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Yazar(lar) (Author(s)): Onur YILMAZ¹, Catalina Natalia CHEABURU-YILMAZ²

ORCID¹: 0000-0002-0992-5937

ORCID²: 0000-0001-5229-8986

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Synthesis and Application of a Low Emulsifier Content Composite Polyacrylic Latex for Leather Finishing

Araştırma Makalesi / Research Article

Onur YILMAZ^{1*}, Catalina Natalia CHEABURU-YILMAZ²

¹Ege University, Faculty of Engineering, Leather Engineering Department, 35100, Bornova, Izmir, Turkey

²Petru Poni Institute of Macromolecular Chemistry of the Romanian Academy, Laboratory of Physical Chemistry of Polymers, 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania

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ABSTRACT

A composite polyacrylic latex via two stage seeded emulsion polymerization with low emulsifier content (0.5 wt.%) was synthesized and characterized by means of particle size and zeta potential analysis, FTIR and differential scanning calorimetry (DSC). The results verified a very uniform particle size distribution and good electrostatic stability. The different phases of the composite polymer were evidenced by DSC analysis with two clear phase transitions. The application of the latex on leathers as coating binder revealed good fastness levels to dry/wet rubbing and water spotting. The synthesized composite latex was found to be good candidate for producing cost-effective waterborne binders with good performance.

Keywords: Composite latex, leather finishing, coating, acrylate, emulsion polymerization.

Deri Finisajı için Düşük Emülgatör İçerikli Kompozit Yapılı bir Poliakrilik Lateks Sentezi ve Aplikasyonu

ÖZ

Kompozit yapılı bir poliakrilik lateks, iki aşamalı tohumlanmış emülsiyon polimerizasyonu ile düşük emülgatör içerikli (ağ. %0.5) olarak sentezlenmiş; partikül boyutu ve zeta potansiyeli analizi, FTIR ve diferansiyel taramalı kalorimetri kullanılarak karakterize edilmiştir. Elde edilen sonuçlar lateksin çok homojen bir partikül boyutu dağılımına ve iyi elektrostatik stabiliteye sahip olduğunu göstermiştir. Kompozit polimerin farklı fazları DSC analizi ile iki net faz geçişi olarak ortaya konmuştur. Lateksin mamul derilerde kaplama binderi olarak uygulanması sonrasında, yaş/kuru sürtme haslıkları ile su damlası haslığı testlerinin iyi sonuçlar verdiği gözlemlenmiştir. Sentezlenen lateksin, iyi performansla sahip, düşük maliyetli su bazlı binderlerin üretimi için iyi bir aday olduğu tespit edilmiştir.

Anahtar Kelimeler: Kompozit lateks, deri finisajı, kaplama, akrilat, emülsiyon polimerizasyonu.

1. INTRODUCTION

Acrylic latexes are widely used as waterborne coating polymers for many industrial applications, especially for paints and coatings [1,2]. Due to resistance to hydrolysis, high block resistance, hardness–softness, good adhesiveness, good film forming properties, resistance to UV light and inexpensiveness of acrylates, they are also the most common commercial binders

used in leather industry [3-5]. On the other hand, the physical and chemical performance of the acrylic polymers are substantially lower than polyurethane based binders leading in general to a reduction in the overall performance of the finish [6]. However, the higher cost of polyurethane based finishing systems encourages the efforts to increase the performance of acrylic based polymers.

In the last decade the composite latex particles are of great importance since their physical properties can be tailored [7]. They are widely used in industrial applications, e.g., coatings, paints, adhesives, paper, textile manufacturing, etc [8-16]. These materials usually have better properties than those of conventional polymers and/or blending of two or more polymer components [17]. Such kind of latexes are commonly known as composite or core-shell latexes and are usually made by emulsion polymerization in a two or multi-stage process where in the first step a seed latex (core) is formed from a monomer composition and in the second step another monomer composition is polymerized over the core to form the shell [16,18]. The polymers with two distinct phases usually have different compositions leading to different properties such as hardness and softness, hydrophobicity, molecular weight, adhesion, etc., which affect the properties of the final polymer. In this way, the advantages of different polymer

