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Influence of the Surfactant on the Hydrotalcite Dispersion in NBR/LDH Composites Produced by Coagulation

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Summary: Dispersions of 10% wt hydrotalcite were prepared by mixing using an ultrasound probe and then incorporated into NBR latex for the purpose of evaluating the influence of the surfactant presence and dispersion stability of the hydrotalcite, both in water and in latex. The surfactant used was Pluronic F-127 and its influence was determined on the size of the agglomerates, the degree of sedimentation and the viscosity of water/LDH dispersions and latex/LDH suspensions. Preliminary results showed the efficiency of the surfactant in promoting dispersion of water/LDH, presenting lower agglomerate diameter values and increased stability of the dispersion. For the latex/LDH suspension, the viscosity of the system containing surfactant was significantly greater due to a better dispersion of LDH. After coagulation, the systems were examined in detail using X-ray diffraction (XRD) and the results did not show differences in the degree of intercalation, but XRD pattern of LDH was not observed, indicating the breakdown of crystallinity and ordering of the clay crystallites. The ash content showed that the presence of surfactant was an important factor to optimize the incorporation of the clay during coagulation. The estimation of Payne effect from shear modulus indicated a better filler dispersion in NBR matrix when using Pluronic F-127, this behavior was also confirmed by FESEM micrographs.

Keywords: dispersion; Latex; LDH; stability; suspension

Introduction

Latex is defined as a colloidal dispersion of polymer particles in an aqueous medium. Butadiene acrylonitrile (NBR) latexes, also called nitrile latexes, are anionic because they present negatively charged polymer particles. Articles obtained from these latexes typically have good heat resistance, and when reinforcing fillers are incorporated, the resulting material exhibits substantial improvement in physical and mechanical properties.[1–3]

Layered silicates are natural or synthetic minerals that have been extensively studied as reinforcing filler for the synthesis of inorganic polymer composites/nanocomposites, due to their high aspect ratio, high cation exchange capacity and low cost. However, the difficulty of controlling the aspect ratio and charge density between the layers limits the use of these clays. Given these disadvantages, layered double hydroxides (LDHs), also known as anionic clays, have attracted attention for their ability to control the anionic exchange capacity, particle size and aspect ratio by simply controlling the reaction conditions.[4] In contrast to cationic clays with negatively charged layers (type 1:1 and 2:1),

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layered double hydroxides (LDHs) are a type of clay mineral that have positively charged layers (1:1 type, brucite-like - Mg $(OH)_2$), compensated with negatively charged interlayers containing anionic species and water molecules.[5,6]

So far, the technology for obtaining rubber/clay composite mainly include melt mixing, in situ polymerization, solution mixing and latex blending. Among these techniques, latex blending is the most promising for manufacturing rubber articles, since it combines low cost of clay with simplicity of the preparation process, meaning high cost/performance ratio, besides being less harmful to the environment than other techniques. However, the preparation of latexes filled with large amounts of clay hybrids requires good aqueous clay dispersion and then co-coagulating the latex with this dispersion during vigorous mixing.[7–8]

It is known that particles with submicron and nanometer size scales have the disadvantage of a strong tendency to agglomerate, especially when in contact with polar liquids such as water. The various types of existing interactions (interparticle attractive forces, or Van der Waals forces, electrostatic forces between oppositely charged sites and strong bonds involving water molecules) are responsible for promoting this process of agglomeration.[9–10] For the purpose of dispersing these micro/nanoparticles, it is common to use a surfactant, also known as a dispersant.

