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To cite this article: E Álvarez and E A Murillo 2019 *J. Phys.: Conf. Ser.* **1386** 012082

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Rheological, morphological, film and thermal properties of emulsions of polyvinyl acrylic resins, carboxymethyl cellulose and titanium oxide

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Abstract. The study of the physical-chemistry properties of dispersions are very important in the coating industry, since of it depend the application and stability of these systems. Therefore, the aim of this investigation was evaluated the influence of the dispersion rate and titanium dioxide content in the rheological (steady and dynamic analyses), colloidal, morphological, films, and thermal properties of waterborne dispersions based on polyvinyl acrylic resin, carboxymethyl cellulose and titanium oxide. In this work were used two proportions of titanium oxide (5.51 wt% and 10.44 wt%) and the following dispersion rates: 900 rpm, 1200 rpm, 1500 rpm and 1725 rpm. The materials were characterized by rheological, dynamic light scattering, scanning electronic microscopy, adherence, hardness, flexibility and thermogravimetric analyses.

1. Introduction

In the coating industry are used waterborne dispersions, since these materials are friendly environmentally due to that they exhibit low amount of volatile organic compounds (VOCs) [1-4]. In this industry is employed titanium dioxide (TiO_2) [5,6], since this material has photochemistry and anti-fouling properties, good chemical stability, non-toxicity and low-cost [1,6,7]. However, the main issue of the dispersions obtained by using TiO_2 is the dispersion of the particles, since during the preparation and post-preparation of the dispersions may occur aggregations, which affect the colloidal stability and rheological and films properties of the dispersions. Furthermore, application properties like leveling out of brush or roller marks need to be improved to make waterborne paints competitive with solvent-based products [8]. Another hand, for the coating industry is important the study of the colloidal and rheological properties of the dispersions, since it is a critical factor for obtaining a good performance of these materials [9,10]. Waterborne dispersions usually exhibit inferior leveling regards to solvent-based paints. However, this behavior is caused by the divergent viscosity–solid content relationship for dispersions and emulsions and by the relatively high evaporation rate of water [8].

In the literature there are some reports of the use of the TiO_2 in the preparation of dispersions [5]. Paint made from acrylic copolymer and TiO_2 , acrylic copolymer/siloxane (60/40) and TiO_2 , were prepared and the evaluation of the photochemical properties and emission of VOCs was realized [5]. In another study were obtained dispersions of a commercial resin (eusolex) and nanometer-sized TiO_2 . These materials exhibited good stability. However, in this study was not evaluated the rheological behavior [11]. In another study was done the stabilization of pickering emulsion with surface-modified TiO_2 for being used in the photocatalytic degradation of red 80 [12].



According to our revision of the literature, there are few reports of the influence of the dispersion rate or TiO₂ content on the rheological, morphological, film, and thermal properties of dispersions of polyvinyl acrylic resins, carboxymethyl cellulose and TiO₂. Therefore, this study will contribute to the art state of this type of material.

2. Materials and methods

The polyvinyl acrylic resins were supplied by Aquaterra factory (solid percentage of 55 wt%), TiO₂ BL R-699 was provided for Henan Billions Chemicals, the particle size is 0.37 μm (d_{50}) and 0.55 μm (d_{90}). The carboxymethyl cellulose (CMC) was supplied by Samsung Fine Chemicals.

2.1. Preparation of the dispersions

This formulation was based in the used by the alvartex factory (Colombia). In order to prepare the dispersions, initially was added the respective proportion of water (38.27 wt%) and then was dissolved the corresponding amount of polyvinyl acrylic resin (10.44 wt%) by using the corresponding dispersion rate during 5 min. Posteriorly was make the addition of the amount of TiO₂ and the system was kept under stirring during other ten min. Finally, was added the CMC amount (0.35 wt%) and the other components (antifoam, water, calcium carbonate, biocide, propylenglycol, texanol, hiresol 180, acuapolymer SA5020, pine oil and nonylphenol etoxylate) during 30 min keeping the stirring. Table 1 presents the dispersion rates and the TiO₂ amounts employed in the preparation of the samples.