*Sorumlu Yazar (Corresponding Author)
e-posta : onur.yilmaz@ege.edu.tr

characteristics can be combined to enhance the final performance of coatings. Some efforts already have been made by using composite technology to increase the performance and functionality of acrylic binders for leather finishing. Krings et al. [6] reported on the development of polyurethane-polyacrylate hybrid materials to be used in finishing application. They marked the improved polymer properties and finishing performance of the urethane/acrylic hybrid polymer dispersions that cannot be achieved by typical polymer dispersions. Qinhuan et al. [19] prepared acrylic core-shell latexes including fluorine containing monomer in the second phase composition and they tested the performance of finished leathers. They used butyl acrylate (BA) and methyl methacrylate (MMA) monomers both in the phase compositions, and dodecafluoroheptyl methacrylate in the second phase. They obtained improved water contact angles and wet rub resistance for composite latex coated leathers. A cationic polyacrylate emulsion with a core-shell structure by seeded emulsion polymerization was reported by Sui et al. [20]. BA and MMA comonomers were used in both core and shell parts and a cationic monomer synthesized by reacting dimethylaminoethyl methacrylate (DMAEMA) and n-butyl bromide used in the shell composition. They observed that the leathers coated with cationic core-shell latex showed many improvements with strong adhesion and resistance to dry and wet rubbing. Liu et al. [21] prepared polyacrylate/nano-SiO₂ core-shell composite latexes via semi-continuous emulsion polymerization stabilized with polymerizable surfactant. They used the core-shell latex for finishing of leathers and obtained better resistance to water uptake, improved water vapor permeability and increased dry and wet rub fastness properties. Another study describing the preparation of a core-shell resin emulsion with styrene, methyl methacrylate, acrylonitrile as monomer; butyl acrylate, methyl methacrylate, acrylic acid as shell monomer was reported by Zhao and Zhao [22]. They also introduced nano-TiO₂ in the shell phase as well as a crosslinking agent in low amounts. They showed that the leathers finished with core-shell emulsion exhibited good resistance to solvent, wet and dry rubbing. In recent studies by Ma et al. [23,24] the syntheses of core-shell structural casein based latexes and their potential application in leather finishing also have been reported. All these studies in the last years show that there is an

increasing interest on synthesis of composite polymeric latexes to obtain high performance leather finishing agents. However, in many studies fluorine or silicone containing moieties have been used to improve the performance of the coating which affects greatly the cost of their production.

Surfactants play a crucial role in the production of emulsion polymers as emulsification of monomers, formation of micelles as polymerization loci and colloidal stabilization of particles. However, they have also tendency to cluster together or migrate either to the film-air interface or the film-substrate interface. In this way they affect the water sensitivity of the coating, as well as the adhesion characteristics especially when they are used in high amounts. The polymerizable surfactants used to overcome this problem often have less reactivity in comparison to the monomer units which may lead to poor incorporation or homopolymerization of the surfactants in water phase [25]. Surfactant-free emulsion polymerization approach took attention the last decade and can also be used to produce latexes. However, they usually result in larger particle sizes, increased amount of coagulum or filterable solids/scraps and decreased shelf-life stability due to the lack of emulsifiers [26]. Therefore, for the production of low particle size and long term stable latexes the use of surfactants to some extent seems unavoidable especially for the latexes used for coating purposes. On the other hand, by proper monomer compositions and control on the polymerization surfactant level can be minimized. Present study describes the synthesis of a stable composite acrylic latex by a two stage seeded emulsion polymerization with low emulsifier content to obtain high performance finishing binder in a cost effective manner by using common and cheap components. The polymer characteristics and the performance properties of the coated leathers were discussed in the study.

