



RESEARCH ARTICLE

ON THE PREPARATION OF POLYACRYLIC BINDER *via* MINIEMULSION
POLYMERIZATION FOR LEATHER PERFORMANCE COATINGS

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ABSTRACT

Polyacrylic copolymer latex composed of butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA) and 1,4 butanediol dimethacrylate (BDMA) was synthesized *via* mini-emulsion polymerization technique. The obtained polyacrylic latex was designed to be used as a binder with good electrostatic stability, low average particle size (83 nm) and narrow size distributions (PDI= 0.12). The FTIR and DSC analyses verified the success of the copolymer's synthesis. The latex was further used as a base coat binder for the coating of shoe upper leathers in a leather finishing application. The performed tests on finished leather showed good dry/wet rubbing performance of the coating as well as excellent flexing endurance. The synthesized latex seemed to be a good candidate as performance binder for leather finishing applications.

Keywords: Mini-emulsion polymerization, Polyacrylate, Latex, Leather finishing, Coatings

1. INTRODUCTION

Acrylate based polymers i.e. emulsions, dispersions are widely used in modern coatings' technology. Due to their excellent durability they are suitable for indoor and outdoor decorative paints, and they can be used as high-resistance coatings for different industrial uses [1, 2]. Moreover, waterborne acrylic latexes are the most commonly used binders in leather finishing due to their good film forming properties, pigment binding capacity, high ultraviolet and block resistance together with their inexpensiveness [3, 4]. However, their mechanical and chemical resistance properties are not at desired level, especially when we compare them with the performance of polyurethane based systems [5]. The solution to overcome these problems could be the partial crosslinking to increase the reactivity between the chains and thus the molecular weight of the acrylic polymer. This is usually done by external crosslinkers that are added to the polymer dispersions just before their application and crosslinking takes place during and after film formation. Most of the industrial applications rely on this technique since it gives high performance coatings. For this purpose, hydroxyl or carboxyl functionalized latexes have been crosslinked with isocyanates [6, 7], polycarbodiimides [8, 9], polyaziridines [10] and polyoxazolines [11, 12]. The final crosslinked films have good mechanical and chemical resistance; however, these external crosslinking agents usually have toxic character and need special care and protection during their application.

Another way to increase the molecular weight of the final polymer is to introduce functional monomers bearing divinyl groups. The addition of a small amount of divinyl based monomers can help to increase the molecular weight and thus the performance of the coating material. On the other hand, synthesis of high molecular weight hydrophobic polymers can cause stability problems in conventional emulsion

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polymerization systems since the diffusion/transport of growing polymeric radicals can be difficult. Moreover, mini-emulsion is a technique in the family of heterophase polymerizations, which allows the modification of polymers in stable nanodroplets. It gives possibility to synthesize hydrophobic and high molecular weight polymer particles with small particle size ranging from 50 nm to 500 nm and high colloidal stability [13, 14].

The present study aims the synthesis of high molecular weight acrylic copolymer latex *via* mini-emulsion polymerization technique and its application in leather finishing as coating binder. Polymer properties and coating performance (e.g. flexing endurance, dry rub fastness, wet rub fastness) were presented in the paper.

2. MATERIALS AND METHOD

2.1. Materials

Mini-emulsion polymerization was performed by reaction of vinyl-based monomers in the presence of a co-solvent, emulsifier, and initiating system. The used acrylic monomers were; butyl acrylate (BA, 99%), methyl methacrylate (MMA, 99%), methacrylic acid (MAA, 99%) and 1,4 butanediol dimethacrylate (BDMA, 95%), all Sigma-Aldrich products. Hexadecane (HD, Sigma-Aldrich, 99%) was the co-solvent while Disponil SLS 101 (Sodium Lauryl Sulphates, BASF product, solid ~30%) was the anionic emulsifier. The system was initiated by potassium persulfate (KPS, Sigma-Aldrich, 99%) and sodium bicarbonate (NaHCO_3 , Merck, 99%) was used to buffer the emulsion. All chemicals were used as received. Ultra-pure water was used for the preparation of emulsions.

Crust bovine upper leather was gifted from Sepiciler Co., Izmir-Turkey to be used for finishing application. Finishing formulation consisted pigment, wax, casein emulsion, aqueous nitrocellulose lacquer and surface modifier and all were supplied from different leather chemical companies.

