

SYNTHESIS AND CHARACTERIZATION OF ACRYLIC RESINS BY THEIR FUNCTIONAL GROUP

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Abstract.

Many types of resins are used in the leather finishing industry, including butadiene, acrylic, urethane resins which when those are aided by auxiliary products such as pigments, contact waxes, etc. give rise to the different articles that are currently marketed. This work is based on the characterization of a very concrete and (at the same time) very extensive group of resins; which are the acrylic resins. The incorporation of different functional groups will be studied from a base polymer, which will give shape to the acrylic resin and consequently; they will give particular properties to the leather finishing. Chemical and physical information is collected from each of the monomers. Finally, a series of comparative tests are performed between the resins obtained to evaluate the particular characteristics from each one.

Keywords: Acrylic resins; functional group; leather; finishing.

1. Introduction

Acrylic resins have been studied deeply since the beginning of the study. The influences that have each of the factors involved in their reaction were studied, as well as the reaction system. The commercialization of acrylic resins was born from a company dedicated to chemicals for leather industry, namely Röhm and Haas, which produced enzymatic products for the hide and they began to produce industrially acrylic polymers. At first, the marketed polymers were intended for other sectors in spite of the leather sector; like paints, and

also to produce "organic glass". It was later that the company began to apply those products in the world of the leather both for wet processing (mainly retanning) and finishing process. [1]

Other authors have extensively studied the effects of different polymerization parameters. Xin Liu, gives an exhibition of different effects of a polymerization of acrylonitrile with methyl acrylate. As it can be the water volume / monomer mass ratios. Effects of initiator concentration, reaction temperature effect and stirring ratio. In this study, it was concluded that a better conversion is obtained increasing water / monomer ratio, initiator concentration and reaction temperature, but did not find significant differences with the stirring ratio, but it was related to the particle size that became smaller. [2]

Other authors have studied the effect of the initiator type and concentration. M. Jain et al. Carried out a synthesis study of a copolymerization between methyl acrylate and ethyl acrylate. In this study, it was used a fully water soluble potassium persulfate (KPS) initiator and a liposoluble substance, 2,2-azobisisobutyronitrile (AIBN). It is concluded that the polymerization initiation began in the aqueous phase and then continued inside the particles. It was also concluded that the molecular weight is influenced by the concentration for the type and the concentration of the initiator. [3]

A good study of an initiator was carried out by N. Kohut-Svelko et al., they make a very exhaustive study of different redox initiators.

They also performed tests by viewing the influence of oxygen from the air as a reaction inhibitor together with the reaction inhibitors contained in the own monomers. By studying the reaction induction times, redox groups containing persulfates, the best couple of trials was the ammonium persulfate and tetramethyl ethylenediamine (TMEDA), terbutylhydroperoxide (TBHP) and sulphonylate formaldehyde (FSS) assisted with ferrous sulphate and EDTA, obtaining conversions of 99%.**[4]**

In another study by Z. Liu et al. the influence of stirring speed was analysed, in this study it was shown how a higher stirring speed achieves higher polymerization temperatures, the explanation given by the authors is based on the droplet size of the emulsion formed during the polymerization. At low revolutions, the droplets are larger than at high revolutions, therefore, it can be concluded that there is more contact zone between phases. They also find differences in the polymerization ratio using different geometries of the stirrer, a sharper stirrer probably produces the same effect of droplets rupture. **[5]**

C.S. Chern gave a very detailed description of the mechanisms of emulsion polymerization, at the same time making a very extensive bibliographical collection of different published studies. They consider that batch polymerization (shots or batch) is one of the techniques used at laboratory scale studying new polymers, also maintains that this technique is slightly used at production scale due to the large amount of heat released in the reactors. In contrast, the polymerization by stages (semi batch) has a more complex reaction mechanisms, although they are much more controllable at large scale, since the addition of monomers is carried out in a staggered way.**[6]**

There are different articles on resin synthesis studying the composition of their monomers. D. Silvestri et al. performed a study of copolymers of methylmethacrylate and butyl acrylate at different compositions and compare them with the corresponding homopolymers. The obtained resins were purified by different washes to extract impurities and different parameters were analysed as well as the particle diameters. They also perform a study of the Tg (glass

transition temperature) obtained in comparison with the copolymer composition, they were compared with the theoretical Tg extracted from the Fox and Gordon-Taylor equations, concluding that the Gordon-Taylor equation had more similarity with the experimental values.**[7]**

