Latex Film Performance of Styrene–Acrylic Particles Functionalized with Acrylic Acid

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ABSTRACT: Latex polymers are frequently used as substitutes for solvent-borne coatings in environmental friendly technologies. However, the relationship between the copolymer composition and the latex film performance must be established. The preparation of a series of styrene–n-butyl acrylate latexes functionalized with different amounts of acrylic acid through semicontinuous emulsion polymerization is presented. In this work, latexes were employed to study the modification of the latex film properties by the addition of acrylic acid during the polymerization; mainly, the adhesion to the substrate, the water vapor permeability, and the electrical film resistance were examined. The most advantageous acrylic acid content was established by a balance of the tested properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 553–557, 2009

Key words: adhesion; coatings; films

INTRODUCTION

The environmental impact of volatile organic compounds has stimulated the substitution of solvent-borne coatings with environmental friendly technologies, such as powder, ultraviolet-cured, and water-borne coatings.[1–3] However, the properties of solvent-borne coatings, such as adhesion to the substrate, low water uptake, and water vapor permeability, as well as the esthetic appearance, cannot be easily obtained with water-borne coatings. In addition, the cost of the raw materials and production processes must remain low.[4]

Latex polymers are an attractive alternative because they use water as a continuum medium, and so they have been studied by the academic and industrial communities. Specifically, styrene–acrylic copolymers have received special attention in the search for high-performance coatings.[5] Often, small amounts of functional monomers are added to formulations to increase specific latex properties. For example, acrylic, methacrylic, and itaconic acids are commonly employed monomers that enhance latex stability and the adhesion of latex films to substrates.[6] Nevertheless, this kind of monomer must be added with care because other important characteristics may be affected.[7–9] Therefore, it is important to establish the appropriate amounts of functional monomers needed to obtain a good balance of the main coating properties.

A common technique for improving the adhesion of latex films involves the use of adhesion promoters. These can take the form of chemical agents or metallic thin films, with different mechanisms responsible for the enhancement of adhesion. Covalent groups can generate interconnecting covalent bonds with the surface layer, but some functional groups bond only to the substrate and enhance adhesion through electrostatic and van der Waals interactions.[10] The former mechanism seems to be important for the way in which acrylic acid (AA) increases the adhesion of polymeric films.

The film formation process from a latex is a complex phenomenon that seriously affects the coating performance. Usually, film formation is divided into many steps.[11,12] First, the polymeric dispersion is applied over the substrate. As water evaporates, the particles tend to pack in an ordered array; the structure achieved in this step is a function of the water evaporation rate and interparticle interaction. If the repulsion between particles becomes stronger, the structure of the film may not be compact enough. The interparticle interaction can be tuned by the addition of salts and by the modification of the particle charge density.[13] Finally, the boundaries between the polymeric colloids disappear by polymer chain interdiffusion.

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TABLE I
Formulation Employed in the Synthesis of Styrene–*n*-Butyl Acrylate
Particles Functionalized with Different AA Contents

Substance	Main reactor (g)	Feeding tank (g)
n-Butyl acrylate	0.0	120.0
Styrene	0.0	120.0, 117.6, 115.2, 110.4, 105.6, 96.0
AA	0.0	0.0, 2.4, 4.8, 9.6, 14.4, 24.0
Ammonium persulfate (5 wt %)	26.0	70.0
Sodium bicarbonate (1 wt %)	2.4	0.0
Abex (10 wt %)	0.0	60.0
Disponil (10 wt %)	0.0	60.0
Water	142.0	0.0

The total amount of the monomer was fixed so that as the amount of AA increased, the same quantity of styrene was removed from the formulation.

In this article, the synthesis by seeded semicontinuous emulsion polymerization of monodispersed styrene–acrylic latex particles functionalized with different amounts of AA is presented. These polymer dispersions were employed to obtain a series of latex films, which then were characterized by standard adhesion methods and electrochemical techniques. It was found that increasing the AA content in the copolymer enhanced the adhesion of the film to the substrate, but barrier properties of the film were seriously affected, as observed by electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Materials

Industrial-grade monomers (Celanese, Mexico)—styrene, *n*-butyl acrylate, and AA—were used without further purification. Ammonium persulfate was used as an initiator, and sodium bicarbonate was used as a buffer; both were reactive-grade (Aldrich, Mexico). A mixture of two nonionic surfactants was employed: Abex 26S by Rhodia (USA) and Disponil EPS by Cognis (USA). Distilled and deionized water was used throughout the synthesis and dilutions of the latex.