2.2. Synthesis of copolymers *via* Mini-Emulsion Polymerization

The copolymer synthesis experimental set-up was presented in Table 1. Prior to the mini-emulsion polymerization, the acrylic monomers i.e. BA, MMA, MAA, BDMA and the co-solvent i.e. hexadecane, were mixed. Separately, SLS and NaHCO_3 were dissolved in distilled water to obtain the pre-emulsion. The monomers mixture was then added to the pre-emulsion mixture and mixed at high speed for 20 min to obtain an oil/water emulsion. The obtained o/w emulsion was then probe sonicated at 70W and amplitude of 80% in an ice bath for 15 min to obtain the mini-emulsion. The resulting emulsion was added to a three-neck glass reactor equipped with a condenser and nitrogen inlet. The dissolved oxygen from the system was removed by bubbling nitrogen gas for 30 min. The reactor was then immersed in a pre-heated oil bath at 80 °C, and then the reaction was initiated by injecting KPS solution. At the end of the 3 h reaction time, the copolymer emulsion was obtained by cooling to room temperature. The conversion was measured gravimetrically and was found to be over 99%.

Table 1. Mini-emulsion polymerization's receipt

Ingredients	Amount
BA	15.5 g
MMA	9.0 g
MAA	0.5 g
BDMA	0.5 g
HD	1.5 g
Disponil SLS-101	4.5 g
NaHCO_3	0.1 g
KPS	0.025 g
Distilled water	68.0 g

2.3. Characterization Methods

The particle size and zeta potential measurement of the latex was done with a NanoZS model (Malvern Instruments UK) zetasizer instrument. A Perkin-Elmer Spectrum-100 ATR-FTIR instrument was used for IR spectrum analysis of the copolymer film by scanning in the range of 600-4000 cm^{-1} . Thermal properties of the film were measured by differential scanning calorimetry (DSC) using a TA DSC Q2000 instrument with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere from -70 to 250 $^{\circ}\text{C}$.

2.4. Application of the Latex in Leather Finishing

The synthesized polyacrylic latex was applied on leathers cut from the coupon part in a rectangular shape (30 × 40 cm). The details of the finishing formulation are given in Table 1. The polymer emulsion was used as the main binder in base coat layers. The coats were applied on leather by hand spraying gun with air pressure of 3 atm followed by a tunnel drying at 90 $^{\circ}\text{C}$ for 3 min. Hot plating was also applied at given intervals. After the finishing the leather was conditioned according to the standard of ISO 2419:2012 [15] for physical testing. Subsequently the performance of the coatings was tested for flexing endurance [16]; colour fastness of leather to To and Fro rubbing [17]. The colour evaluation of the specimens was done using Grey Scale Standard (IUF 131-132) which gives a rating between 1 and 5 (5: means no colour change, and 1: means failure).

Table 2. The finishing recipe used for coating of leathers

Coats	Components	Application	Description
Base Coat	Pigment	10	
	Acrylic dispersion	25	
	Polyurethane dispersion	5	Spray x 3 times
	Wax emulsion	12	Hot plate 100 $^{\circ}\text{C}/70$ bar
	Casein emulsion	5	Spray I x 3 times
	Isopropyl alcohol	0.5	
	Water	50	
Topcoat	Aqueous NC Lacquer	10	
	Silicone Surface Modifier	0.5	Spray x 2 times
	Water	20	Hot plate 100 $^{\circ}\text{C}/50$ bar

3. RESULTS AND DISCUSSIONS

The particle size distribution curve of the mini-emulsion was given in Figure 1 and other parameters, e.g. Z-size diameter, zeta potential and polydispersity index, were summarized in Table 2. The average particle size diameter of the latex was found to be ~83 nm. The PDI value of the latex was also low as 0.12 showing that the emulsion had homogenous particle size distribution. Zeta potential value of the latex was measured as -39,2 mV exhibiting a good electrostatic stability. The results showed that a stable mini-emulsion latex was obtained with low particle size diameter and narrow particle distribution, which can be sometimes a challenge for mini-emulsion polymerizations.

