SYNTHESIS OF POLYURETHANES WITH LOW VOLATILE ORGANIC COMPOUNDS CONTENT FOR UPHOLSTERY AND AUTOMOTIVE ARTICLES

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The manufacture of upholstery and automotive articles is linked to the release of Volatile Organic Compounds (hereinafter VOCs) during their manufacture, which have short and long-term effects on the health of users and the environment. In the leather sector, around 40 kg of VOCs are generated per 1000 kg of raw skin. This research work has focused on the synthesis of new and more sustainable urethane-based polymers that, in turn, allow the quality requirements of the finish to be met, which vary depending on the leather article manufactured. The main objective of the study is to minimize the content of VOCs in the different aliphatic polyurethanes synthesized in a pilot-scale reactor, making small modifications to the synthesis formulations. The synthesis route developed is based on the preparation of polymers of ionomeric polyurethanes and their subsequent dispersion in water. In the synthesis processes developed, the content of coalescing solvents and neutralizing agents, which directly contribute to the concentration of VOCs of the urethane polymers, is eliminated and / or minimized as much as possible. The new urethane-based polymers obtained have been analyzed according to the parameters of pH, viscosity, density and percentage of solids in the resin. Likewise, organoleptic tests (color, transparency, hardness, touch and tacking) and physical tests (tensile strength, water absorption, hardness and color change at 100°C for 24 hours) have been carried out on the film corresponding to each synthesized polyurethane resin. These products will be introduced in finishing formulations designed to obtain high-performance upholstery and automotive leather with minimal impact in terms of VOC content at the pilot level. Tests of fastness and physical resistance have been carried out to evaluate the performance of these leathers.

Keywords: VOCs, resin, film, finishing.

INTRODUCTION

This work details the synthesis procedures for new more sustainable polyurethane polymers, and more specifically, aliphatic polyurethanes of the polyester, polyether, polycarbonate and polyether-polyester blends.

Polyurethanes are polymers or macromolecules formed from the catalyzed reaction between a polyisocyanate and a polyol. The simple reaction between an alcohol and an isocyanate produces the urethane (or carbamate).

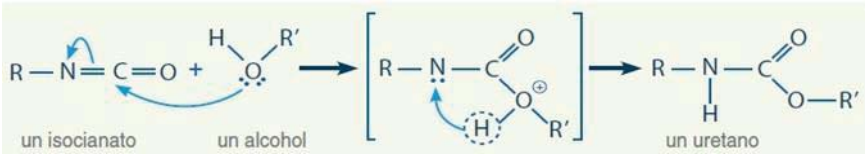

Figure 1. Urethane formation reaction

Conventional polyurethanes are not compatible with water, for this reason some modifications are necessary in the production process in order to allow the generation of an aqueous dispersion. For the production of the aqueous polyurethane dispersion, two differentiated stages are carried out: 1) formation of pre-polymer chains, either in mass or in solution; and, 2) dispersion of the prepolymer in water. (Szycher, 2012; Noble, 1997).

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The synthesis process carried out must be careful and strict, starting from completely dry material and using a nitrogen atmosphere in the reactor throughout the process. The variables to reduce VOCs are based on the elimination of coalescing solvents in the formation of pre-polymer chains and on the minimization of neutralizing agents in the process of dispersing the pre-polymer in water.

Water-based polyurethanes have gained commercial relevance in recent years. The main reason for this fact is the growing concern for the environment regarding solvents and volatile organic compounds (VOCs) which are emitted into the atmosphere, causing the deterioration of the ozone layer, acid rain and a possible chemical imbalance in the ecosphere of the Earth. The secondary reasons are related to the economic costs derived from the consumption of raw material (substitution of solvents for water) and the scope of benefits equivalent to those provided by solvent-based polyurethanes (Szycher, 2012).

MATERIALS AND METHODS

Materials

The raw materials for the synthesis of polyurethanes are: N, N-Diethylethanamine; 2,2-Bis (hydroxymethyl) propionic acid; Hexanedioic acid 1,6-bis (2-methylpropyl) ester; 3- isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate; Dipropylene Glycol Dimethyl Ether; Hydroxy compound, polyester oligomer containing: Dimethyl adipate, Dimethyl glutarate and Dimethyl succinate; Neopentyl glycol butanediol polyadipate; Polyol polypropylene linear ether; Polyol polypropylene linear ether; Polycarbonate diols based on 1-Hexanediol; Polycarbonate diols based on 1-Hexanediol; Tin dibutyl dilaurate; 1,2-benzisothiazolin-3-one solution in dipropylene glycol and water.

There are two glass reactors tailor made by the V. Forné Mechanical Workshops, with a volumetric capacity of 5 L, arranged in a chain. The first reactor has a double cover heated by means of oil in a thermal bath. This thermal bath regulates the temperature of the reactor. The thermal bath temperature adjustment systems do not allow to exceed 150°C.

The first reactor is connected to a nitrogen flow that allows an inert medium to be obtained inside and that allows the achievement of the pre-polymer safely and thoroughly.

The first reactor is located in a higher position than the second, in order to take advantage of the gravity effect to transfer the contents of the first reactor to the second. Both reactors have an adjustable stirring system.