Synthesis of the styrene–acrylic emulsions

A series of polymer particles consisting of copolymers of *n*-butyl acrylate and styrene with different amounts of AA were synthesized as previously reported.[14] The latex formulation is given in Table I. Emulsion polymerization was carried out in a semicontinuous reactor composed of a 1000-mL glass vessel and a feeding tank under an atmosphere of N_2. The main reactor was loaded as shown in the formulation, except for the initiator. Once the reaction temperature was reached, the initiator solution was added. Then, after 10 min, the addition of the pre-emulsion from the feeding tank started. To obtain large-particle diameters, the synthesis of a seed was not used. The addition time was about 180 min. The final solid content of all polymer dispersions was close to 40 wt %, as designed. The latex particle size distribution was determined by quasielastic light scattering (QELS) with a Malvern Autosizer 4800 spectrometer with a Coherent Innova 90 c laser device; a diluted sample was used. All latex samples were neutralized with a concentrated NaOH solution.

### Preparation of the latex films

Four different latex films were prepared on AISI 1018 low-carbon steel for electrochemical analysis; the metal plates were sanded with 600 paper and cleaned with acetone. They were dried at room temperature (25°C and 50% relative humidity) for 5 days. All coatings reached a thickness between 90 and 150 μm as determined with an Elcometer 345 coating thickness gauge.

A series of latex films, prepared on a glass substrate, were employed to measure the adhesion with ASTM Standard D 3359-02,[15] which reports the percentage of the residual area. In a parallel experiment, a second series of latex films were carefully peeled from the glass substrate to obtain free films, which were used to measure the water vapor permeability with ASTM Standard E 96/E 96M-05[16] (specifically the wet cup method). These films were obtained at the same temperature and relative humidity.

All experiments were run with three different samples, and the mean values are reported. The standard deviation is of the order of the symbol size.

Measurements of the electrochemical coating properties

EIS was carried out with a Gill potentiostat in the frequency range of 10^4–10^{-1} Hz with an amplitude of 10 mV. The electrolyte was a 3 wt % NaCl
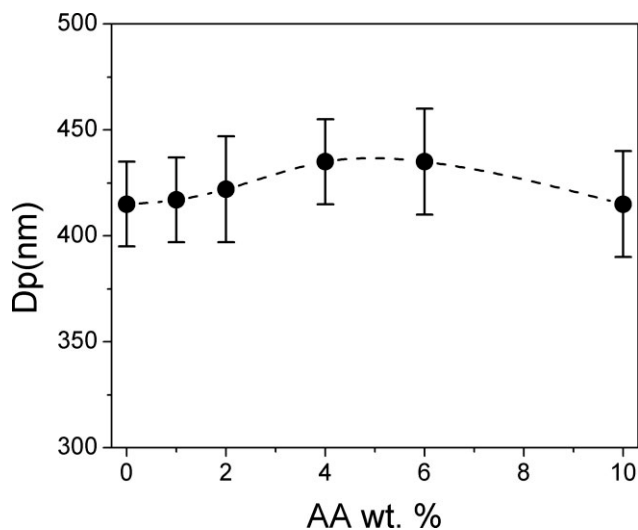
Figure 1 Particle diameter (D_p) obtained by QELS as a function of the AA content. All the polymeric particles achieved a polydispersity index lower than 1.09.

solution in a typical three-electrode arrangement with a saturated calomel reference electrode and graphite as the counter electrode. All impedance measurements were carried out in a Faraday cage to minimize external interference with the studied system. The data analysis was interpreted under the assumption of an R(RC) equivalent circuit at a high frequency range with Zview software,[17] and the resistance of the films is reported.