2. MATERIALS AND METHODS

2.1. Materials

For the synthesis of acrylic latex, butyl methacrylate (BMA), 2-hydroxyethylacrylate (HEA), butyl acrylate (BA) and methacrylic acid (MAA) were supplied from Aldrich and used as monomers. The other necessary chemicals; sodium dodecyl benzene sulfonate as emulsifier (SDBS, C₁₈H₂₉NaO₃S, tech. grade), potassium

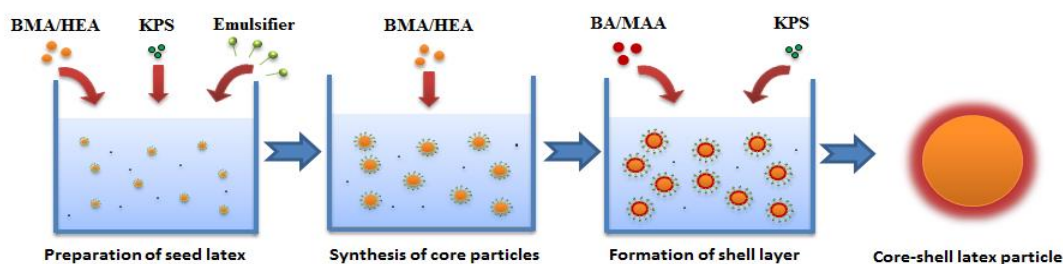


Figure 1. Synthesis route of the core-shell latex

persulfate (KPS, $K_2S_2O_8$, $\geq 99\%$) as initiator, sodium bicarbonate ($NaHCO_3$, $\geq 99.5\%$) as buffer and sodium hydroxide ($NaOH$, $\geq 99\%$) as a general alkaline were also supplied from Aldrich. All chemicals were used as received without any further purification.

A crust bovine upper leather was supplied from a regional tannery company (Sepiciler Inc. Co., Izmir-Turkey) and was used for leather finishing application. Other necessary commercial chemicals for finishing such as pigment, wax, aqueous nitrocellulose lacquer and surface modifier were supplied from different leather chemical suppliers.

2.2. Synthesis of the Composite Acrylic Latex

The composite latex was designed to have a hard polymer core (phase-I) that consist of BMA and HEA monomers in a weight ratio of 59:1, and a second phase (phase-II) including BA and MAA with a ratio of 38:2 (w:w). The ratio of the different phases (hard/soft) was chosen as 60:40 by weight, respectively. For the preparation of composite latex particles, selected amount of SDBS emulsifier, $NaHCO_3$, half of KPS initiator solution were first dissolved in water and mixed in the reactor for 15 min under nitrogen flow. One third (1/3) of phase-I monomers were first introduced in the system and purged with N_2 to remove the dissolved oxygen and they were polymerized at 70 °C for 45 min to prepare the seed polymer particles. Afterwards, the remaining of the phase-I monomers was dropped into the system within 1 h and kept for another 1.5 h to obtain the first phase latex particles. After the completion of first phase synthesis, the phase-II part monomers were added dropwise into the reactor within 1 h which was followed by the addition of remaining initiator solution. The reaction was kept for additional 2 h at 80 °C for completion of the reaction. At final, the system was cooled down to room temperature and the composite latex was obtained with a total solid content of 25% and a conversion ratio over 99% (measured gravimetrically). The general route of the synthesis was presented in Figure 1. The copolymer films necessary for analysis were obtained by casting the emulsion on a glass substrate and drying at room temperature for 3 days and in oven at 70°C for 1 day.

2.3. Experimental Methods

A nanoZS model (Malvern Instruments UK) zetasizer instrument was used for the measurement of particle size and zeta potential of the latex. The IR spectra of the

copolymer film were recorded with a Perkin-Elmer Spectrum-100 ATR-FTIR instrument by scanning in the range of 600-4000 cm^{-1} . Differential scanning calorimetry (DSC) thermographs were recorded with a Perkin Elmer Diamond DSC instrument at a heating rate of 10 °C/min under N_2 atmosphere from -70 to 120°C. The imaging of the finish layer of the leather samples was performed by Hitachi TM-1000 Table-Top scanning electron microscope and the magnitudes are given on the images.