Synthesis Methods

The synthesis of eight polyurethanes with the functional groups shown in Table 1 have been carried out.

Table 1. Synthesized polyurethane type

Polyurethane type	Nomenclature
Polyester (PES)	PES NV001
	PES NV002
	PES NV003
	PES NV004
Polyether (PET)	PET NV005
Polyester-Polyether (PES-PET)	PES-PET-NV006
Polycarbonate (PC)	PC NV007
	PC NV008

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After the synthesis of each pre-polymer, the following phases of the polymer synthesis process were carried out: neutralization, elongation of the polymer and aqueous dispersion.

Film Resin Test Methods

For the characterization of the emulsions resulting from each synthesis process, the following chemical tests have been carried out: pH, density (g / mL), percentage of solids (%) and viscosity (s). For a more exhaustive characterization of the different polymers generated, the film for each one of them has been elaborated, taking into account the percentage of solids obtained in the characterization of the emulsion. To create a film layer that allows the subsequent characterization of the material formed, plastic material molds are used in which a certain amount of each polymer is allowed to dry at 30-35°C until the formation of a film layer is observed.

To evaluate the new synthesized resins, organoleptic tests are carried out: color, degree of transparency, hardness and tacking, and physical tests according to the standards:

-ISO 3376 (tensile strength);
-ISO 5403-1 (water absorption for 1 hour);
-ISO 868 (hardness of plastics and ebonite);
-ISO 17228 (color change at 100°C for 24 hours).

Application of the New Synthesized Resins

The aim of this part of the work is to evaluate the fastness and physical resistance that these polyester and polyether resins provide once sealed to the leather surface and to analyze whether the partial and total substitution of DMM for DBE 3 is reflected in any way in the leather finish. A finishing formula consisting of a base coat and a top coat is used. A black color has been selected as the pigment to more clearly visualize the differences in the transfer of color in the tests of rub fastness, flex strength and adhesion of the finish.

The base coat integrates each of the synthesized resins. Finally, the same top formulation has been applied to all leathers to provide a pleasant touch. The physical and fastness tests selected for the comparison of the finishes made with the different synthesized resins have been the following:

-ISO 5402-1 (dry / wet flex strength);
-ISO 11640 (dry / wet rub strength);
-ISO 15700 (water drop absorption);
-ISO 11644 (dry / wet finish adhesion).

RESULTS

Results of the Synthesized Urethane Emulsions

Table 2 shows the values obtained in the different tests carried out on the resins in emulsion state.

Table 2. Results obtained from the analysis of polyester polyurethane resins

	PES-NV001	PES-NV002	PES-NV003	EPES- NV004
pH	10.0	7.3	7.1	7.2
Viscosity (s)	14	18	15	140
Density (g/mL)	1.01	1.01	1.02	0.97
Solids (%)	29.9	31.6	29.9	33.4

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	PET- NV005	NV006	PC-NV007	PC- NV008
pH	10.6	7.2	10.6	8.3
Viscosity (s)	18	19	14	18
Density (g/mL)	1.01	1.03	1.02	1.00
Solids (%)	22	41.8	27.9	29.9

Upon completion of the synthesis process, the resulting polyurethanes should include the following specifications: percentage of solids (30 ± 2% in PES, PET and PC; 40 ± 2% in PES-PET) and pH (7.8 - 8.8). pH values higher than 8.8 denote an excess of TEA in the neutralization carried out in the second reactor, while values lower than 7.8 denote a lack of the same product for neutralization. Regarding the value of the percentage of solids, most of the resins meet this specification, with the exception of the PET-NV005 emulsion which presents a much lower value. The viscosity parameter marks an obvious difference from the PES-NV004 emulsion, with a Ford Cup number 4 value of 140 seconds much higher than the rest of the tested resins. The density of all the resins oscillates between 0.97 and 1.03 g / mL, presenting the minimum value the PES-NV004 emulsion.

Results of the Study of the Films

The resulting films have the same solid content, which makes it possible to compare the results of the organoleptic tests (color, degree of transparency, hardness and tacking) and of the physical tests carried out on the formed polymers or resins.

The results of the organoleptic parameters of the resins in the film-forming state are shown in Table 3.

Table 3. Results of the organoleptic analysis of the resin film

Parameter	PES-NV001	PES-NV002	PES-NV003	PES-NV004	PET-NV005	PES-PET-NV006	PC-NV007	PC-NV008
Color	Color-less	Color-less	Yellow-ish	White	White	Color-less	White	White
Transparency degree	Trans-parent	Trans-parent	Semi opaque	Semi trans-parent	Semi trans-parent	Trans-parent	Semi opaque	Semi opaque
Hardness	Very hard	Very hard	Very hard	Hard	Very soft	Hard	Very hard	Hard
Tacking	No	No	Yes	No	No	No	No	No
	Film PES-NV001	Film PES-NV002	Film PES-NV003	Film PES-NV004	Film PET-NV005	Film PES-PET-NV006	Film PC-NV007	Film PC-NV008
Tensile strength - Load (N)	7.3	5.1	(1)	2.2	41.0	5.6	(1)	(1)
-Elongation mm	254.9	223.6	(1)	671.6	520.5	520.8	(1)	(1)
Water absorption (%) / 1 hour	55.1	27.2	11.5	6.2	90.0	6.6	(1)	9.3
Hardness(^{0}ShA)	92	93	92	78	19.2	77	(1)	65
Color change at 100ºC/ 24 hours	5	5	3	5	4/5	5	(1)	4