Table 1. Dispersion rate and TiO₂ content employed in this study.

Samples	Dispersion rate (rpm)	TiO ₂ (wt%)
M1	950	5.51
M2	1150	5.51
M3	1450	5.51
M4	1725	5.51
M5	950	10.44
M6	1150	10.44
M7	1450	10.44
M8	1725	10.44

2.2. Characterization of the blends

Rheological analyses under steady and oscillatory conditions were realized in a rotational rheometer of TA instruments using a plate-plate geometer whose diameter was 20 mm and at room temperature. The gap was of 1 mm. The oscillatory analysis was done at angular frequency between 1 Hz and 100 Hz and a deformation of 0.2%. Dynamic light scattering (DLS) analysis was done at room temperature in a Nano-ZS of Malvern Instruments by employing a wavelength of 633 nm and an incidence angle of 173°. For it were used solutions (1 wt%) of the dispersions. Scanning electronic microscopy (SEM) analysis was executed in a Jeol JSM-6490LV. Samples obtained were made conductive by the deposition of a layer of gold. The analysis was realized to the dry films using a beam acceleration voltage of 20 kV. The analysis of the film properties was based on american society for testing and materials (ASTM); adherence (ASTM D 3359) [13], hardness (ASTM D 3363) [14] and flexibility (ASTM D 522) [15]. The TGA analysis was executed in a TA Instruments SDT Q600 equipment using a heating rate of 20 °C/min. from room temperature until 600 °C employing a purge of nitrogen.

3. Results and discussion

Figure 1 shows the rheological behavior of the samples under steady conditions. The samples exhibited a thinning shear behavior; it was possibly due to disentanglements of the chains and dissociation of the interactions. The same behavior has been observed for dispersions obtained using TiO₂ [16]. The samples obtained with the proportion of 5.51 wt% of TiO₂ (M1, M2, M3 and M4) did not show a trend with the dispersion rate, this may be due to different interaction degree between components and to the

number of aggregations. The same behavior was exhibited by the samples prepared employing 10.44 wt% of TiO_2 (M5, M6, M7 and M8). However, these samples presented higher kinematic viscosity (η) than those obtained using the lowest amount of TiO_2 (5.51 wt%), which possibly is related with the particle size of these materials.

The rheological behavior of the samples under oscillatory conditions (Figure 2) did not show dependence with the dispersion rate, but the behavior of the complex viscosity (η^*) was different than that observed under steady conditions, since it was detected a reduction on η^* , but then it increased, this means that probably was carried out a formation of a microstructure which is able to elastically deform. This phenomenon was not observed in the analysis done under steady conditions because during this analysis happens the destructure of the chains. Therefore, the system is not recovered, because this analysis is not realized in the linear viscoelastic region, but the oscillatory analysis if it is performed in this region.

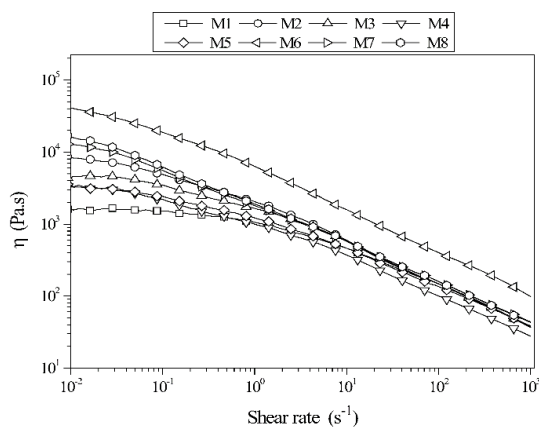


Figure 1. Graphs of η vs shear rate of the samples.

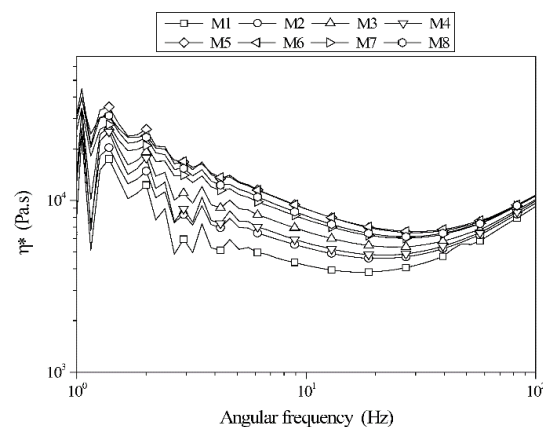


Figure 2. Graphs of η^* vs angular frequency of the samples.

