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SYNTHESIS OF POLYMER NANOCOMPOSITES USING LAYERED HYDROXIDE SALTS (LHS)

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Abstract - In this work latexes of poly (methyl methacrylate) were synthesized via emulsion polymerization using layered hydroxide salts (LHS) as reinforcements: zinc hydroxide nitrate ($Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$) and copper hydroxide acetate ($Cu_2(OH)_3CH_3COO \cdot H_2O$). The LHSs were characterized by X-ray powder diffraction (XRPD). Mastersizer analysis indicated the particle diameter of the latexes. Molecular weights and conversion data were also obtained.

Keywords: emulsion polymerization, layered hydroxide salts, poly (methyl methacrylate), nanocomposites, reinforcements

Introduction

In recent years, there has been great interest on the development of nanostructured composites. These materials exhibit better mechanical, thermal, gas permeability, among other properties, when compared to traditional materials. Obtaining polymeric nanocomposites by using reinforcements is in the interests of the productive sector.

Layered Hydroxide Salts (LHS)

Layered materials have been extensively studied in recent years due to the wide range of properties that can be tailored by intercalation and functionalization (surface chemical modification) reactions, allowing them to be used in different fields of science and technology [1].

Layered hydroxide salts (LHS) are derivative compounds of the brucite-like structure. In this case, part of the structural hydroxyl groups can be substituted by water molecules or by other oxoanions, generating residual positive charge in the layers. In both cases, these compounds undergo anionic exchange reactions [2] and, potentially, surface chemical modifications [3]. The general formula of LHS is $M^{2+}(OH)_{2-x}(A^{m-})_{x/m} \cdot nH_2O$, where M can be one or two types of divalent cations and A represents a hydrated counter ion with m^- charge. Studies which use LHS as layered hosts are quite rare and most published works involve their structural characterization [4].

Zinc hydroxide nitrate (ZHN - $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$), which is one of the most extensively studied LHS, has a CdI_2 -type structure and is classified by [5] as an IIB type. In this structure, one-quarter of the octahedrally coordinated zinc cations are displaced from the main layer to tetrahedral

sites located above and below each empty octahedron. Three vertices of the tetrahedron are occupied by hydroxyls shared with the octahedral sheet and the apex by a water molecule (Fig 1). The nitrate ions are situated between the layers and are surrounded by water molecules but not coordinated to the zinc atoms [6]. As far as the authors known, investigation of using LHSs as reinforcements of PMMA are absent in the literature.

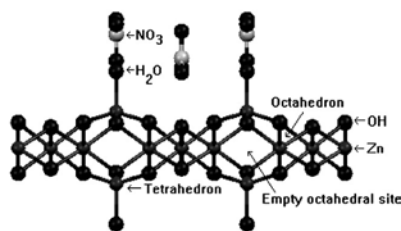


Figure 1 - Zinc hydroxide nitrate structure side view. Hydrogen atoms were removed from the zinc hydroxide nitrate structure to facilitate visualization [1].

Emulsion Polymerization

Polymer nanocomposites have been prepared by four main processes: exfoliation-adsorption, template synthesis, melt intercalation and in situ intercalative polymerization. Several techniques such as solution, suspension, bulk, emulsion [7] and miniemulsion [8] polymerizations have been used to prepare polymer nanocomposites by in situ intercalative polymerization. When using either of these techniques the clay is normally first modified to increase the interlayer spacing and turn its surface organophilic and consequently with better physico-chemical affinity with the monomer or polymer.

In spite of the many advantages of continuous stirred tank reactors (CSTR), complex dynamics, essentially oscillation mechanisms and multiple steady states, have restricted their commercial use. The oscillations produce heterogeneous polymer and make production control difficult. An increase in the polymer concentration can cause an increase in the molecular weight and branching of the polymer, and create problems in the processing. Further, the sudden decrease in surfactant concentration can produce coagulation of the latex. In addition, the new nucleations create a large number of small particles increasing the viscosity of the system that can originate agitation and heat transfer problems. The oscillatory behavior arises as a result of the role of the surfactant in particle nucleation and can be avoided by modifying the nucleation mechanism. In emulsion polymerization, particle nucleation takes part in the micelles where a steady state operation condition is achieved, reducing the oscillatory behavior.

Experimental

LHS Synthesis

Zinc hydroxide nitrate and copper hydroxide acetate were synthesized by the salt-base method [9]. For zinc hydroxide nitrate, a solution was prepared with 300 mL of distilled water, containing 44.61 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. A solution of NaOH 0.5 mol.L^{-1} was then added dropwise under stirring to the above solution. For copper hydroxide acetate, a solution was prepared with 300 mL of distilled water, containing 15.52 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. A solution of NaOH 0.2 mol.L^{-1} was then added dropwise under stirring to the above solution. Both syntheses were stopped when the pH reached around 7.0. Solids were then washed with 50 mL of water, separated by centrifugation at 4000 rpm for 5 min (this process repeated five times), and dried at 60°C in a vacuum oven until constant weight.

