

ENCAPSULATION OF VEGETABLE OILS BY MINIEMULSION POLYMERIZATION: MATHEMATICAL MODELING

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ABSTRACT – Miniemulsion polymerization reactions of MMA were conducted with encapsulation of vegetable oils, using different types (linseed and andiroba oil) and amounts of oils. It was observed a decrease in the reaction rate that was proportional to the number of double bonds present in the oil. Polymers with lower molecular weights were obtained when oils with higher number of double bonds were used. A mathematical model was developed to represent the kinetics of these reactions, including all the other kinetic mechanisms associated to free radical miniemulsion polymerization. The model was able to predict the variation in the polymerization reaction rate depending on the type and amount of the vegetable oil.

1. INTRODUCTION

Polymeric nanoparticles for encapsulation of solids or liquids are frequently obtained by miniemulsion polymerization. When the miniemulsion polymerization reaction is conducted in the presence of a high concentration of a hydrophobic liquid, phase separation and the formation of particles with a core-shell morphology may occur. The encapsulation of hydrophobic ingredients (organic liquids or solids dispersed in hydrophobic liquids) allows obtaining functional materials, with the core product protected and stabilized by a polymeric shell. In this sense, polymeric nanocapsules are used to encapsulate materials as perfumes, pharmaceuticals, cosmetics, fabric treatment products, fluorescent dyes, printing inks, heat regulating agents, coating pigments, UV stabilizers, among others (Landfester, 2009; Samyn *et al.*, 2012; Weiss; Landfester, 2010).

When unsaturated compounds are incorporated by miniemulsion polymerization, grafting reactions are expected to occur, leading to the formation of hybrid polymers. In the last years, the hybrid miniemulsion polymerization has been applied for several systems including combinations of acrylic polymers with alkyd resins, unsaturated polyester resins, epoxy resins, oil modified polyurethane resins, resins derived from vegetable oils or even the pure vegetable oils (Tsavalas *et al.*, 2003). The grafting reaction can take place either by addition to the double bonds in the resin or by abstraction of allylic hydrogen of the resin. Although the addition process is energetically favored over abstraction, the structure of groups surrounding reactive site of the unsaturated molecule and the steric features of the polymeric radical can make abstraction preferable to addition during the reaction. With monomers like methyl methacrylate, that has a methyl group adjacent to the vinyl and has steric hindrance to react directly with the double bonds of the resin, grafting takes place

preferentially by hydrogen abstraction. This chain transfer produces a relatively stable radical, which has a lower capability to propagate than the polymeric radicals. This is the origin of degradative chain transfer in these systems, which causes the decrease of the polymerization rate. Furthermore, monomers like butyl acrylate, without the steric hindrance of the methyl group, can form radicals with higher reactivity. The polymeric radicals with butyl acrylate terminal unit can attack the double bonds of the resin by direct addition forming a grafted chain. They can also participate in chain transfer reactions with hydrogen abstraction (Guo; Schork, 2008; Hudda *et al.*, 2005). Vegetable oils have similar curing capabilities as alkyd resins because of similar double bonds content, but they have significantly lower molecular weight. Hence, the hybrid particles with oil have better homogeneity than those from alkyd resin, due to better miscibility (Guo; Schork, 2008). The type of encapsulated vegetable oil influences the degree of grafting because the number of double bonds is directly related to the concentration of possible reactive sites. Additionally, if a reaction occurs via free radical polymerization, the conjugated double bonds form more stable radicals, due to the delocalization of the electrons, what decreases the polymerization rate. Therefore, slower reactions are obtained when oils with a higher number of conjugated double bonds are used (Uschanova *et al.*, 2008).

In this work, encapsulation of vegetable oils by miniemulsion polymerization was carried out in order to evaluate the effect of the degree of unsaturation of the oil molecules on the reaction rate and on the molecular weight of the hybrid polymer. A mathematical model was used to describe the kinetic mechanisms involved in these reactions with vegetable oils.

2. EXPERIMENTAL

The miniemulsion polymerization reactions were conducted using the monomer methyl methacrylate (MMA, from Merck), freshly distilled. The surfactant sodium lauryl sulfate (SLS, from Merck) and the initiator 2,2'-azobis-2-methyl butyronitrile (V59, from Wako Chemicals) were used. Hexadecane (HD, from Sigma-Aldrich) was used as costabilizer, or it was substituted by a vegetable oil: andiroba oil (AND, from Beraca - Brazil) or linseed oil (LIN, from Aldrich). These vegetable oils are composed by a mixture of triglycerides with an average composition of different fatty acids, as shown in Table 1. Demineralized water was the continuous phase. Tetrahydrofuran (THF, from Merck) was used as solvent in the gel permeation chromatography analysis and deuterated chloroform in the nuclear magnetic resonance analysis (HNMR).