2.4. Application of the Composite Latex in Leather Finishing

For finishing application rectangular leather specimens (30 × 40 cm) were cut from the coupon part of the leather. The formulation of finishing mixture consisted of a pigmented coat and a top coat (Table 1). The coating layers were applied by a hand spraying gun with air pressure of 3 atm. After the application of each cross spray, the leathers were dried at 90 °C in a drying tunnel for 3 min and hot plated at given intervals. The formulation was prepared as simple as possible for an easier evaluation of the effect of the composite binder on finish properties. The finished leathers to be tested by physical methods were conditioned according to the standard of ISO 2419:2012 [27]. The efficiency of finishing applied on leathers was evaluated by the physical tests of; flexing endurance [28]; color fastness of leather to To and Fro rubbing [29]; color fastness to water spotting [30]. The evaluation of all the tests related to color change was done according to the Grey Scale Standard (IUF 131-132) which gives a rating between 1 and 5 (5: means no color change, and 1: means failure).

3. RESULTS AND DISCUSSION

3.1. Design of Latex Particles

The selection of monomer phases and their ratios were made according to the softness, adhesion and abrasion resistance of the final polymer. Because the leather is a flexible material, the final polymer had to be soft enough to be compatible with the substrate. Therefore, monomers of the first phase were selected to give a relatively hard polymer in nature (glass transition temperature- T_g near room temperature) with a higher weight percentage (60%) in respect to the total polymer mass whereas the second phase (T_g below 0°C) was chosen to give a soft polymer. The hard part defines the

Table 1. The finish formulation applied on the leathers

Components	Application Steps		Descriptions
	Basecoat (I) (parts)	Topcoat (II) (parts)	
Water	35	20	Spray I x 3 times
Pigment	10		Hot plate 80°C/100 bar
Wax	5		
Acrylic Latex	20		Spray I x 3 times
Isopropyl alcohol	0.5		
Aqueous NC Lacquer		10	Spray II x 1 time
Silicone Surface Modifier		0.5	Hot plate 80°C/70 bar

mechanical performance of the latex and the soft part increases the elasticity of the polymer and its adhesion to the substrate. A harder phase could also be chosen having a much higher T_g (~ 100 °C) to increase the mechanical performance further, however, in this case the final polymer would be brittle with a higher minimum film forming temperature that could cause difficulties in finishing applications. The small portions of the monomers of HEA and MAA were used to increase the hydrogen bonding capacity of the final polymer which contributes to the adhesion and also to increase the stability of latex due to their hydrophilic character.

3.2. Particle Size and Stability of the Latex

The average particle size diameter of the latex particles was found to be 123 nm with a very low polydispersity index of 0.030. The particle size distribution of latex obtained from dynamic light scattering analysis is given in Figure 2. The low particle size latexes below 500 nm can penetrate better into the collagen fibers and enhances the adhesion of the coating as well as keeping the natural look of the grain. Besides, they have better pigment binding efficiency than coarse latex particles, thus increasing the physical properties of the finish. From this point of view, the synthesized latexes with low emulsifier content of 0.5 wt% (based on total monomer amount) exhibited low particle size and very homogenous size distribution for being a good candidate to use as binder in leather finishing.

The zeta potential of the latex was measured as -44.1 mV which showed a good electrostatic stability for the particles. It is known that especially core-shell latexes usually require high concentrations of surfactants just as normal emulsion polymers [25]. High amount of surfactant can contribute negatively to film appearance and film properties by their wetting and migration properties. In the study only 0.5 wt% of anionic emulsifier was used for micelle formation. The low amount of hydrophilic monomers (HEA, MAA) used in the different phases separately contributed to the stability of the particles with the location of hydroxyl and carboxyl groups towards the water phase from the surface of particles. As it's known small portions of carboxylic acid and hydroxyl monomers helps to improve the stabilization of the latexes [31], the freeze-thaw and mechanical stability [32,33], enhances adhesion and increases the critical pigment volume concentration value [34]. In addition, the seeded emulsion polymerization, which was used for the synthesis, usually give a better control for particle growth stage and decreases the risk of coagulation [35,36]. With the given method low emulsifier containing, stable and low particle size composite latex was synthesized successfully.