Pedraza et al. worked with resins synthesized from methyl methacrylate, butyl acrylate, and increased concentrations of 2-hydroxyethyl methacrylate or methacrylic acid. They performed a study of the obtained particles and the traction increase and the increase of the elasticity increasing the carboxylic function of the polymer was indicated in their summary.**[8]**

In the thesis from Ricardo Santillan Pérez about the effects of the carboxylic groups expressed that the properties of the polymer are given by the functional groups, these functional groups are responsible of reacting with other particles of the medium, they can absorb smaller chemical compounds and can modify their volume by absorbing water molecules. The monomers used were butyl acrylate, methyl methacrylate and acrylic acid. They described the processes for shots and semi-continuous processes. **[9]**

Other authors studied the synthesis of other monomers in different proportions and used similar techniques in their synthesis. Thus, M. Corea et al. performed a synthesis of ethyl acrylate and methyl acrylate in different proportions by studying the conversion at different reaction temperatures. They concluded that the reaction temperature is determinant in the reaction time. Below 60°C the reaction is extended to 100 min while above 60°C the reaction becomes more difficult to control. They use the Fox equation to predict the Tg of the obtained polymers and compare them with the experimental results.**[10]**

A.Reza Mahdavian et al. defended in their work the effects of the carboxylic groups on the surface of the leather. According to the authors, these groups improve the compatibility of the resins with the pigments, increasing the traction and the adhesion of the film to polar substrates. Also they are reactive points before crosslinking. In their study, they made copolymers which by means of different "shots" or additions being able these

carboxylic groups to react at the end of the synthesis becoming to the external form as well as possible. They performed a study of the reaction kinetics as well as the amount of carboxylic acid reacted by titration. [11]

2. Experimental

The objective of this work is to identify the characteristics offered by the functional groups to the acrylic resins. As it was explained, the work is focused on the monomers which are suitable for their application in the bottom coating due to their properties. In the literature, it has been found that the addition of small amounts of functional monomers are enough to provide special characteristics to the acrylic resins.

Different characteristics of the film were evaluated, to identify the differences caused by the functional monomer itself.

The chosen method for the synthesis of resins was the polymerization by emulsion. Within the polymerization methods we take the shots method. The resin synthesis system for shots is based on reacting the entire monomer in a short time. For this reason, water, surfactant, monomer and initiators are added in the same reactor. A controlled exothermic reaction takes place, being double the role of water; on the one hand it acts as a dispersion medium for the

monomers (aided by the surfactant) and on the other hand, it absorbs the generated heat. This method also has some drawbacks, the largest is that the resins which are synthesized have a solids content of about 25%. This is because if higher monomer/water ratios were made (adding more monomer to the reactor), the heat released by the reaction would be so large, and it could be difficult to control since the reaction could reach the boiling point of water in some cases. In addition, the redox pairs can be affected by high temperatures. This method also allows to calculate a priori the thermal jump of the reaction by means of the reaction heat of the monomers, its heat capacity and molecular weight.

The experimental part of this work was based on the synthesis of an acrylic resin which will be taken as a reference. This acrylic resin does not contain any reactive functional group. It is composed by butyl acrylate and methyl methacrylate, in such a way that the synthesized resin itself fulfil with the necessary requirements for the application in the bottom coating of the finishing leather process. Once this resin was produced, a series of resins were made by adding monomers with particular functional groups. These monomers are described in Table 1.

Monomer	N° CAS	Molecular weight	Tg	Functional group	Density
Butyl acrylate	141-32-2	128.17	-54	- - -	0.89
Methyl methacrylate	80-62-6	100.12	105	- - -	0.93
Acrylonitrile	107-13-1	53.06	125	-CN	0.8
Methacrylic acid	79-41-4	89.09	228	-COOH	1.01
Acetoacetoxy ethyl methacrylate (AAEM)	21282-97-3	214.22	18	CO	1.12
Acrylamide	79-06-1	71.08	165	NH ₂	1.12
2-dimethyl amino ethyl methacrylate (MADAME)	2867-47-2	157.21	19	-N(CH ₃) ₂	0.93
Glycidyl methacrylate	106-91-2	142.15	46	EPOXI	1.07

Table 1. Physical parameters from the different monomers used

The redox system formed by an oxidizing agent (Ammonium persulfate) and a reducing agent (sodium metabisulphite) was chosen as the initiator. An activating agent (ferrous sulphate) was also used. This agent does not directly participate in the polymerization, but has a

great influence on the free radicals generation. Table 2 shows the synthesized resins.

