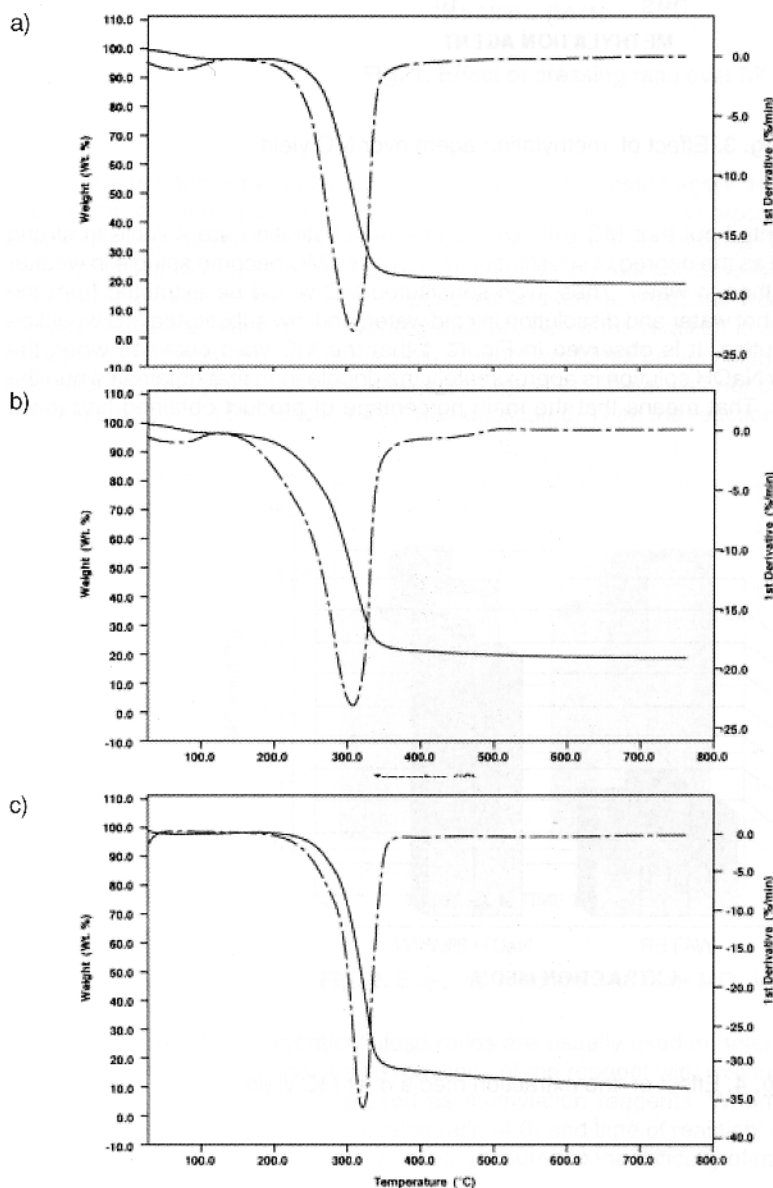


Fig. 5. TGA of a) MC water extracted, b) MC alkali extracted, and c) MC 25 cPs (Sigma) used as standard

higher the thermal stability (15). The beginning of the thermal degradation process was proposed to be accelerated by the presence of sample impurities (16). Compared to the thermal decomposition behavior showed by the commercial sample, the broader peaks and the lower temperatures determined for the water and alkali extracted MC fractions obtained in the present work may be attributed to some impurities or to their lower molecular weights, or to both factors.

To investigate the origin of the differences in thermal stability, the viscosity average molecular weights (M_v) of the water extracted fraction and of the commercial MC sample were determined. (M_v) values of 88,450 and 91,270 were determined for the water extracted and for the commercial MC sample, respectively. The lower decomposition temperature found for the MC water extracted may be attributed to the presence of impurities.

It was studied the effect of the reaction temperature and the extraction media over the solution properties under steady shear of MCs obtained and compared with commercial MC sample.

Figure 6 shows a typical Newtonian behavior for the commercial sample (MC25 mPas). The MCs

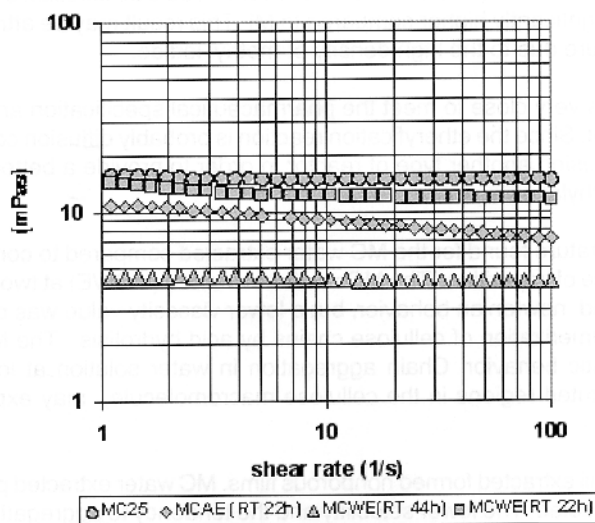
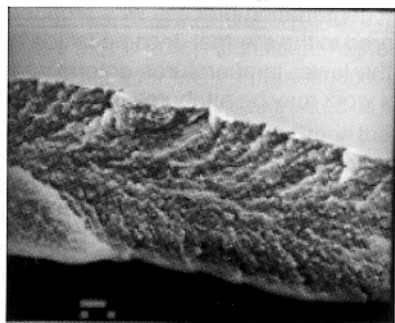


