

SYNTHESIS OF HIGHLY CARBOXYLATE ACRYLIC RESINS FOR LEATHER IMPREGNATION

by

L. OLLÉ, M.M. SOLÉ, A. SHENDRIK¹ L. LABASTIDA, A. BACARDIT*

Igualada Engineering School (EEI). Universitat Politècnica de Catalunya (UPC)

PLAÇA DEL REI, 15. 08700-IGUALADA, SPAIN

¹*Biochemistry Faculty. Ukraine Donetsk National University*

UNIVERSITY ST., 24. 83055 - DONETSK, UKRAINE

ABSTRACT

This work describes the synthesis of new leather finishing acrylic resins. Four resins were synthesized varying the concentration of ethyl acrylate, butyl acrylate, and methacrylic acid. Sodium lauryl sulphate was used as emulsifying system. By means of an experimental design, an optimal resin for leather impregnation was defined. The results obtained indicated that the variation of the monomer concentration influences the resin properties, the hardness of the film, and the penetration into the leather. Most importantly, this new highly carboxylate acrylic resin enables leather impregnation without the use of surfactants or penetrating agents.

RESUMEN

Este trabajo describe la síntesis de un nuevo acabado de resinas acrílicas para cuero. Cuatro resinas fueron sintetizadas variando la concentración de acrilato de etilo, acrilato de butilo y ácido metacrílico. Lauril sulfato de sodio fue empleado como sistema emulsionante. Por medio del diseño experimental, una resina óptima para la impregnación de cuero se ha definido. Los resultados obtenidos indicaron que la variación de la concentración del monómero influye en las propiedades de la resina, la dureza de la película, y la penetración en la piel. Lo más importante, esta nueva resina acrílica altamente carboxilada permite la impregnación de cuero sin el uso de tensoactivos o agentes de penetración.

INTRODUCTION

The impregnation technique involves the application of thermoplastic polymer dispersions that penetrate the leather and form a bond between the grain layer and the reticular layer, or between the buffed grain layer and the reticular layer. Nowadays, impregnations are carried out in aqueous media due to their versatility and easy handling. Additionally, impregnations do not produce toxic or inflammable vapors. Three conditions have to be met in impregnations: (a) the dispersion must humidify the leather; (b) it must penetrate rapidly and avoid the coalescence before obtaining sufficient penetration; (c) it must penetrate with the sufficient intensity so as to enable the welding between the reticular layer and the grain layer (i.e., 1/3 of leather thickness). With these conditions in mind, the addition of surfactants or penetrating agents is commonly required.¹

This work describes the synthesis of new leather finishing acrylic resins for impregnation avoiding the use of surfactants and/or penetrating agents.

The synthesis was carried out by free-radical polymerization. This is the most widely practiced method of chain polymerization and is used almost exclusively for the preparation of polymers from olefinic monomers of the general structure $\text{CH}_2 = \text{CR}^1\text{R}^2$, where R^1 and R^2 are two substituent groups which may be identical, although they are often different. The procedure by which an emulsion polymerization is carried out has a significant effect upon the resulting polymer and its properties. Indeed, polymers with quite different performance characteristics can be produced from the same reaction formulation by appropriately controlling the type of polymerization process and the conditions. In this work, the batch process was used to perform the polymerization since, with this type of process; polymers with higher molecular weight are obtained.²⁻⁷

*Corresponding author e-mail: anna.bacardit@eei.upc.edu; Tel.: +34-93-803-5300; Fax: +34-93-803-1589

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EXPERIMENTAL

Material

The monomers used in the polymerization were methyl acrylate acid (MAA), buthyl acrylate (BA), and ethyl acrylate (EA), and were supplied by Dow Chemical. Kao Corporation supplied sodium lauryl sulphate, used as surfactant.

Preparation of acrylic emulsions

The batch process was used to perform the polymerization. All the products (67.5 % water, 2% surfactant, and 25% monomers in the proportion described in Table I) were added to the reactor flask (1 liter capacity). Then, nitrogen was applied to the reactor, ensuring that all oxygen was dissipated. Afterwards, 0.0006% ferrous sulphate heptahydrate was added to the reactor to promote the reaction in a redox system (i.e., 0.1% ammonium persulphate and 0.07% sodium metabisulphite). The reaction was maintained at 85°C for 30 minutes. Ferrous sulphate heptahydrate and ammonium persulphate were supplied by Dow Chemical. Sodium metabisulphite was supplied by BASF.