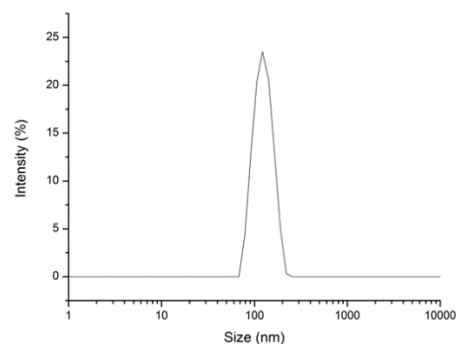


Figure 2. Particle size distribution of the core-shell acrylic latex

3.3. IR Spectrum of the Composite Latex

The IR spectrum of copolymer film is given in Figure 3. Corresponding characteristic absorption peaks of poly(BMA-co-HEA) / poly(BA-co-MAA) composite polymer appeared at 2960 (1), 2933 (2), 2873 (3), 1726 (4), 1450-1465 (5), 1154 (6), and 1063 (7) cm^{-1} , which can be attributed to the asym stretching of $-\text{CH}_3$ (1), asym (2) and sym (3) stretching of $-\text{CH}$ groups of CH_2 ; $\text{C}=\text{O}$ stretching (4), $-\text{CH}_3$ bending (5), O-R stretching (6), and C-O-C stretching (7). The characteristic peaks of MAA and HEA was difficult to observe in the spectrum due to their low amount on the main copolymer backbone. However, the low intensity peaks observed at 3445 and 3290 cm^{-1} can be attributed to the $-\text{COOH}$ and $-\text{OH}$ groups indicating their presence on the polymer. In addition, the characteristic peak of $\text{C}=\text{C}$ usually appears at 1645 cm^{-1} due to the residual monomers was not observed in the spectrum showing the success of the reaction.

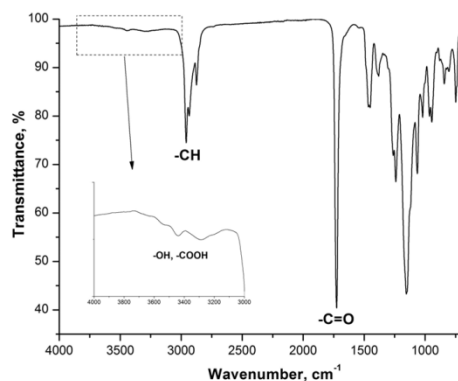


Figure 3. IR spectrum of the poly(BMA-co-HEA) core / poly(BA-co-MAA) shell latex film

3.4. Differential Scanning Calorimetry (DSC)

DSC curve of the composite polymer is given in Figure 4. From the thermal behavior of the polymer two clear phase transitions were observed which can be attributed to the different compositions of the different phases of the polymer. The first transition was observed at around $-38\text{ }^{\circ}\text{C}$ for soft part and the second at $25\text{ }^{\circ}\text{C}$ for the hard part with a larger transition. The obtained values were found to be close to the theoretical T_g values of each phase composition indicating that a two-phase polyacrylic latex was synthesized successfully.

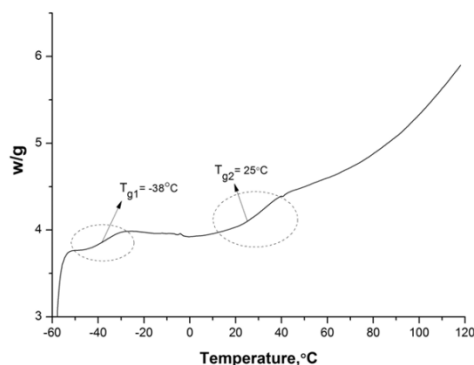


Figure 4. DSC curve of the synthesized core-shell latex film

3.5. Finishing Performance of the Latex

The finishing formulation (Table 1) was kept simple to evaluate the performance of the composite latex. In addition, one leather sample was finished without applying any topcoat to evaluate the performance of the composite latex alone. The results obtained from the physical tests are given in Table 2. The flexing endurance of the leathers was perfect after 100.000 times of flexing. This showed that the hard phase of the latex did not impair the flexibility of the final coating. The dry and wet rub fastness of the leathers finished with the composite latex gave satisfactory grey scale values even without a top coat layer. To assess further the water behavior of the leathers, a water spotting test was also employed on the composite latex coated leather samples. The results showed that after 30 min the water droplet still remained on the leathers with a partial absorption (Figure 5A), however, there was no color change or a spot on the leather after 16h (Figure 5B).