By DLS analysis was observed that all samples exhibited aggregations and the distributions were polymodal (Figure 3 and Figure 4). This result is according with that observed by rheological analysis. According to the results, none dispersion rate was able for obtaining a monomodal system since in all cases was observed two or more size distributions, it also may be associated with the proportion used of surfactants and dispersants which possibly were not enough to make a good dispersion and stabilization of the particles.

Table 2 shows the particle size exhibited by the samples where can be observed that similar to results of the rheology were not observed a dependence with the dispersion rate and TiO_2 amount.

Figure 5 and Figure 6 exhibit the micrographs of the samples M6 and M7 respectively, which were obtained by SEM analysis. It can be observed the morphology of the particles is not completely spherical since during the solvent evaporation, the superficial tension increased. Despite of it, the formation of the films is good because the samples evaluated presented a continuous form.

The adherence of the samples obtained with 5.51 wt% of the TiO_2 was higher than those obtained using a 10.44 wt% (Table 2). In the case of the hardness (Table 2), the values did not show a great difference. According to the results it can be seen that the adherence and hardness did not exhibit a trend with dispersion rate, which possibly is related to aggregations and different degree of interactions between components.

The flexibility of the samples was good since none sample was broken during the analysis. The behavior observed by rheological analysis, DLS, adherence and hardness was the same showed in thermal stability since the decomposition temperature (T_d) of the samples, which was determined by TGA analysis (Figure 7) did not follow a trend with dispersion rate and TiO_2 content. However, these materials presented an acceptable thermal stability (Table 2). In a study was observed that the thermal

stability of the waterborne dispersions increased with the TiO₂ content [1]. In the present study it only was saw to the samples M6, M7 and M8, which is possibly due to the interaction between the components, which has been observed to system of TiO₂ and calcium carbonate [17].

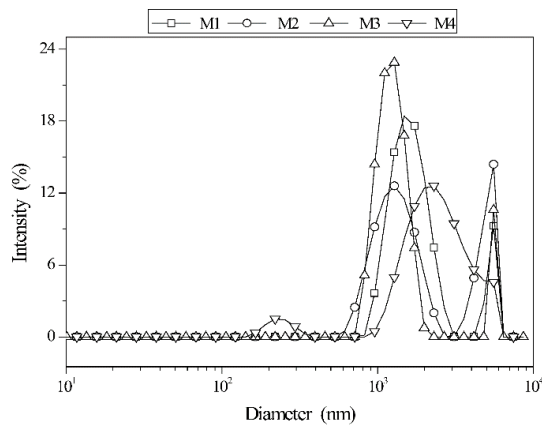


Figure 3. Distributions of size of the samples obtained with 5.51 wt% of TiO₂.

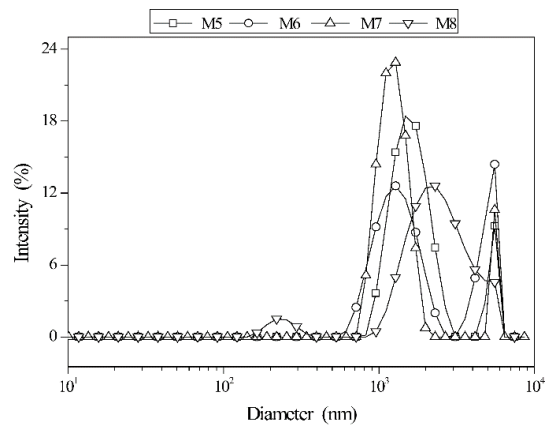


Figure 4. Distributions of size of the samples obtained with 10.44 wt% of TiO₂.