The word surfactant is a term applied to molecules which combine in the same structure two opposite polarity regions: one polar (hydrophilic) and nonpolar (hydrophobic). These molecules acting on the surface, usually in an aqueous solution, have strong adsorption at the interface, leading to changes in the characteristics of the resulting material. These changes promote deagglomeration, thereby enabling the dispersion of the particles in the aqueous medium. Surfactants can be classified according to the chemical structure of their hydrophilic groups, which can be anionic, cationic or nonionic.[9,11]

Rheology is a very important tool to study the behavior of emulsions during processing. Among the rheological properties, viscosity is particularly important, especially when working with polymer composites. The rheological behavior of composites depends on the clay dispersion, which is directly related to the filler-polymer interactions. Therefore, the degree of clay dispersion in the polymer matrix not only affects the final properties, it also influences the rheological behavior of the matrix.[12]

This study focuses mainly on a nonionic block copolymer of poly (ethylene oxide-co-propylene oxide-co-ethylene oxide) (PEO-PPO-PEO) as the dispersant in an aqueous suspension of LDH for subsequent co-coagulation of NBR latex. The suspension properties were investigated by particle size distribution, sedimentation testing and rheological behavior in order to detect the action of the surfactant on the deagglomeration of LDH particles in aqueous media. After coagulation, the systems were examined in detail using X-ray diffraction (XRD), ash content measurement and, Payne effect (dynamic mechanical properties) and scanning electron microscopy (FESEM) to complement the study of the surfactant influence on the dispersion stability.

Experimental Part

Materials

NBR- 615B latex with antioxidant was obtained from Nitriflex S/A Indústria e Comércio, Brazil. NBR is a copolymer of acrylonitrile and butadiene with acrylonitrile content of 33% and Mooney viscosity of (ML (1 +4) 100 °C 48). The Mg/Al layered double hydroxide (LDH, synthetic hydrotalcite, Mg/Al $\approx$ 3:1) and the nonionic surfactant Pluronic F-127 were supplied by Sigma-Aldrich. A solution of ultrapure 30% aluminum sulphate was obtained from Reagan Ltda., Brazil, and used as coagulating agent to NBR latex.

Preparation of NBR latex/LDH Composites

Latex/LDH Suspension (step 1)

Aqueous clay was prepared using 10% wt of LDH dispersed in deionized water with 0.5% wt of Pluronic F-127. This suspension was made with the help of an ultrasound probe for 15 min at 60% amplitude in an ice bath using Hielscher UP400S. Pluronic F-127 was used to facilitate stabilization of the clay aggregates in the aqueous media. Thereafter, the clay dispersion was mixed with NBR latex under vigorous agitation for 2 hours by a propeller mixer.

Latex/LDH Co-Coagulation (step 2)

To prepare latex/LDH composites by the latex-coagulation method, latex/LDH suspension was coagulated by 30% wt aqueous solution of aluminum sulphate acidified with sulfuric acid and then washed with water and dried in an air oven for 1 hour at 100 °C.

Test Methods

The particle size distributions in the aqueous LDH dispersions were determined by the dynamic light scattering (DLS) method (Microtrac – Zetatrac). The stability of the emulsion was observed immediately after ultrasonic probe mixing by the sedimentation method.

Rheometric measurements were carried out with an oscillatory rheometer (MARS II from Thermo Haake) equipped with coaxial-cylinder at 25 °C, to obtain the viscosity curve of the aqueous LDH and latex/LDH suspensions by varying the shear rate from 0.1 to 100 s^{-1}.

Strain sweep experiments in the strain range of 0.28-100% were performed on NBR/LDH gums (uncured) using a RPA 2000 rubber process analyzer (Alpha Technologies) at 100°C and 0.1 Hz, with the aim to determine the Payne effect.

The degree of rubber intercalation in the clay layers was evaluated using XRD in a scan 2θ range from 1° to 50° at a scan rate of 2° min^{-1} with a Rigaku Miniflex diffractometer with CuKα radiation ($\lambda = 0.1504$ nm), voltage of 40 KV and current of 30mA.

The ash content was determined according to ASTM D5630 at 600 °C after system coagulation. The ashes were weighed and the exact amount of hydrotalcite in each system was determined by Equation (1).

$$\text{Ash content}(\%\text{wt}) = 100^{*}[(w3 - w1)/(\text{w2} - \text{w1})] \quad (1)$$

Where W1 is the mass of the empty crucible; W2 is the mass of the crucible with the sample before burning; and W3 is the weight of crucible and sample after burning.