RESULTS AND DISCUSSION

The content of AA in different styrene–*n*-butyl acrylate emulsions was varied to study its influence on the coating properties. The characterization of the polymeric dispersions by QELS showed that all the latexes were monodisperse in size, with a polydispersity index lower than 1.09. The effect of the functionalization with AA on the final particle size is reported in Figure 1. At first, there is a slight increase in the particle size as a function of the AA content. This could be due to the hydrophilic nature of AA, which tends to form a hairy corona around the polymeric particles. After reaching a maximum at about 4 wt % AA, the particle diameter decreases as a result of the saturation of carboxylic negative charges on the particle surface, causing shrinkage of the polymer particles.[18,19] However, the particle diameter variation does not seem to be very large, and the modification of the coating properties can be attributed to the other parameters discussed next.

The main properties that we evaluated to determine the best combination for coating performance were adhesion to the substrate, water vapor permeation, and coating electrical resistance. In Figure 2, the film adhesion with glass as the substrate is pre-

sented. In this test, the residual area covered by the film after the removal of a pressure-sensitive tape was determined. With no AA content (0 wt % AA), we can observe that most of the film is removed by the pressure-sensitive tape because only about 20% of the tested area is still covered by the latex film. By increasing the AA content in the formulation, we can observe a linear augmentation of the adhesion as a function of AA. Nonetheless, after 6 wt % AA, the film completely adheres to the glass substrate. This is a clear indication that the addition of AA increases the adhesion to the glass substrate. This phenomenon might be related to the polarity increase of the copolymer with the addition of AA, which increases the van der Waals interactions with the substrate.[20]
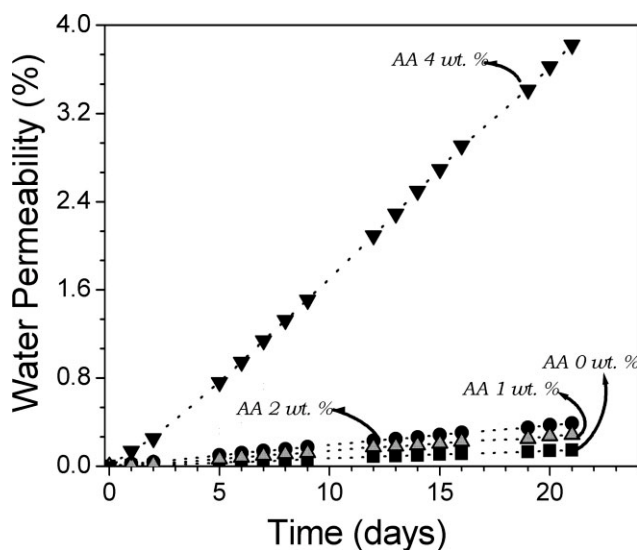
In Figure 3, the water vapor permeability, studied by the wet cup test, is presented. Among several experimental techniques used to determine the latex film structure, water vapor permeability and gas sorption offer inexpensive and nonlaborious ways of correlating some film properties with the film structure. In the figure, we can see that the lowest permeability is achieved by the system unfunctionalized with AA. Afterward, increasing the amount of AA in the formulation enhances the passage of water vapor through the film. The data for the films with 6 or 10 wt % AA are not reported because it was not possible to obtain free films without defects on account of their high adhesion to the substrate. All the latex films were prepared in the same way, so the main difference in the coating properties was a result of the AA content. As mentioned previously, the addition of AA increases the repulsion between polymeric particles during film formation, so a noncompact structure is generated during latex film
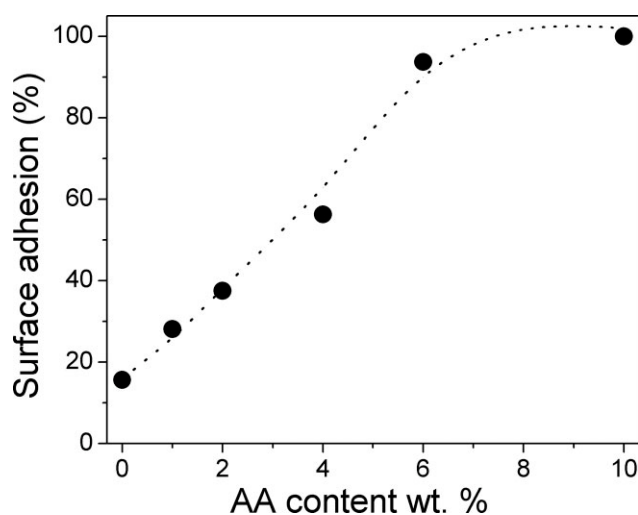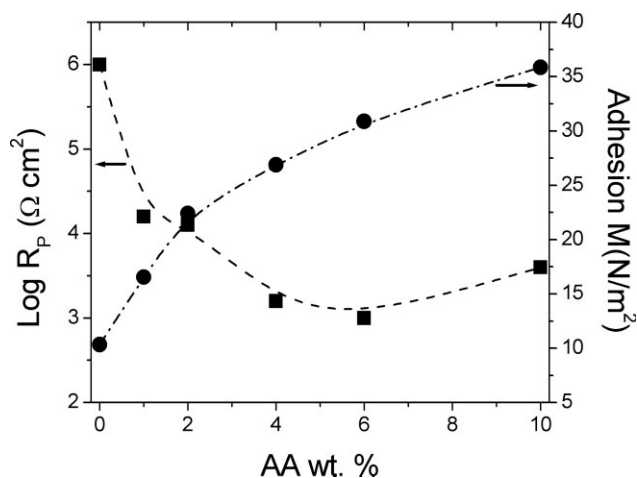