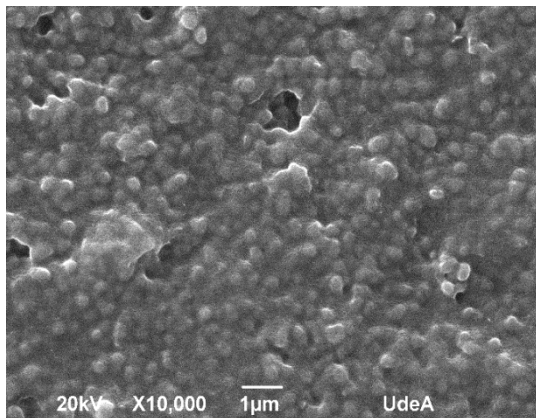


Figure 5. Micrograph of the sample M6.

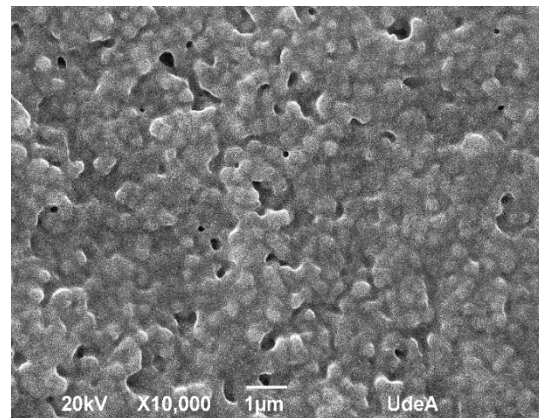


Figure 6. Micrograph of the sample M7.

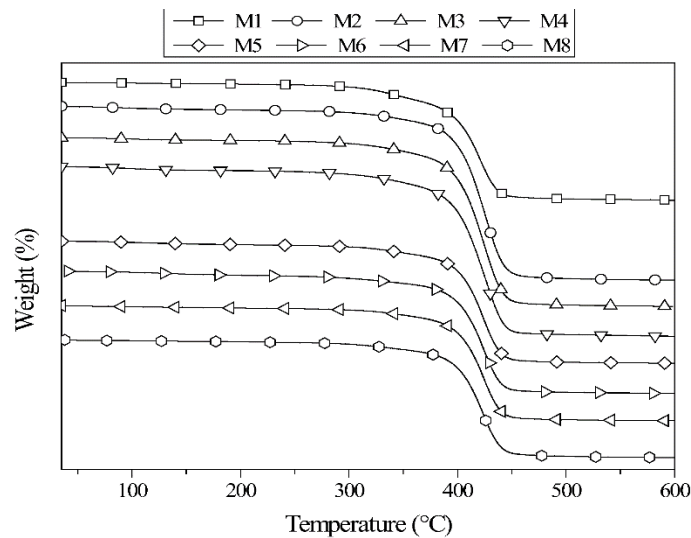


Figure 7. TGA thermograms of the samples.

Table 2. Values of particle diameter, adherence, hardness, flexibility and T_d of the samples.

Samples	Particle diameter (nm)	Adherence	Hardness	Flexibility	T_d ($^{\circ}$ C)
M1	1347-5497	4B	2B	Passed	293
M2	1287-4201-203	5B	B	Passed	297
M3	996-5381	4B	2B	Passed	276
M4	760-5560	4B	B	Passed	285
M5	1700-5420	2B	B	Passed	280
M6	1319-4994	3B	2B	Passed	298
M7	1240-5560	1B	B	Passed	295
M8	238-2649	3B	B	Passed	296

4. Conclusions

In this study were obtained waterborne dispersions based mainly in polyvinyl acrylic resins, CMC and TiO_2 . The effect of the dispersion rate and the TiO_2 content were evaluated. The rheological behavior of the samples was mainly pseudoplastic. All samples exhibited two or more distributions, which indicated that the samples presented aggregations. By SEM analysis was observed that the analyzed samples exhibited a continuous form. The rheological, thermal and film properties of the sample did not show a trend with the dispersion rate and TiO_2 content, this was possible due to aggregations and different interaction degree between the components. However, the film properties evaluated to these samples were acceptable.

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