The nature of filler dispersion in the NBR matrix was also investigated using a field emission scanning electron microscope (FESEM) (Quanta FEG 450 manufactured by FEI). The samples were hot-pressed at 70 °C at 12 MPa for 5 minutes. These films were then coated with platinum (sputter method).

Results and Discussion

The ultrasound probe was used to reduce the size of the clay particles and thus improve the dispersion of LDH in the aqueous medium, since such particles tend to agglomerate in aqueous media. The mechanism of ultrasound action is based on microturbulences caused by fluctuation of pressure and cavitation, while high shear forces are responsible for dispersion and reduction of the particle size.[13] The addition of surfactant stabilized this LDH aqueous dispersion as shown by photographs of LDH suspensions with and without surfactant, after mixture with the ultrasound probe (see Table 1). It is apparent that LDH dispersion without surfactant (water/LDH) was not well dispersed because of the large volume of the suspended material. In contrast, the dispersion of LDH in the presence of the surfactant was more stable.

In the surfactant system shown in Figure 1 (b), the particle size was effectively reduced (diameters around 0.87 micrometers) and

Table 1.
Effect of surfactant on the LDH aqueous dispersions.

Period	Dispersions (water/LDH)	
	Without surfactant	With surfactant
Immediately after ultrasound probe mixture (T_{oh})		

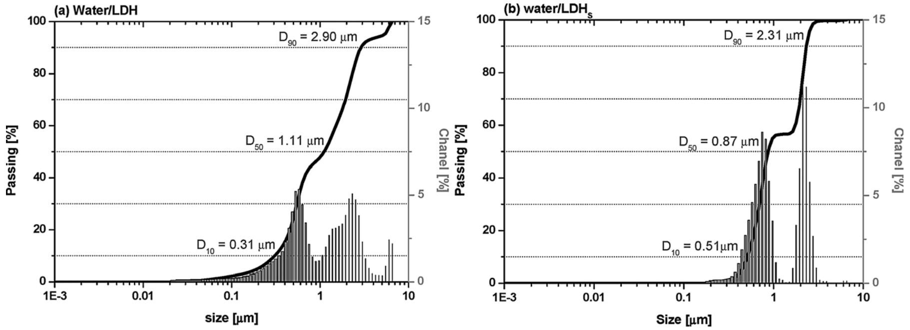

Figure 1.
Particle size distributions of dispersions: without surfactant (a) and with surfactant (b).

the dispersion of the particles had bimodal behavior of agglomerates. On the other hand, without surfactant it was not possible to break the high potential attraction between the particles, so that the result was slightly larger particle size (agglomerate size larger than about 1.11 micrometers), as seen in Figure 1(a), with the appearance of a new mode.

However, it is possible to verify that the LDH aqueous dispersion caused broader modes, suggesting a wider range of particle sizes, i.e., a more heterogeneous dispersion. On the other hand, the water/LDH$_s$ system (dispersion with surfactant) produced narrower modes, indicating more homogeneous particle diameters due to the process of deagglomeration promoted by the surfactant.

The stabilization of the LDH suspension is a result of surfactant (block copolymer of PEO-PPO-PEO) adsorption through hydrogen bonding between hydrophilic groups of the PEO and the hydroxyl groups of the lamellar surface. This nonionic surfactant has been successfully applied as a stabilizing agent because it has the ability to cause steric stabilization. As a consequence, the lower polarity group PPO (tail micelle) free in solution promotes a steric barrier between the dispersed hydrotalcite particles, keeping them suspended longer and hindering the formation of agglomerates. This means that the PEO-PPO-PEO block copolymer acts as a steric stabilizer by promoting the formation or hydrotalcite particles with smaller diameters. A previous study by Palla and co-workers[14] confirmed that steric stabilization occurs due to the presence of physical barriers adsorbed on particles that prevent the particles from coming close enough to allow the van der Waals attractive forces between them to dominate.