Table 1 – Average composition of fatty acids in the vegetable oils

	<i>Fatty acid (wt%)</i>				
	<i>C16:0</i> (<i>palmitic acid</i>)	<i>C18:0</i> (<i>stearic acid</i>)	<i>C18:1</i> (<i>oleic acid</i>)	<i>C18:2</i> (<i>linoleic acid</i>)	<i>C18:3</i> (<i>linolenic acid</i>)
Andiroba oil	25.04	13.51	44.66	12.49	-
Linseed oil	7.09	6.53	23.45	18.49	43.41

Reference: Melo (2010).

The organic phase was prepared mixing the initiator V59, the monomer MMA and the costabilizer (HD or a vegetable oil: AND, LIN), under magnetic stirring for 5 minutes. The aqueous phase, which was previously prepared mixing SLS and water, was added to the organic phase, and the

mixture was submitted to magnetic stirring at 1000 rpm for 60 minutes. The formulations used are shown in Table 2. The ratio monomer/costabilizer was equal to 50/50 or 75/25. The initiator concentration was maintained constant at 0.12 mol% (related to monomer) for all formulations. After mixing, the emulsion was sonicated using a Branson Sonifier (model W450, digital, 400 W), being cooled with an ice bath to prevent heating and the early onset of polymerization during sonication. The dispersion conditions, as well as the surfactant concentrations, were varied in order to obtain droplets with similar diameters in the reactions (see Table 2).

Table 2 – Formulations and dispersion conditions employed in miniemulsion polymerizations

Reaction	Reagents (g)					Dispersion conditions	
	<i>MMA</i>	<i>V59</i>	<i>HD/AND/LIN</i>	<i>SLS</i>	<i>Water</i>	<i>Time*</i>	<i>Amplitude</i>
HD50	3.0	0.005	3.0	0.060	24.0	2 min	70 %
AND50	3.0	0.005	3.0	0.060	24.0	2 min	70 %
LIN50	3.0	0.005	3.0	0.060	24.0	3 min	70 %
LIN25	4.5	0.009	1.5	0.015	24.0	1 min	60 %

*Pulse 10 s ON/5 s OFF

An aliquot of 0.5 g of the miniemulsion was then transferred to a vial, which was placed into the aluminum block of a reaction calorimeter (Micro Reaction Calorimeter, from Thermal Hazard Technology). The reactions were conducted inside the calorimeter at 72°C under magnetic stirring, with temperature control and with data acquisition of heat flow for each second of the reaction time. The data acquisition was interrupted when the heat flow was back to zero, indicating the end of the reaction. Monomer conversion, as a function of reaction time, was calculated by integration of the reaction heat curves, using the Origin® program. All these experiments were done in duplicate.

Intensity average diameters of polymer particles were measured using the dynamic light scattering (DLS) equipment Nanophox, from Sympa. The latex samples were diluted with demineralized water prior to DLS analysis. The molecular weights were measured by gel permeation chromatography, using the HPLC from Agilent Technologies, model 1260 Infinity, equipped with three columns in series and a refractive index detector. The samples were dried under vacuum for 24 hours and then dissolved in THF. The analyses were performed at 30°C, using THF as eluent at a flow rate of 1 mL/min. PMMA standards were used. HNMR analyses were conducted in order to determine the number of double bonds in the vegetable oils and in the latex samples. The samples were dissolved in deuterated chloroform prior to analysis.

3. MATHEMATICAL MODEL

The mathematical model used to describe the kinetics of miniemulsion polymerization reactions with encapsulation of vegetable oils was based on the mathematical model previously developed by Costa *et al.* (2013). This model was shown to represent very well the kinetics of miniemulsion polymerization reactions using oil-soluble initiators and allows to verify the effect of the variation on the particle diameters on reaction kinetics. The model includes mass balances for monomer, polymer and initiator in both organic and aqueous phases, and radical balances in the aqueous phase. A population balance also included in the model exhibits a detailed description of the radicals' entry and

exit from polymeric particles. This model also includes equilibrium equations, in order to represent the partition of the compounds in this heterogeneous system, and correlations to represent the gel and glass effect occurring during the reaction. To represent the encapsulation reactions, a mass balance for the vegetable oil was included in the model (Equation 1), considering that the oil can be consumed due to chain transfer or addition reactions to the polymeric chain radicals:

$$\frac{dO}{dt} = - \frac{\sum_{n=1}^{n_{max}} (nN_n)[O]^p N_{db} k_{fo}}{N_A} - \frac{\sum_{n=1}^{n_{max}} (nN_n)[O]^p k_{ad} P_M^p}{N_A} \quad (1)$$

where N_n is the number of particles with n radicals, $[O]^p$ is the concentration of the vegetable oil in the organic phase, N_{db} is the number of double bonds of the oil, k_{fo} is the rate coefficient for chain transfer to the oil, k_{ad} is the rate coefficient for addition of oil to the polymeric chain and P_M^p is the probability of having a radical with a monomeric terminal unit in the organic phase, which is calculated using the Equation 2:

$$P_M^p = \frac{k_{p2}[M]^p + k_{p1}[M]^p}{k_{p2}[M]^p + k_{p1}[M]^p + k_{ad}[O]^p + k_{fo}[O]^p N_{db}} \quad (2)$$

where $[M]^p$ is the concentration of monomer in the organic phase, k_{p1} is the rate coefficient for propagation of a single radical formed from an oil molecule and k_{p2} is the rate coefficient for propagation of radicals with an oil terminal unit. As the single radical obtained from an oil molecule is very stable due to conjugation with adjacent double bonds, this radical is much less reactive (Tsavalas *et al.*, 2003), and then $k_{p1} < k_{p2}$. The rate coefficients used to represent the reactions with andiroba oil or linseed oil are presented in Table 3.

Table 3 – Rate coefficients for reactions with vegetable oils

Parameter	Value	Unit
k_{ad}	$2 \times 10^{-2} k_{p(MMA)}^*$	$\text{cm}^3/\text{mol.s}$
k_{fCE}	$2.34 \times 10^{-4} k_{p(MMA)}^{[1]}$	$\text{cm}^3/\text{mol.s}$
k_{p2}	$2.5 \times 10^{-4} k_{p(MMA)}^*$	$\text{cm}^3/\text{mol.s}$

[1] Hudda, Tsavalas e Schork (2005); *Estimated.

In addition, in the mass balance for the monomer MMA, according to the previously developed model (Costa *et al.*, 2013), the consumption of monomer by propagation with radicals with an oil terminal unit was also considered.

4. RESULTS AND DISCUSSION

Comparing the miniemulsion polymerization reactions conducted with 50 % of vegetable oil or hexadecane (Figure 1), the differences in the reaction kinetics can be observed. As the vegetable oils used in these reactions have double bonds in their triglyceride molecules, the free radical present in the polymerization can either react with these double bonds or perform chain transfer to the oil, leading to a decrease in the reaction rate (Guo; Schork, 2008; Hudda *et al.*, 2005). Since hexadecane

has no double bonds, the reaction conducted with hexadecane (HD50) presented the highest reaction rate, when compared with reactions with vegetable oils. The linseed oil has more double bonds than the andiroba oil. So, reactions with andiroba oil (AND50) were faster than reactions with linseed oil (LIN50) and were also slower than reaction with hexadecane (HD50). These results agree with the literature reports. Higher levels of unsaturation and, in particular, conjugated unsaturation produce greater quantities of abstractable hydrogen. Additionally, higher degrees of unsaturation support greater electron delocalization and increase the resonance stability of the radicals, thereby promoting chain transfer reactions. The activation energy for free radical formation is lower in linoleic and linolenic acid than in oleic acid because of the active methylene group situated between the double bonds that leads to enhanced allylic radical stability (Black *et al.*, 2011). Linseed oil has about 43 % of linolenic acid, 18 % of linoleic acid and 23 % of oleic acid, which contain respectively three, two and one double bond. Andiroba oil has about 12 % of linoleic acid and 45 % of oleic acid. In this sense, chain transfer reactions are expected to occur more for linseed oil. Black *et al.* (2011) showed similar results for MMA/BA solution polymerization reactions using 33 wt% of soybean oil, linseed oil or tung oil. According to these authors, chain transfer greatly retarded the polymerization rate in reactions conducted in the presence of vegetable oils, with the effect increasing in order of soybean oil, linseed oil and tung oil (which contains about 70 % of a fatty acid with three conjugated double bonds). Cardoso *et al.* (2013) performed styrene miniemulsion polymerization reactions using 50 % of hexadecane, jojoba oil or andiroba oil. A decrease in the polymerization rate was obtained when andiroba oil was used, because of the reactions of free radicals with the double bonds in the oil.