Figure 2 Adhesion of the latex film measured according to ASTM Standard D 3359-02 as a function of AA with glass as the substrate.

formation, and the water vapor can permeate films with high AA contents without much difficulty. In addition, a significant amount of AA on the polymeric particle surface could be responsible for the formation of hydrophilic channels between the particles.[6] Therefore, the higher the amount of AA is, the greater the water vapor permeability is.

Because EIS can be used to evaluate film properties without the removal of the film from the substrate, it is a practical technique that provides useful information about the performance of the substrate/coating system. For example, the film resistance can be related to the mobility of the hydrated ions inside the film, and this can provide information about the ability of the film to isolate the substrate from its environment. High film resistance means that the ions are not able to move easily because the film might be compact or have a low defect content or its hydrophilicity is rather low. In Figure 4, the film resistance after 12 h of continuous immersion is plotted as a function of the AA content. High film resistance is attained with 0 wt % AA because in this system the null number of carboxylic groups on the particle surface might generate a film with a compact structure. By the addition of 1 wt % AA to the formulation, the film resistance drastically decreases (the film resistance is given on a log scale), that is, by 2 orders of magnitude. This behavior could be explained in terms of the greater repulsion between the polymeric particles with the addition of carboxylic groups, which acquire a negative charge. Therefore, the higher the number of surface charges is, the higher the repulsion among the particles is. This effect may be responsible for the formation of a noncompact structure during film formation. Also,

Figure 4 Behavior of (■) the film electrical resistance (R_p) and (●) the adhesion of the film to the metallic substrate as a function of the AA content.

the addition of AA enhances the hydrophilic nature of the copolymer, so the electrolyte uptake is augmented as well. In the same figure, we can observe that with the addition of more than 4 wt % AA to the copolymer, there is a decrease in the film resistance, but the order of magnitude of the film resistance remains the same.

In the same figure, the adhesion of the latex film to the metal substrate is reported on the right-hand axis, as measured by the ASTM D 4541 method.[21] The same behavior found with the glass substrate can be observed; that is, the higher the amount of AA is, the better the adhesion of the latex film is to the metallic substrate. However, in this test, a linear increase in the adhesion is not observed; however, after approximately 4 wt % AA, there is not a significant increase in the adhesion. At 4 wt % AA, the particle diameter reaches a maximum (see Fig. 1), and this means that the particle surface is saturated with the charges of the carboxylic group. It has been reported that the addition of carboxylic acid sticker groups abruptly enhances the adhesion of polybutadiene to aluminum.[22] Therefore, the saturation of the particle surface with carboxylic groups improves the adhesion of the latex film to the metallic substrate.

Figure 3 Water vapor permeability of the latex films functionalized with different percentages of AA as a function of time.

CONCLUSIONS

In this article, the modification of styrene–acrylic latex film properties by AA has been presented. The tested properties include adhesion to the substrate, water vapor permeability, and film resistance. It has been observed that there is a compromise between the adhesion of the film and its barrier properties. The adhesion increases with the addition of AA up to approximately 4 wt %; afterwards, this property remains nearly constant. However, the addition of

AA diminishes the barrier properties of the latex films, as revealed by water vapor permeability and electrochemical measurements. It can be concluded that the best combination of film properties for this system occurs around 4 wt % AA.

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