Resin	Monomer	Proportional quantity	Total quantity
1	Butyl acrylate	60	15%
	Methyl methacrylate	40	10%
	Sodium lauryl sulphate	1	1%
2	Butyl acrylate	60	15%
	Methyl methacrylate	15	3.75%
	Acrylonitrile	25	6.25%
	Sodium lauryl sulphate	1	1%
3	Butyl acrylate	60	15%
	Methyl methacrylate	35	8.75%
	Methacrylic acid	5	1.25%
	Sodium lauryl sulphate	1	1%
4	Butyl acrylate	60	15%
	Methyl methacrylate	38	9.5%
	AAEM	2	05%
	Sodium lauryl sulphate	1	1%
5	Butyl acrylate	60	15%
	Methyl methacrylate	38	9.5%
	Acrylamide	2	0.5%
	Sodium lauryl sulphate	1	1%
6	Butyl acrylate	60	15%
	Methyl methacrylate	36	9.5%
	MADAME	4	1%
	Sodium lauryl sulphate	1	1%
7	Butyl acrylate	60	15%
	Methyl methacrylate	38	9.5%
	Glycidyl methacrylate	2	0.5%
	Sodium lauryl sulphate	1	1%

Table 2. Synthesized Resins

The assembly shown in figure 1 has been used to synthesize acrylic resins.

- 1- 1L reactor with 3 vertical necks
- 2- Zero displacement thermometer
- 3- Mechanical stirrer with speed control
- 4- Nitrogen producer
- 5- Glass elbow to add post-reaction products
- 6- Reflux condenser
- 7- Heating mantle

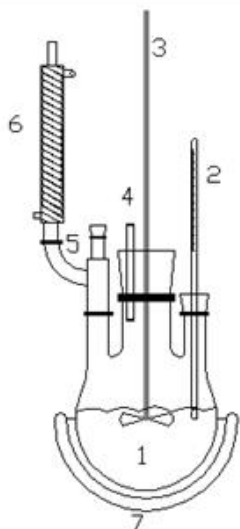


Figure 1. Assembly of the reactor for the resins synthesis

In order to compare the differences between the seven synthesized resins, each one is characterized, and the corresponding films.

The following measurements are made to characterize the resins:

- Initial pH (at the end of the synthesis).
- Final pH of adjustment (with sodium hydroxide 25%).
- Viscosity Ford cup n° 4.
- Dry matter.
- Density.

The following assays were made to characterize the films:

- Film color by Datalog spectrophotometer.
- Percentage of elongation by IUP-6.
- Tensile strength by IUP-6.
- Elasticity module by IUP-6.
- Hardness of films using a durometer.
- Water absorption at 1h and 24h.
- Fastness to yellowing.

3. Results

The comparative results of the synthesized resins with different functional groups can be seen in Table 3.

RESIN	Synthesis Final pH	pH adjustment	Dry matter (%)	Density (g/ml)	Viscosity CF 4 (s)
1	2.5	8.0	27.1	1.0190	10.84
2	3.1	7.4	24.8	1.0155	10.59
3	2.7	7.1	27.4	1.0200	10.91
4	2.7	7.5	26.4	1.0187	10.73
5	2.7	7.4	26.9	1.0190	10.74
6	8.6	9.1	26.8	1.0185	9.65
7	2.7	7.7	25.5	1.0178	9.83

Table 3. 2 Resins parameters

The comparative results of the films obtained from the synthesized resins are shown in Table 4 and from Figure 2 to Figure 8.