Figure 2 shows the viscosity curve as a function of shear rate, after stirring the ultrasound probe. Figure 2(a) compares the viscosity of water and viscosity of the water/LDH and water/LDH_s dispersions. It can be seen that the presence of surfactant led to smaller and more homogeneous particles after the ultrasound process (see Figure 1(b) – $D^{50} = 0.87\,\mu m$ and narrow modes). The smaller particle sizes reduced the flow resistance when submitted to rheology analysis, which is directly related to the viscosity of the system. Therefore, the viscosity of the system with surfactant (water/LDH_s) declined slightly in comparison with the system without surfactant (water/LDH), with viscosity equal to that of pure water. This result corroborates the result shown in Figure 1, where the system without surfactant has larger particles with more variable sizes, causing an increase in viscosity (greater flow resistance) during the rheology assay. Thus, the agglomerates are responsible for an increase in flow resistance. This behavior was also observed by Palla and co-workers, who stated that the presence of surfactant promotes steric stabilization, so that dispersions with high solids exhibit relatively low viscosities.[14]

Referring to Figure 2 (b), the viscosities of the latex/LDH suspensions with and without surfactant were compared to those of pure latex. Reduced viscosity of the suspensions was expected, since the latex was added to the aqueous dispersion of LDH, favoring the dilution of the system and, consequently, reducing its viscosity. However, when comparing the latex/LDH suspension with and without surfactant, it was found that the latex/LDH_s suspension showed higher viscosity at low shear rate, probably due to the greater contact between clay particles and rubber chains in the latex, which led to greater latex-LDH interaction, favored by the smaller diameter of the agglomerates. Deposition of LDH particles was observed in the system without surfactant, thus reducing the system viscosity.

After the coagulation process, the strain sweep data of the NBR/LDH gum with and without surfactant were studied using the rubber process analyzer. The results are shown in Figure 3. The unfilled NBR (NBR gum) showed no indication of nonlinearity, after adding the LDH the low strain modulus (G_0) increased more than the high strain modulus (G_∞), resulting in nonlinear viscoelastic behavior. That behavior observed in each of these systems is known as the Payne effect, and is measured by the difference G_0 - G_∞.

This routine was performed with experimental shearing not exceeding ~ 100%, and according to Payne, in the low strain region

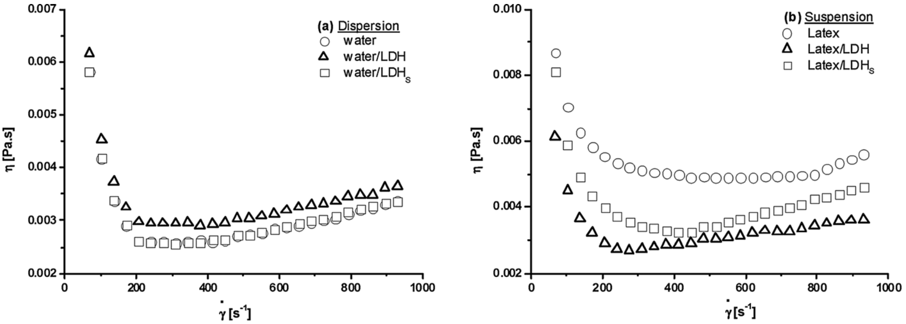

Figure 2.
Viscosity of LDH aqueous dispersions (a) and latex/LDH suspensions (b).

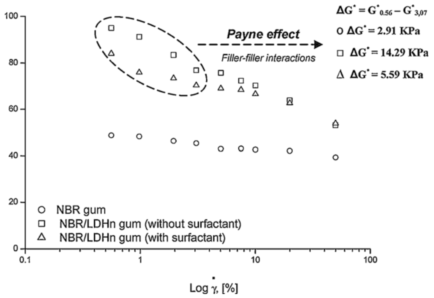

Figure 3.
Effect of surfactant on the dynamic modulus depending on the shear rate (Payne effect) in NBR gum and NBR/LDH$_n$ gum after coagulation.