Experimental design

The simplex method was employed in order to optimize the working conditions to perform the synthesis. This method is an optimization technique that involves an experimental design network. The simplex method is an optimization approach based on the one devised in 1962 by Spendley, Hext, and Himsworth.⁸ The convenience of this approach encourages some modifications which lead to several derived simplex methods like the one used in this work. The monomer ratios chosen for the experimental design are shown in Table I.

TABLE I
Experimental design

Resin	Ethyl acrylate	Buthyl acrylate	Methyl acrylate acid
1	0.7	0.25	0.05
2	0.55	0.4	0.05
3	0.5	0.4	0.1
4	0.7	0.2	0.1

The amount of surfactant (i.e., sodium lauryl sulphate) was kept constant in all four synthesis carried out, using a 2 wt%. Once the resins were synthesized, they were applied to buffed bovine chrome-tanned leather using a rollcoater. Impregnation consists of buffing dry leathers with buffing paper of 180 grit size; then, the dust is removed and leathers are impregnated using a solution of resin (i.e., 25% of resin in water). Leathers are left to stand for 24 hours to facilitate the even distribution of the solution.

Evaluation

To characterize the emulsion, the following parameters were determined:

- Percentage of solids, gravimetric.
- pH, by pH Meter.
- Viscosity, by Ford viscosity cup 4 mm.
- Glass transition temperature, theoretically calculated.
- Density, by volumetric system.

To characterize the films obtained, the following properties were analyzed:

- Water absorption, by Kubelka method.
- Hardness, by a shore durometer.
- IR spectra were recorded by the IR Spectrum One (serial number 57458), manufactured by PerkinElmer (Beaconsfield, UK) and equipped with an ATR module of internal reflectance (universal sampling accessory, serial number P0DL01101418) and Fourier transform infrared spectra (FTIR).

To determine the applied properties of the resins obtained:

- Penetration time of the resin solution droplet was measured.
- Loss in leather softness by BLC Tester.

RESULTS AND DISCUSSION

Table I presents the results for each of the properties detailed on the next page.

All four resins have a bluish white final color, which is an indication of small particle size. The composition of solids is around 25%, pH is ~ 3 , viscosity is of 11 seconds, and the density of 1.02g/cm³. The theoretical calculation of the glass transition temperature gives different results depending on the percentages of monomers used, with ranges between -20 and -31°C. We observed differences between the resins synthesized with 5% of MAA and those synthesized with 10% of MAA. The films of the resins synthesized with 5% of MAA appeared to be more elastic, stickier, and with less water absorption. On the other hand, those synthesized with 10% of MAA were harder and it took longer for them to penetrate into the leather. The infrared spectra of all four resins show the characteristic bands of each functional group (see Figure 1).

Statgraphics Plus was used to analyze the results, which included hardness of the film, penetration time and loss of leather softness. The experimental design used to evaluate monomer blends was the Simplex method. This method is applied when the sum of the percentages of two or more

TABLE I
Resin characterization

Resin	#1	#2	#3	#4
Percentage of solids (%)	26.6±0.1	24.3±0.2	24.9±0.1	24.4±0.3
pH	2.9±0.2	3.1±0.1	3.0±0.1	3.3±0.2
Viscosity (seconds)	11.0±0.3	10.3±0.1	11.3±0.2	12.0±0.1
Glass transition T (°C)	-27	-32	-27	-21
Density (g/cm ³)	1.0228±0.001	1.0157±0.002	1.0173±0.001	1.0209±0.002
Water absorption (%)	106.2±0.2	83.1±0.1	121.7±0.3	195.9±0.1
Hardness (°ShA)	50.0±0.1	53.0±0.3	56.5±0.1	55.3±0.2
Time penetration (sec.)	28±1	31±2	67±1	77±2

factors or ingredients of a blend must be 100%. Therefore, the levels of the factors are not independent and their variation can determine the properties of the final product. The geometric description of the space of the factors for 3 components will be a triangle whose vertex represents one single component and the sides are the design coordinates for mixtures of two components and a $x_i=0$. The coordinates inside the triangle represent the mixtures of two components, where $x_1 > 0$, $x_2 < 0$ and $x_3 < 0$. Any proportional combination

of components for the mixture experiment must be placed either in the frontier or inside the triangle of coordinates. Through the design of experiments, we have defined 3 variables (hardness of the film, penetration time and loss in leather softness) for three factors or components (EA, BA, and MAA) in a simplex model. Results were analyzed for each variable in order to obtain the optimal response and the equation of the model fitted.