Resin	ΔL	Δa	Δb	
1	--	--	--	Reference
2	0.70	-1.59	4.40	Yellower and lightly greenish
3	4.46	-0.25	-1.03	Lightly bluer
4	1.89	-0.29	-0.61	Very similar in colour
5	1.15	-0.16	-0.82	Lightly bluer
6	3.57	-0.82	-0.89	Lightly bluer / greenish
7	2.39	-0.17	-2.04	bluer

Table 4. Colour in relation to resin nº 1

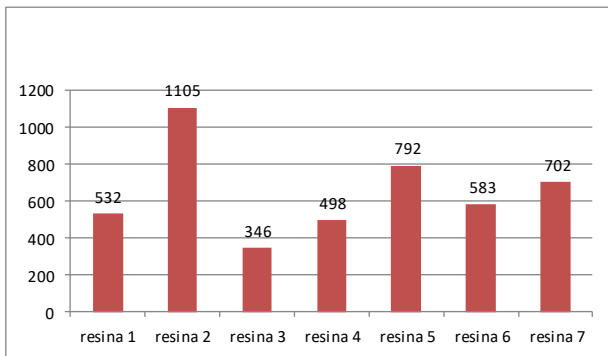


Figure 2. Elasticity to break (%)

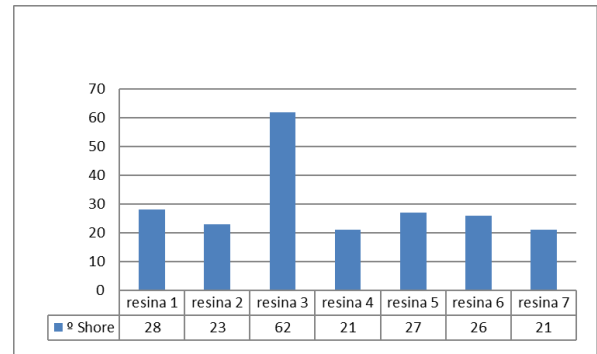


Figure 5. Shore hardness of resins

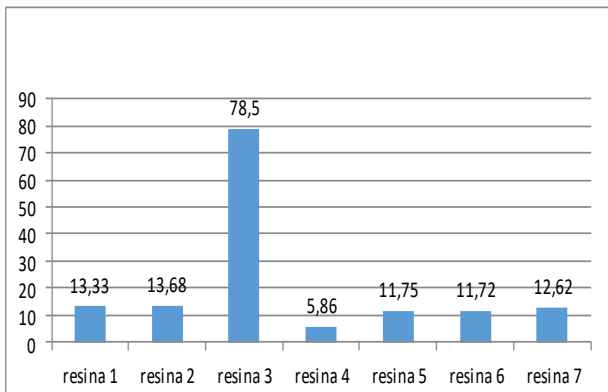


Figure 3. Tensile strength (N/mm)