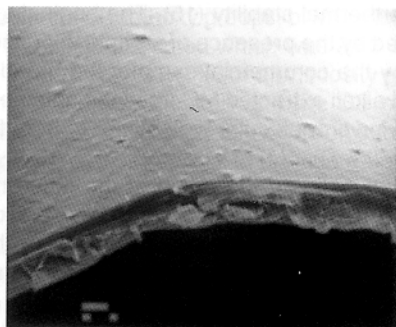
Fig. 6. Steady shear behavior of MC samples

water extracted (MCWE) at two different reaction time (RT =22 and 44 h) showed also newtonian behavior, but a lower viscosity value was observed at longer time of reaction due to depolymerization of cellulose chain by acid hydrolysis. This acid media is produced by sulfuric acid generated from a lateral reaction between DMS and water present in the alkalicellulose. The MC alkali extracted (MCAE) showed pseudoplastic behavior. Chain aggregation in water solution at low shear rates, probably resulting from unsubstituted regions in the cellulose macromolecule, may explain this effect.

The MC water extracted and MC alkali extracted were analyzed by SEM. The micrographs are shown in Figure 7. Both films are nonporous. The MC water extracted produced a thicker film. The lower solubility and the tendency to aggregation of the MC alkali extracted may explain the lower thickness of its film.



a) MC water extracted (scale bar = 10 μ m)



b) MC alkali extracted (scale bar = 10 μ m)

Fig. 7. SEM micrographs of a) MC water extracted and b) MC alkali extracted (scale bar = 10 μ m)

CONCLUSIONS

The effects of the pressing ratio, reaction time and type of methylation agent were studied. The effect of the pressing ratio was no significant on MC yield, also there was not observed significant effect of the reaction time even if the reaction time was duplicated. Then the reaction could be diffusion controlled. The MC yield obtained with DMS was significantly higher compared to MI. This result may be attributed to the difficulty of mixing the reaction mixture due to the high density of methyl iodide.

The DS of MC water extracted is very close to meet the pharmaceutical specification and that of MC alkali extracted was not too far from it. Since the etheryfication reaction is probably diffusion controlled, the DS obtained could be improved by using another type of reactor in order to provide a better contact between the alkalicellulose and the methylation agent.

The lower decomposition temperature found for the MC water extracted compared to commercial sample may be attributed to the presence of impurities. The MCs water extracted (MCWE) at two different reaction time (RT =22 and 44 h) showed newtonian behavior, but a lower viscosity value was observed at longer time of reaction due to depolymerization of cellulose chains by acid hydrolysis. The MC alkali extracted (MCAE) showed pseudoplastic behavior. Chain aggregation in water solution at low shear rates, probably resulting from unsubstituted regions in the cellulose macromolecule, may explain this effect.

Both MC water extracted and alkali extracted formed nonporous films. MC water extracted produced a thicker film compared to MC alkali extracted. The lower solubility and the tendency to aggregation of the MC alkali extracted may explain the lower thickness of its film.

ACKNOWLEDGEMENTS

The authors thank Red Latino Americana de Química (RELAQ-UNESCO) for a fellowship for Cristián Tapia.

REFERENCES

1. K. Hiéta, S. Kuga, M. Usuda. *Biopolymers.*, 28, 1807 (1984).
2. S. Salmon, S.M. Hudson. *Journal of Macromolecular Science, Reviews in Macromolecular Chemistry and Physics.*, C37, 199 (1997).
3. E.K. Just and T.G. Majewickz. In: *Encyclopedia of Polymer Science and Engineering*, vol 3, pp.227-269. John Wiley & Sons, New York, USA, 1985.

4. H. Kern, S.W. Choi, G. Wenz, J. Heinrich, L. Ehrhardt, P. Mischnick, P. Garidel, A. Blume. *Carbohydrate Research.*, 326, 67 (2000).
5. M. Rinaudo, M.P. Lowys, J. Desbrières. *Polymer.*, 41, 607 (2000).
6. G.K. Greninger In : *Encyclopedia of Chemical Technology*, Kirk-Othmer, vol 5, pp.149-153. John Wiley & Sons, New York, USA, 1979.
7. H. Utz. In: *Cellulose sources and exploitation*, pp. 273-283. J.F. Kennedy, G.O. Phillips, P.A. Williams (editors), UK, 1989.
8. C. Tapia, J. Sapag-Hagar, P. Siches, F. Valenzuela, C. Basualto. *Lat. Amer. Appl. Res.*, 26, 221 (1996).
9. C. Tapia, J. Sapag-Hagar, F. Morales, F. Valenzuela, C. Basualto. *Bol. Soc. Chil. Quím.*, 46, 161 (2001).
10. K. Hodges, W. Kester, D. Wiederich, J. Grover. *Analytical Chemistry.*, 51, 2172 (1979).
11. W. Neely. *Journal of Polymer Science: Part A*, 1, 311 (1963).
12. K.G. Denbigh and J.C.R. Turner. *Introducción a la Teoría de Reactores Químicos*, pp. 151-153. Editorial Limusa, México, 1990.
13. G.K. Greninger, R.W. Swinehart, A.T. Maasberg. *Industrial and Engineering Chemistry.*, 47, 156 (1955).
14. *US Pharmacopeia 24*, United States Pharmacopeial Convention, Inc., Rockville, MD, pp. 1079. 2000.
15. M.E. Calahorra, M. Cortazar, J.J. Eguiazabal, G.M. Guzmán. *J. Appl. Polym. Sci.*, 37, 3305 (1989).
16. P. Yang, S. Kokot. *J. Appl. Polym. Sci.*, 60, 1137 (1996).