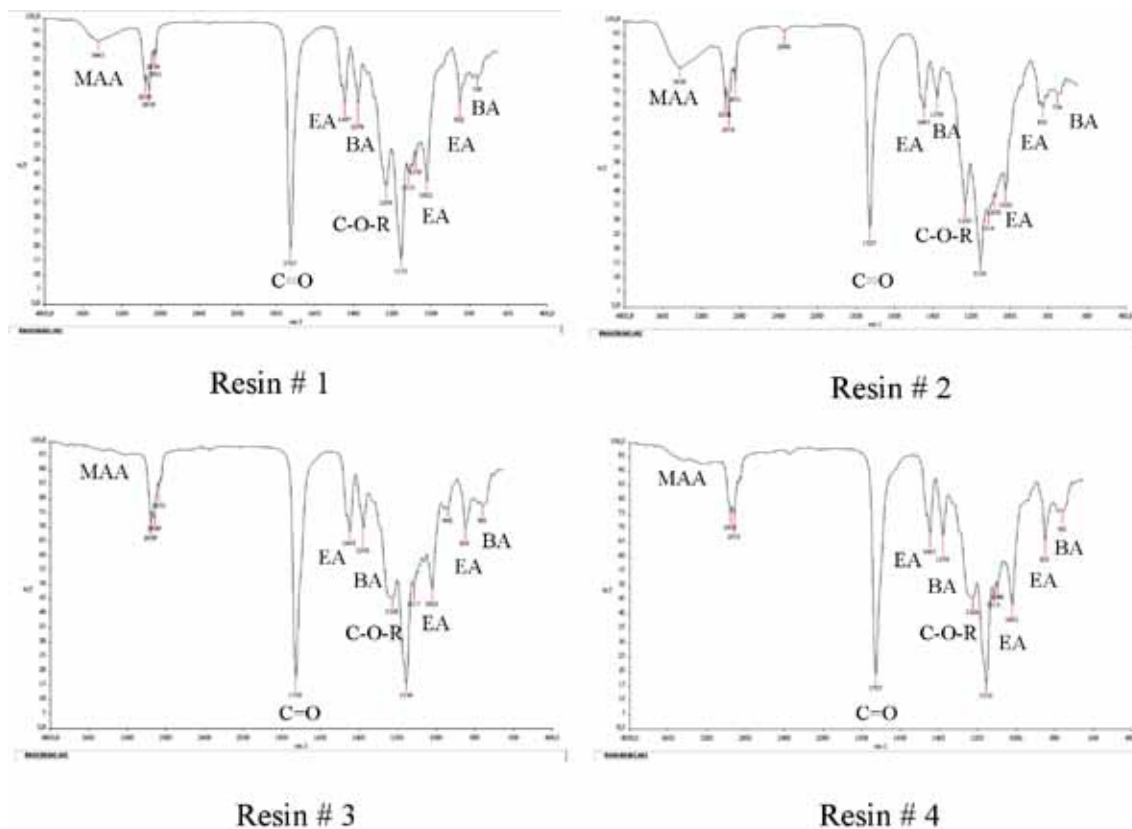


Figure 1. Infrared spectra of the synthesized resins

The equation of the model fitted for hardness of the film is:

$$\text{Hardness} = 50.1 \cdot \text{EA} + 52.9 \cdot \text{BA} + 73.5 \cdot \text{MAA}$$

The estimated response surface for hardness is shown in Figure 2.

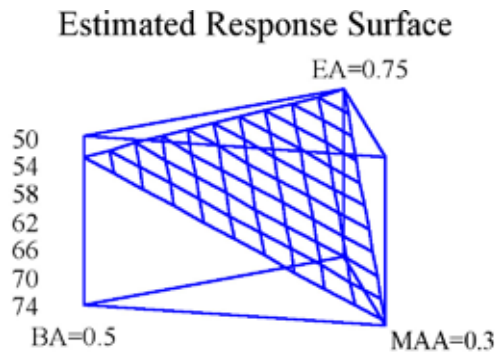


Figure 2. Estimated response surface for hardness

Figure 3 shows the optimum blend to obtain minimum hardness.