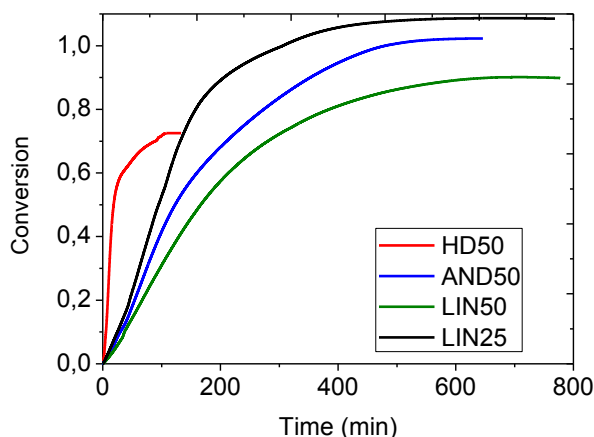


Figure 1 – Evolution of conversion for miniemulsion polymerization reactions with hexadecane, andiroba oil and linseed oil.

In reactions conducted with different linseed oil/MMA ratio (Figure 1), it was observed that the reaction rate increases when the oil concentration is decreased. This result clearly shows that the reaction rate decreases proportionally with an increase of oil concentration or an increase in the number of double bonds in the system, and agrees with those results presented for different oils. The same behavior was found by Guo and Schork (2008) in MMA and BA miniemulsion polymerization reactions when the concentration of sunflower oil was varied. The average particle diameters measured in the end of these reactions are shown in Table 4.

Table 4 – Intensity average diameter (D_p), number average (M_n) and weight average (M_w) molecular weight of polymer obtained in miniemulsion polymerizations with vegetable oils or hexadecane

Reaction	HD50	AND50	LIN50	LIN25
D_p (nm)	142.7±0.1	131.4±9.1	132.3±1.6	150.7±24.9
M_n (×10 ³ g/mol)	2356	173	36	96
M_w (×10 ³ g/mol)	3337	491	56	225

The number of double bonds per oil molecule quantified by HNMR, for samples of pure oil and samples obtained after MMA/oil polymerization reactions, are shown in Table 5. A pronounced decrease in the number of double bonds per oil molecule was observed for all reactions conducted with the unsaturated vegetable oils. This result suggests that addition reactions of monomer or polymer radicals to the oil did occur, consuming the double bonds, besides of chain transfer reactions to the oil. Similar result was shown by Gooch *et al.* (2000) for MMA/BA miniemulsion polymerization using 20 to 50% of an unsaturated resin. They showed that only 60-70% of double bonds of the resin were preserved.

Table 5 – Average number of double bonds per oil molecule (N_{db}) quantified by HNMR analysis

Sample	N_{db} - before polymerization	N_{db} - after polymerization	Double bonds preserved after polymerization (%)
AND50	2.0	1.4	70
LIN50	6.6	3.4	52
LIN25	6.6	0.1	2

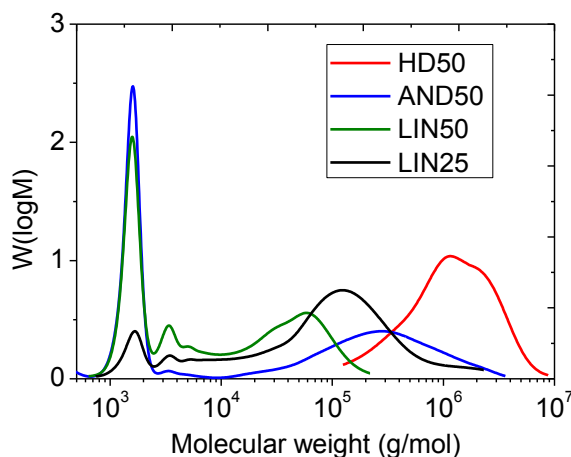


Figure 2 – Molecular weight distributions obtained in miniemulsion polymerizations with hexadecane, andiroba oil and linseed oil.

The occurrence of reactions with double bonds can also be noticed in the molecular weight distributions (MWDs) shown in Figure 2. In this figure with multimodal MWDs, the high molecular weight peak corresponds to PMMA and the low molecular weight peak corresponds to the pure oil. In addition, a fraction of intermediate molecular weight (around 10^4 g/mol) was formed by reaction between the polymeric chains and the oil molecules, forming a graft polymer. This grafting is observed in all reactions with vegetable oils and is more pronounced in reactions with linseed oil, due to its high degree of unsaturation.

As the number of double bonds in the oil increases, an increase in the grafting degree is observed and the formed polymer tends to have lower molecular weight. Thus, the highest molecular weights were obtained in the reaction with hexadecane and the lowest ones were obtained in reactions with linseed oil, as shown in Table 4. This effect on the molecular weight was also observed by Black *et al.* (2011), especially when oils with conjugated double bonds were used.