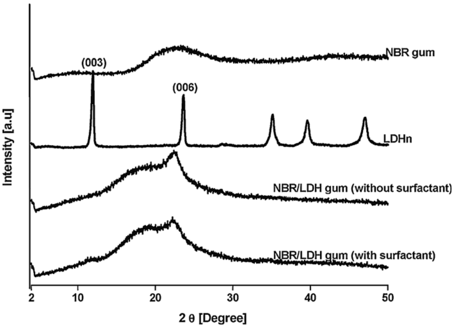

Figure 4.
XRD patterns for NBR, LDH and NBR/LDH composites (with and without surfactant).

(strain ~ 0.1%), the dynamic mechanical properties of filled rubbers are less strain-dependent. Payne suggested the presence of a yield point at these low strains.[15] But in this work that effect was noted for strains up to 3%.

It can be seen that the addition of the surfactant in the aqueous dispersion of clay for further coagulation with latex promoted more efficient dispersion, with smaller LDH particles. This behavior can be proved by the Payne effect, which showed a substantially lower value ($\triangle G^* = 5.59$ KPa) than the system without surfactant ($\triangle G^* = 14.29$ KPa). This results suggests the poor dispersion of the system without surfactant. According to Bezerra and co-workers, the higher the value ΔG^*, the greater the filler-filler interaction, indicating the need for stronger forces to break these interactions when the dispersion of filler is present in the form of large agglomerates in the elastomeric matrix.[16]

XRD was used to compare the degree of rubber chain intercalation between the clay layers in the materials produced from water/LDH suspensions (with and without surfactant). The diffractograms are shown in Figure 4. The XRD patterns of both composites showed low diffraction peaks when compared to the pure LDH. This behavior is understandable, since 10% wt of LDH (theoretical value) was incorporated in the NBR matrix. Comparing the peaks of the composites, there are remnants of the LDH basal reflections (003 and 006) superimposed on the amorphous halo characteristic of NBR. Visually, it is difficult to compare the degree of clay dispersion produced by the addition or not of the surfactant from the diffractograms given by the two composites. But it can be seen that the crystalline pattern of LDH disappeared, suggesting the intercalation of NBR between the clay layers. Therefore, transmission electronic microscopy (TEM) and other measurement techniques are needed to confirm these observations.

The ash content shown in Table 2 indicates the content of inorganic matter incorporated in the polymer after the burning of organic matter. The results showed higher LDH incorporation in the matrix of NBR in the presence of surfactant. Thus, this experiment confirmed the greater stability of hydrotalcite in solution as a result of the addition of Pluronic F-127.

To further evaluate the dispersion of LDH in the NBR matrix, FESEM (field-emission gun scanning electron microscopy)

Table 2.
Ash content of composites.

Composites	Ash content (% wt)
NBR/LDH$_n$ (without surfactant)	3.55
NBR/LDH$_s$ (with surfactant)	6.80

(*) Theoretical value of LDH in the matrix equal to 10% by weight.

was performed on the samples. The micrographs are shown in Figures 5 and 6, NBR/LDH$_n$ (without surfactant) and NBR/LDH$_s$ (with surfactant) respectively.

It can be clearly seen that in NBR/LDH$_n$ [Figure 5], LDH particles are mainly present as aggregated, thus supporting the rheology results. The poor dispersion of the system without the presence of surfactant shows the importance of using a dispersant (surfactant) to improve the stability of the dispersed particles of the LDH in aqueous medium and reduce agglomeration in the subsequent coagulation step (as seen in Figure 6).

Conclusion

The results show that the use of an ultrasound probe and addition of surfactant worked synergistically to break down LDH aggregates, yielding stable aqueous dispersions. The ultrasound process provides the required energy to break down the clay aggregates. However, the presence of Pluronic F-127 was essential to improve the dispersion of LDH particles in the aqueous suspensions and delay the subsequent particle sedimentation.