Polymerization

Methyl methacrylate (30 g) were placed in a container with 0.3 g of LHS and stirred for 24 h (swelling time). The organic phase was poured under strong agitation with 400 g of deionized water and 0.87 g of sodium dodecyl sulphate (DDS) into an 1000-mL stainless steel reactor equipped with nitrogen purging tube, temperature controller, and stirrer. To start the polymerization, the temperature was increased to 60°C , and a solution of 0.15 g of sodium persulphate in 170 g of deionized water was added. The reactor was continuously purged with nitrogen during polymerization which was carried out for 1h. Samples of 4 g were removed periodically from the reactor for conversion analysis [10]. This procedure was followed for polymerizations with LHS (1 wt%). One experiment was carried out with no LHS addition for reference. The formula used in this case was different: Methyl methacrylate (40 g), deionized water (400 g), sodium dodecyl sulphate (1.16 g) and sodium persulphate (0.2 g).

Results and Discussion

Table 1 shows the three runs made. Conversion profiles for all runs are shown below in Fig 2. Conversion was calculated by mass difference (gravimetry). Molecular weights (number average and weigh average) profiles are obtained only for Run 1 (no LHS) and presented in Fig 3 as reference, since the GPC cannot analyze samples of polymers with clays in it. The GPC (Viscotek TDA 302) used is equipped with a triple detector: refraction index (RI), viscosimeter and right-angle laser light scattering (RALLS). Two columns (ViscoGEL I-series) having dimensions of 7.8 mm x 30 cm were used. These columns separate polymers with molecular weights of up to 10 million.

Table 1 - Experimental Runs

Run	Monomer	LHS
1	MMA	-
2	MMA	LHS Zn
3	MMA	LHS Cu

In Fig 2, it is possible to see that the final conversion obtained in run 1 is the highest one (95%) comparing to run 2 (50%) and 3 (80%). This may be explained by the presence of a higher amount of monomer in the reactor used in run 1 than the one used in run 2 and 3. Also, the presence of LHSs, which were not chemically modified, could affect/block monomer groups in their course to grow the polymeric chain.

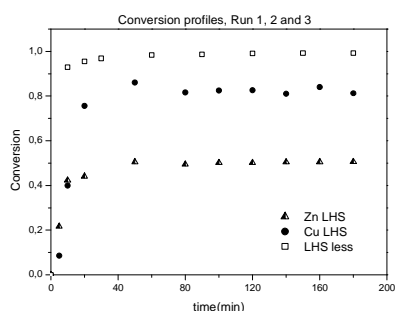
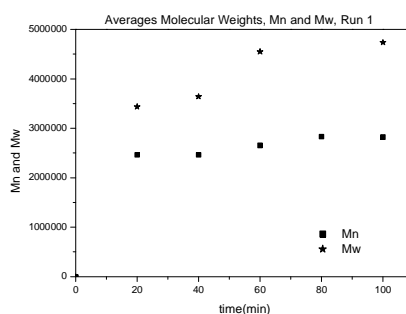
**Figure 2** - Conversion vs. time.**Figure 3** - Averages Molecular Weights, Mn and Mw vs. time.

Fig 3 presents the final values of number and weight average molecular weight obtained for run 1, 3×10^6 and 5×10^6 , respectively. These are high values of molecular weights and may grant to the final product, the polymer itself, properties like resistance and rigidity. In order to have some knowledge of both LHSs, X-ray diffraction characterizations were performed. Fig 4 shows the XRD patterns for zinc hydroxide nitrate and copper hydroxide acetate, respectively. The XRD patterns were obtained by scanning the range of 1.5 to 70° theta, at a rate of $2^\circ / \text{min}$. The equipment used was Shimadzu XRD-7000, with copper cathode (1.54060 Å), voltage 40 kV and electric current of 30mA.

Table 2 presents the basal spacing of the two different LSHs.