Factor	Low	High	Optimum
EA	0,5	0,75	0,75
BA	0,2	0,45	0,2
MAA	0,05	0,3	0,05

Figure 3. Optimum blend to obtain minimum hardness

As can be seen, the optimum value of minimum hardness in order to obtain the best combination of monomers is 75% of EA, 20% of BA, and 5% of MAA.

The equation of the fitted model for penetration time is:

$$\text{Penetration time} = 32.6 \cdot \text{EA} + 26.4 \cdot \text{BA} + 242.0 \cdot \text{MAA}$$

The estimated response surface for penetration time is shown in Figure 4.

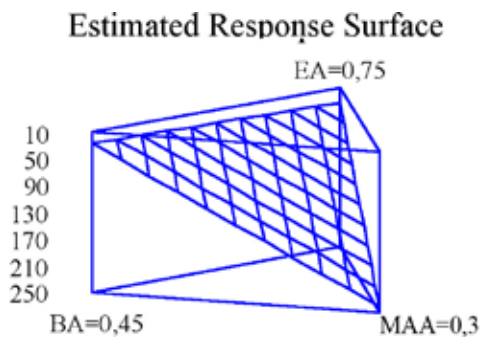


Figure 4. Estimated response surface for penetration time

Figure 5 shows the optimum blend to obtain minimum penetration time.

Factor	Low	High	Optimum
EA	0,5	0,75	0,5
BA	0,2	0,45	0,45
MAA	0,05	0,3	0,05

Figure 5. Optimum blend to obtain minimum penetration time

As can be seen, the optimum value of minimum penetration time in order to obtain the best combination of monomers is 50% of EA, 45% of BA, and 5% of MAA.

The equation of the fitted model for loss in leather softness is:

$$\text{Softness} = -0.42 \cdot \text{EA} - 0.58 \cdot \text{BA} - 2.0 \cdot \text{MAA}$$

The estimated response surface for loss in softness is shown in Figure 6.

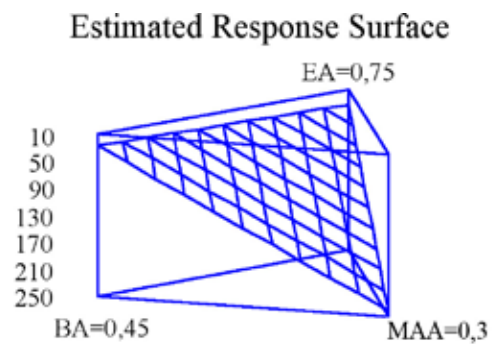


Figure 6. Estimated response surface for loss in leather softness

Figure 7 shows the optimum blend to obtain minimum loss in leather softness.

Factor	Low	High	Optimum
EA	0,5	0,75	0,75
BA	0,2	0,45	0,2
MAA	0,05	0,3	0,05

Figure 7. Optimum blend to obtain minimum loss in leather softness

As can be seen, the optimum value of minimum loss in leather softness in order to obtain the best combination of monomers is 75% of EA, 20% of BA, and 5% of MAA.

In all the three properties studied (i.e., hardness, penetration time and loss in leather softness), the most influential monomer is MAA. This leads us to conclude that to obtain less hard resins with faster penetration into the leather lower amounts of MAA (i.e., 5% of MAA) need to be handled.

Therefore, we assume that in order to obtain a well-balanced resin in these three properties (i.e., hardness, penetration time and loss in leather softness) the optimal resin is formed by 65% of EA, 30% of BA, and 5% of MAA.

CONCLUSIONS

According to our findings, several conditions must be met to obtain optimal impregnation resins. These include rapid penetration into the leather and avoiding hardness while maintaining good grain firmness. Using 5% of methyl acrylate acid, we can obtain resins which are highly carboxylated. These resins are less hard and penetrate faster into the leather without requiring any additional surfactant or penetration agent in its application. Also, by finding a balance between the functional group hydrophilic acid and the emulsifying system, we manage to obtain better grain firmness.

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