Table 2. Average particle size, polydispersity and zeta potential values of the copolymer latex

Mini-emulsion	Z-average diameter (nm)	Polydispersity index (PDI)	Zeta Potential (mV)
EM	82.9	0.120	-39.2

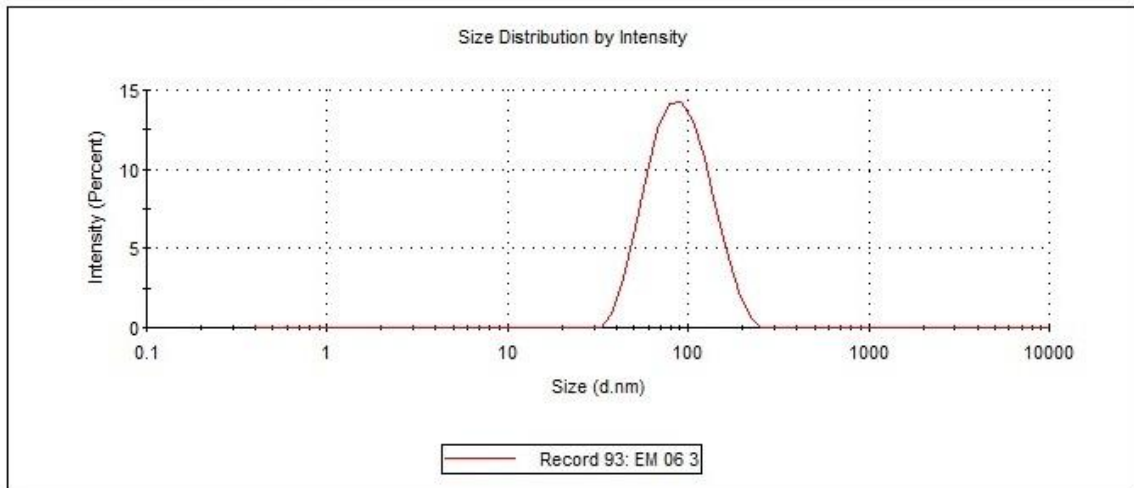


Figure 1. Particle size distribution of the latex

Figure 2 shows the IR spectrum of copolymer film. The characteristic vibration peaks of poly(BA-co-MMA-co-MAA-co-BDMA) copolymer appeared at 2985 (1), 2937 (2), 2875 (3), 1725 (4), 1447-1380 (5), 1155 (6), and 1021 (7) cm^{-1} , which could be assigned to the asymmetric (asym) stretching of $-\text{CH}_3$ (1), asym (2) and symmetric (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 vibration peaks of MAA were difficult to be determined in the spectrum due to low amount against the other constituents. However, the low intensity peaks observed at 3445 cm^{-1} could be attributed to the $-\text{COOH}$ groups indicating their presence on the polymer. In addition, the characteristic peak of $\text{C}=\text{C}$ from 1645 cm^{-1} due to the residual monomers was not observed in the spectrum indicating that the vinylic groups were polymerized and transformed into CH and CH_2 of the polymeric chain.

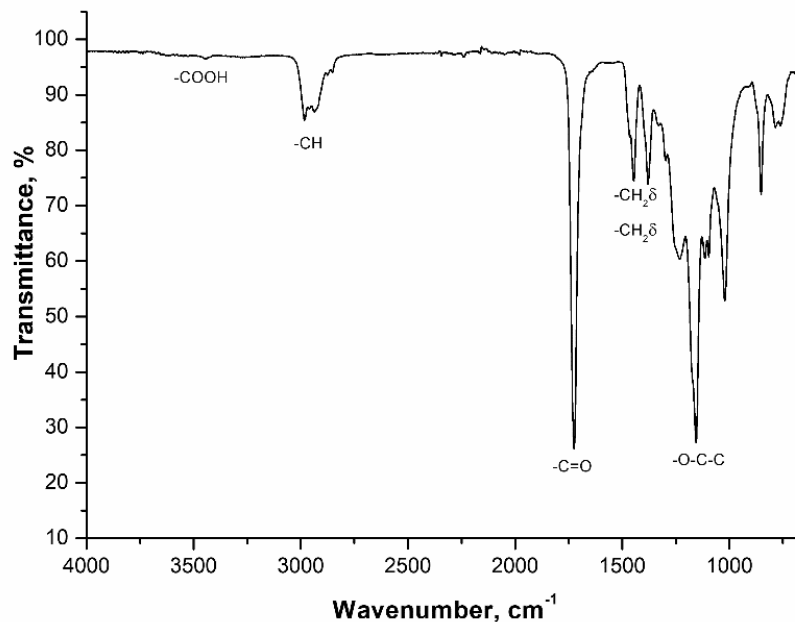


Figure 2. The FTIR spectrum of the copolymer

In Figure 3 DSC curve of the copolymer film was given. The film was obtained by casting the latex in a Petri dish and drying at room temperature for 3 days. From the thermogram a phase transition could be observed at $-2.3\text{ }^{\circ}\text{C}$ which can be attributed to the glass transition temperature of the copolymer. This temperature was found to be higher than the theoretical T_g value ($T_g = -11\text{ }^{\circ}\text{C}$) possibly due to the high molecular weight of the copolymer that decreases the mobility of the chain and thus free volume. On the other hand the film was still elastic being below $0\text{ }^{\circ}\text{C}$ that is proper for leather applications. In the thermogram, the endo peak observed at $+19\text{ }^{\circ}\text{C}$ was possibly due to the melting of hexadecane remained within the film since its melting temperature is known to be at $+18\text{ }^{\circ}\text{C}$.