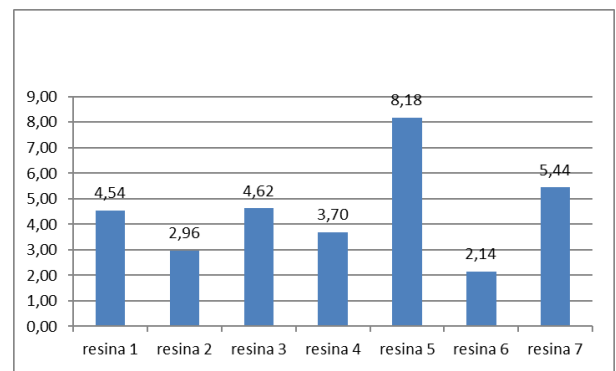


Figure 6. Water absorption at 1 h

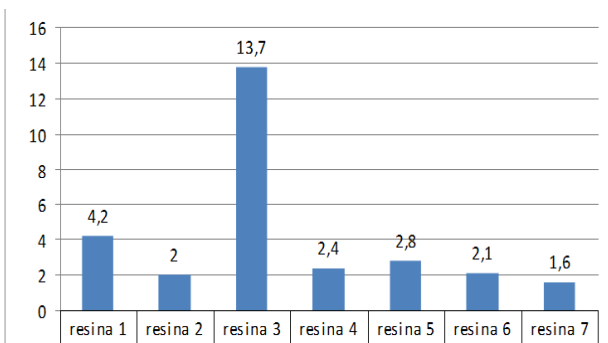


Figure 4. Elasticity modulus 100%

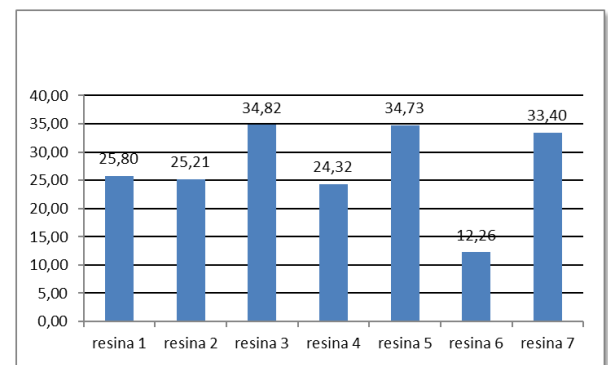


Figure 7. Water absorption at 24 h

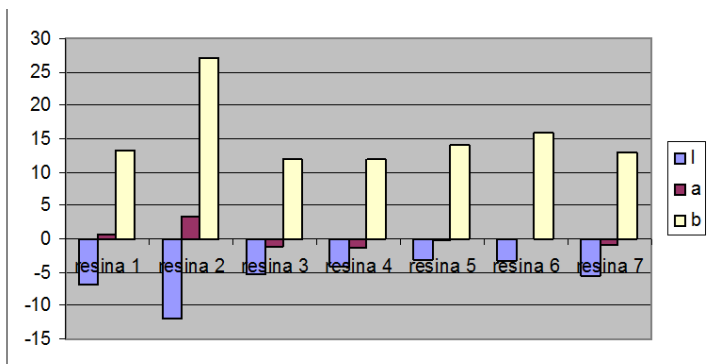


Figure 8. Graph of the increments L, a, b to compare the degree of yellowing

From the results obtained, it is possible to emphasize that the resin n°1 without functional groups is a light transparent resin, it has intermediate film values compared to other resins, as in the film form it does not stand out for any particular property.

The resin n°2 functionalized with acrylonitrile stands out as it is a resin which from the beginning already has a yellower colour in comparison to the others. In the resistance of the yellowing to the heat, it is the one which look yellow.

Another peculiarity of this resin is that it is the most elastic resin to the touch and in the elongation at break, with a very high yellowing, this great elongation causes that it has a very low elasticity modulus. It has an elevated water absorption at 24 h.

The resin n°3 functionalized with methacrylic acid is the hardest resin for touch and hardness °Shore, which is difficult to be bended, is less elastic to the touch and has no tacking, these results can also be observed with the tensile strength, it is the resin having the highest tensile strength, on the other hand it has the minimum elongation at break, this implies a very high modulus of elasticity. It is the resin that has higher values of water absorption at 24 hours, due in part to the fact that the acid group is very polar and it allows the hydrolysis of the resin. It is observed that the water absorption is slow since during the first hour this is not the resin that absorbs more water.

Resin n°4 functionalized with carbonyl group is the second in softness from all synthesized resins. It is the one that presents more tacking

jointly with the resin n°7 functionalized with the epoxy group. It is the resin that has a lower tensile strength.

The resin n°5 functionalized with amide group is the resin that presents intermediate values in all the tests carried out. Higher water absorption rate, since it is the resin with higher values after one hour, but instead, it does not present high values after 24 h compared to other resins.

Resin n°6 functionalized with tertiary amino group presents intermediate values in all the tests carried out. No particular highlight in any of the trials.

The resin n°7 functionalized with glycidyl group presents a very soft touch, the resin which has a lower hardness. It presents some tacking and it is the one that yellows less. It also stands out for its fast speed of water absorption, being also the resin that more water absorbs after 24 hours.

4. Conclusions

It has been found that acrylic resins offer a wide range of characteristics due to their own monomers that they are composed. The functional group of the monomer used affects the characteristics obtained.

The nitrile group causes a very high yellowing. The most yellowing ones are nitrogen-containing functional groups such as acrylamide and MADAME. It is a functional group that should be taken into account for articles with good colour performance with heat. In contrast, the nitrile group has a high elasticity of the film.

The acid and carbonyl groups provide low finishing adhesion and low water droplet absorption time. They also absorb more water over time.

The glycidyl group improves the adhesion. It gives less yellow resins. The glycidyl group resin is the softest resin tested.

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