The results obtained in the simulations of miniemulsion polymerization reactions conducted with linseed oil are shown in Figure 3a. In order to represent the grafting reactions, the rate coefficient for chain transfer to the oil was used as proposed by Hudda *et al.* (2005) for MMA polymerization reactions with alkyd resins. The values for the rate coefficient for addition reactions and the rate

coefficient for propagation of oligomeric radicals with an oil terminal unit were estimated to represent these reactions. It is observed that the simulation results were well adjusted to the experimental data for both reactions with 50 % and 25 % of oil and was able to describe the effect of the variation in the concentration of oil on the evolution of conversion. In the simulation of conversion for reaction with andiroba oil, the same rate coefficients were used. The evolution of conversion obtained in the simulation was very similar to that obtained experimentally (Figure 3b). These results show that the mathematical model can be adequately used to describe the kinetics of miniemulsion polymerization reactions with encapsulation of vegetable oils.

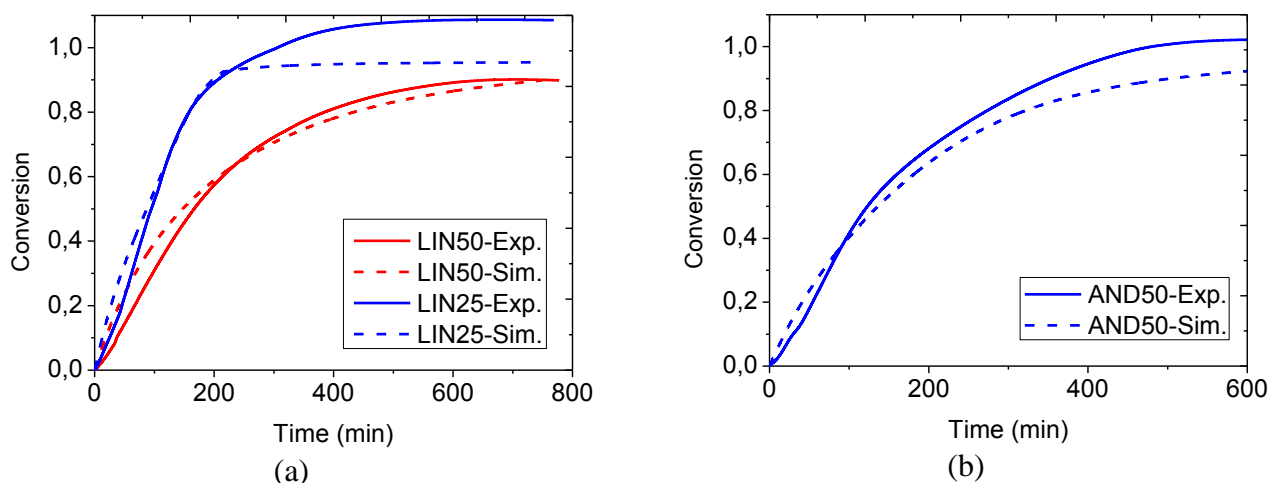


Figure 3 – Simulation of conversion for MMA miniemulsion polymerization reactions with (a) 50 % or 25 % of linseed oil; (b) 50 % of andiroba oil.

5. CONCLUSION

Miniemulsion polymerization reactions for monomer MMA with encapsulation of hexadecane, andiroba oil or linseed oil were conducted. It was observed a decrease in the reaction when the unsaturated oils (andiroba or linseed oil) were used and this decrease was proportional to the number of double bonds of the oil. Additionally, the reaction rate decreased when the amount of oil was increased. This reaction rate decrease was attributed to grafting reactions occurring between the polymeric growing chains and the unsaturated oil, due to its double bonds. HNMR analyses were performed to verify the consumption of double bonds of the oil molecules in these reactions. The formation of a hybrid polymer due to grafting reactions was also observed in the molecular weight distribution results, showing a peak of intermediate molecular weight, between the pure oil molecular weight and the PMMA molecular weight. Beyond the formation of hybrids with molecular weights around 10^4 g/mol, the molecular weights of polymer PMMA were lower in reactions with unsaturated oils. A mathematical model was developed to represent the kinetics of these reactions, including all the other kinetic mechanisms associated to free radical miniemulsion polymerization. The model included both addition and chain transfer mechanisms proposed to describe the grafting reactions occurring due to the double bonds of the vegetable oils. The results of conversion obtained in the simulations were very similar to those obtained experimentally. The model was able to predict the

variation in the polymerization reaction rate depending on the type of the vegetable oil and on the concentration of the vegetable oil in the reaction medium.

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