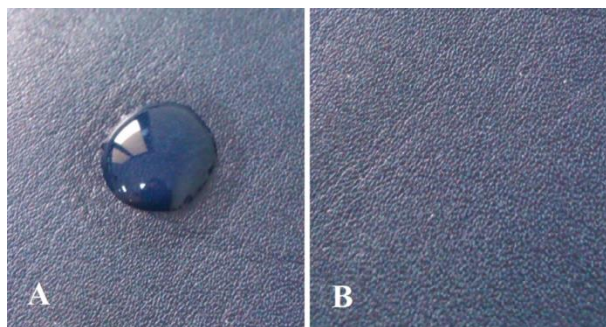


Figure 5. The photographic images of the core-shell latex coated leathers during wet spotting test (A: after 30 min; B: after 16 h)

In Figure 6 the SEM images obtained from the cross-section of finished leathers with and without topcoat layer are given. In Figure 6a,b the homogenous pigmented coating layer deposited on the leather surface can be seen with different magnification. The thickness of the finish layer was found to be less than $20\text{ }\mu\text{m}$ indicating that not a heavy finish was applied on leathers. The topcoat layer as a more rigid and very thin film structure could also be observed over the pigment layer (Figure 6c,d) with a more opaque appearance. The overall finish layer was thin enough to support the natural look of the leather grain and thick enough to improve the surface properties of the leathers.

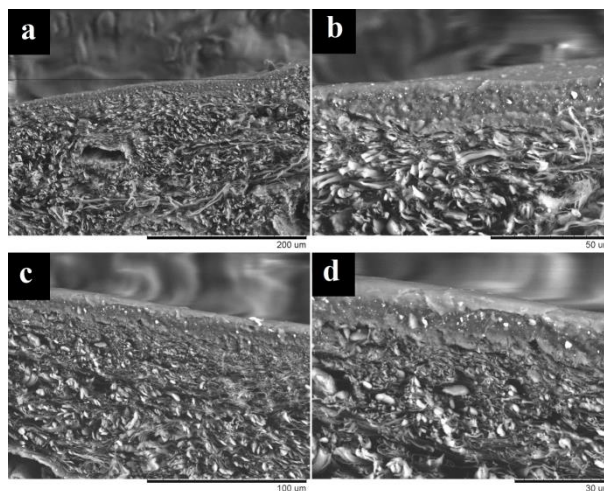


Figure 6. SEM images of the cross-section of coated leathers without (a,b) and with (c,d) the topcoat layer.

4. CONCLUSION

A composite polyacrylate latex with low emulsifier content (0.5 wt%) was synthesized successfully via two stage seeded emulsion polymerization technique. The latex had good electrostatic stability with low average particle size and narrow size distributions. The two different polymer phases of the latex was confirmed by DSC analysis. The application of the composite latex in a basic finishing formulation showed that they were successful as base coat binders for leather finishing by offering good film forming properties, elasticity and pigment binding efficiency as well as glossy and natural look of the leathers. The leathers coated with the composite latex exhibited good fastness levels to dry/wet rubbing and water spotting. The synthesized composite latex was found to be proper for industrial applications as a waterborne acrylic binder in leather finishing providing improved properties with inexpensive production conditions.

Table 2. The results of the performance tests applied to the finished leathers

Leather Sample	Flexing endurance (x100.000)	Fastness level 500 rubs (dry)		Fastness level 10 rubs (wet)		Fastness level 25 rubs (wet)		Fastness level after water spotting (16h)
		Leather	Felt	Leather	Felt	Leather	Felt	
C-S latex without topcoat	Excellent	4	3	3/4	2	2	1/2	5
C-S latex with topcoat	Excellent	5	4	5	4	4	3	5

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