The dynamic light scattering (DLS) and rheology analyses showed that hybrid

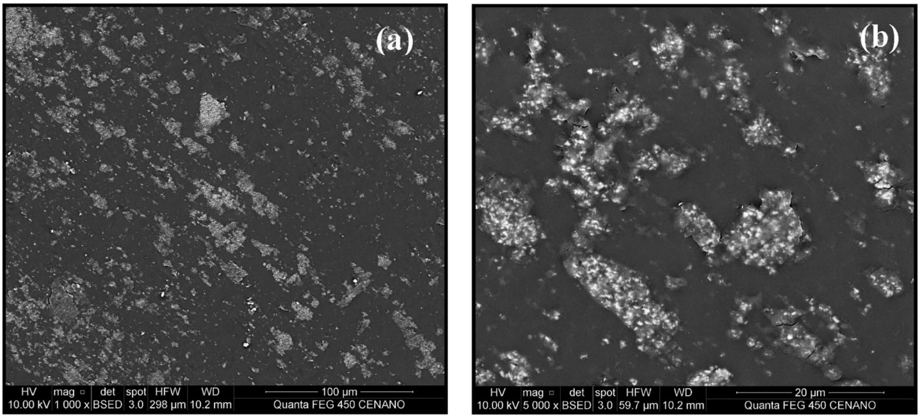

Figure 5.
SEM images of NBR/LDH$_n$ without surfactant: (a) magnification = 1000x and (b) magnification = 5000x.

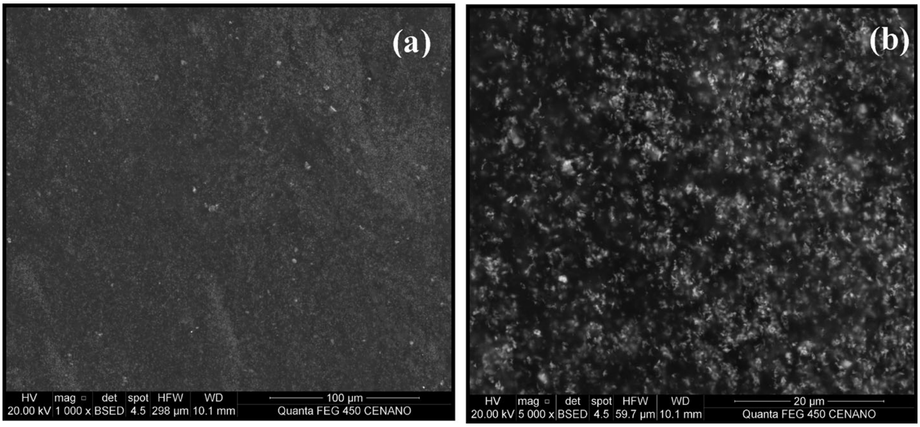

Figure 6.
SEM images of NBR/LDH with surfactant: (a) magnification = 1000x and (b) magnification = 5000x.

particles can cause agglomeration of aqueous dispersions without surfactant. Even a small amount of surfactant (0.5% wt) is capable of optimizing the LDH dispersion in NBR latex by reducing the particle size. Simultaneously, the viscosity results showed a slight increase in viscosity of the latex suspensions, which can be related to stronger filler-rubber interaction.

For the coagulated systems, it was not possible to differentiate the degree of dispersion of the composites by X-ray diffraction, since the results were similar. However, it was possible to confirm the stability of the clay dispersion with greater incorporation of filler in the matrix in the presence of surfactant, by measuring the ash content. The same behavior was found for the theoretical prediction of filler dispersion given by Payne effect. The smaller the value of $\triangle G^*$, the stronger the filler-matrix interaction (Payne effect), indicating better dispersion of the particles in the matrix. For the systems with surfactant, $\triangle G^*$ was lower, suggesting better dispersion. This result agrees with the FESEM-FEG micrographs, which show more homogeneous dispersed particles.

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