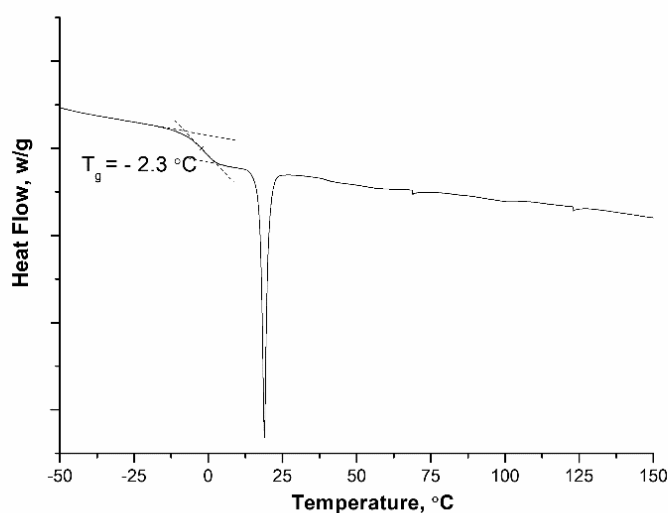


Figure 3. The DSC thermogram of the copolymer film

The finishing formulation was summarized in Table 1 and the results of the performance tests were given in Table 3. The flexing endurance of the leathers was tested, and the results were very good even after 50.000 times of flexing showing that the high molecular weight of copolymer did not impair the flexibility of the final coating. The dry rub fastness of the leathers was very good since no visible damage on the leather and/or colour transfer to felt was observed (Figure 4). The wet rub fastness of the leathers gave average grey scale values. Although there was no significant damage on leather a slight colour transfer to the felt was observed. However, the overall performance of the finishing considering its simplicity, the results were very satisfactory.

Table 3. The results of the performance tests applied to the finished leathers

Leather Sample	Flexing endurance (x50.000)	Fastness level 500 rubs (dry)		Fastness level 25 rubs (wet)	
		Leather	Felt	Leather	Felt
EM	Excellent	5	5	4	3

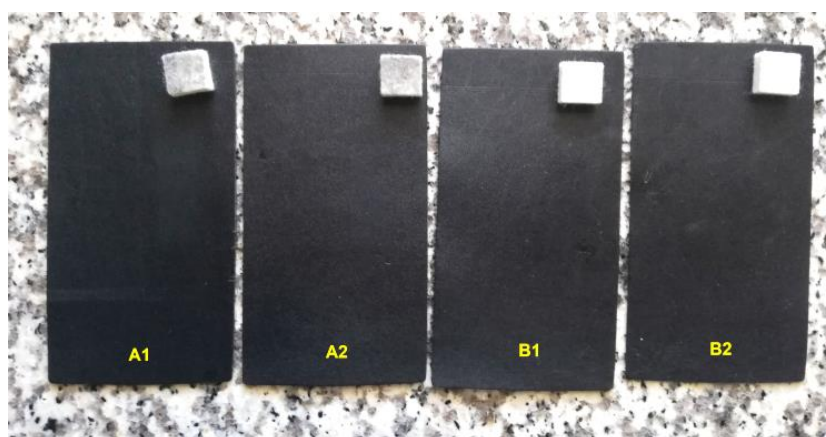


Figure 4. The images of the leather samples after abrasion test (A1,2 – after wet rubbing, B1,2 – after dry rubbing test)

4. CONCLUSIONS

A polyacrylate latex was successfully synthesized *via* mini-emulsion polymerization technique. The latex had good electrostatic stability with low average particle size and narrow size distributions which sometimes can be a challenge in mini-emulsion polymerizations. The synthesized latex was further used as a base coat binder in a leather finishing formulation and the results showed that the leathers exhibited good fastness levels to dry/wet rubbing action. The synthesized latex was found to be proper for industrial applications as a good performance waterborne acrylic binder in leather industry without using external crosslinkers.

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