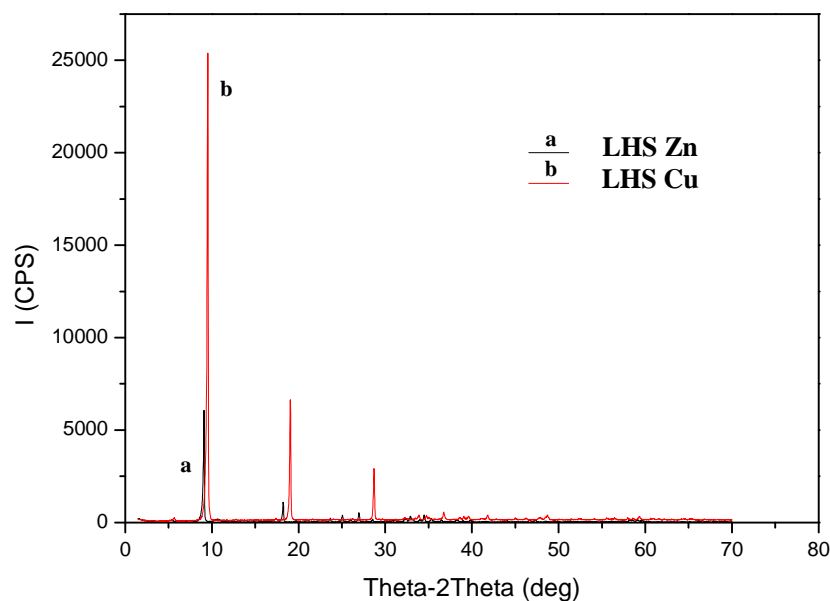


Figure 4 - XRD patterns of zinc hydroxide nitrate (a) and copper hydroxide acetate (b).

Table 2 - Basal Spacing (d)

Material (LHS)	Basal spacing (nm)
zinc hydroxide nitrate	0.98 ($2\theta = 9.04^\circ$)
copper hydroxide acetate	0.94 ($2\theta = 9.45^\circ$)

From Fig 4, it was possible to obtain the basal spacing for both LHSs (Table 2). It can be noticed that the values are very similar. So, it may be expected that when the LHSs were to be added to the polymer matrix, they would disperse alike although copper hydroxide acetate has more hydrophobic character.

Particle size measurements were carried out on a Malvern ZETASIZER NANO ZS ZEN 3600 (red badge: wavelength 633nm). Table 3 presents the particle size of the latexes (DP is the average volumetric diameter. It is the diameter of the sphere which possesses the same average volume of the constituent particles of system).

Table 3 - Latexes Particle Size

Run	Monomer	LHS	DP (nm)
1	MMA	-	63.08
2	MMA	LHS Zn	53.51
3	MMA	LHS Cu	60.69

From Table 3 is possible to see the variation in particles size. It is possible to see that latexes with both LHSs have their particle size decreased. The effect was more intense for latex with LHS Zn than for latex with LHS Cu. This decrease may be explained by the fact that probably both LHSs are yet hydrophilic and did not suffer any organic modification or interaction during the 24h stirring time in the monomer. They are probably still dispersed in the water, so most likely they are not located within the monomer droplets that would explain an increase in particle size.

Conclusion

Poly (methyl methacrylate) latexes, to which 1wt % zinc hydroxide nitrate and 1 wt% copper hydroxide acetate were added, have been synthesized by in situ emulsion polymerization.

Conversion profiles were presented and the experimental results showed that maybe the addition of LHSs did influence the polymerization kinetics. Molecular weights profiles were presented as a reference for further physical properties analyses. Analysis of XRD patterns showed the expected basal spacing values for both LHSs. The Zetasizer analyses showed the decrease in particle size when using the LHSs. That might indicate that the LHSs did not have their structure exfoliated.

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References

1. G. G. C. Arizaga; A. S. Mangrich and F. Wypych *J. Coll. Interf. Sci.* 2008, 320, 238.
2. M. Meyn; K. Beneke and G. Lagaly *Inorg. Chem.* 1993, 32, 1209.
3. F. Wypych and K. G. Satyanarayana *J. Coll. Interf. Sci.* 2005, 285, 532.
4. G. G. C. Arizaga; K. G. Satyanarayana and F. Wypych *Sol. Stat. Ion.* 2007, 178, 1143.
5. M. Louër; D. Louër and D. Grandjean *Acta Crystallogr. Sect. B Struct. Scie.* 1973, 29, 1696.
6. W. Stählin and H. R. Oswald 1970, *Acta Crystallogr. Sect. B Struct. Scie.* 1970, 26, 860.
7. N. N. Herrera; J. L. Putaux and E. B. Lami *Prog. Solid State Chem.* 2006, 34, 121.
8. Z. Tong and Y. Deng *Ind. Eng. Chem. Res.* 2006, 45, 264.
9. R. Marangoni, Ph.D. Thesis, Federal University of Parana, 2009.
10. R. P. Moraes; A. M. Santos; P. C. Oliveira; F. C. T. Souza; M. Amaral; T. S. Valera and N. R. Demarquette *Macromol. Symp.* 2006, 245, 106.