(1) It is impossible to punch out and therefore makes it impossible to perform any test

All polyester polyurethane films are very hard and all of them except PES-NV003 do not present tacking. At the level of transparency, the first two (PES-NV001 and PES NV002) are transparent, the PES-NV004 film is semi-transparent while the PES-NV003 film is semi-opaque. Polyether polyurethane resin film (PET-NV005) is softer than

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polyester urethane resin films. Likewise, it is characterized by its white color, the absence of tacking and high water absorbance. The PES-PET-NV006 film turns out to be hard and solid to light, but it is not the most resistant. The PC-NV007 film is impossible to analyze as it fragments and is not consistent. The PC-NV008 film is white, semi-opaque, without tacking and, in addition, softer than polyester urethane resins or mixed (PES-PET).

Application of the New Synthesized Resins

After applying polyester polyurethane and polyether polyurethane on the leather surface, the leather was left to rest for 24 hours before starting the physical tests mentioned in the previous section.

The finished leathers present a similar appearance between them. At an organoleptic level, it can be pointed out that the leather finished with the PET-NV005 base has some tacking, while the rest of the leather shows the silicone touch of the top finishing layer applied.

The results obtained in the physical tests can be seen in Table 4.

Table 4. Results of the finishing tests

	PES- NV001	PES-NV002	PES-NV003	PET-NV005
Dry Flex (100.000 flexs)	Little breaks	Little breaks	Little breaks	Little breaks
Wet Flex (50.000 flexs)	Breaks	Breaks	Breaks	Breaks (a)
Dry Rub (mark) 500	1 1/2	4 4/5	1 1	2/3 3
Wet Rub (mark) 10	2	4/5	1	1
Wet Rub (mark) 20	1	2	1	1
Drop water absorption	1min 2 se. (L.O.)*	2min 32 sec (M.O)*	12 min 02 sec (M.O)*	3 min 10 sec (M.O)*
Dry finishing adherence	2.2	1.5	2.1	5.1
Wet finishing adherence	0.9	0.7	0.8	2.1

(a) The finish is peeling off
*(L.O.) Slight darkening
*(M.O.) Moderate darkening

According to the results observed in Table 13, it is observed that after the dry flexion test, all samples present small ruptures, which are increased if they are tested in wet. In the case of leathers with PET-NV005 in the base coat, the finish peeling off. Regarding dry rubbing, PES-NV002 has a high rubbing fastness value. The rest of the synthesized resins applied have a low rub fastness value. The fastness to the drop of water is conditioned by the study area of the leather, but in general terms none of the resins reaches the 30 minutes established in the test. Furthermore, darkening occurs in all resins, light in the case of PES-NV002 resin and moderate in the rest. In either case, loss of gloss occurs. Synthesized polyol ester resins have lower finish adhesion values compared to polyol ether based polyurethane resin.

CONCLUSIONS

In this work, new finishing products of the aliphatic polyurethane type in aqueous dispersion have been developed. Certain variables, specifically, the hydroxylated compounds (polyether oligomers and polyester oligomers and polycarbonates) and the type of solvent (DMM and DBE-3) have been modified in order to obtain minimal or no volatile substances.

The new polymers obtained have been analyzed according to the parameters of pH, viscosity, density and percentage of solids. In general terms, most resins have a low viscosity, less than 20 seconds measured with a Ford cup, with the exception of the

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PET-NV005 sample. Polyester polyurethane resins have a solids percentage of around 30%. The polyether polyurethane resin has a pH greater than 8.8. This fact is due to incomplete prepolymer transport in the dispersion reactor, as well as an excessive addition of triethylamine. As a consequence, the percentage of solids is around 20% and the resin gives off an odor of the products added in the second reactor.

Finally, a polycarbonate polyurethane type synthesis was carried out, which resulted in polycarbonate urethane resin (PC-NV007). During the filtration of the same previous packaging, a carbonic cloud was observed when contacting the dispersed resin with the air. This synthesis has not been satisfactory as a consequence of the incompatibility of monomers in the prepolymerization reactor.

In the synthesis of polycarbonate urethane resin (PC-NV008), a single polycarbonate polyol monomer has been used. In organoleptic terms, the PC-NV008 resin is similar to the results of the other resins, that is of polyester or polyether origin.

For reasons of fastness and high content of VOCs, the study with PES-NV001 resin was refused. The best results of the physical tests were obtained in the leathers finished with the PES-NV002 resin. A possible future way of study would consist in the application of this resin combined with other commercial resins, as well as its application in different layers of the finish. Not to be underestimated is PES-NV003 urethane resin synthesized using a lower volatile solvent in the prepolymerization process. Polyether urethane resin (PET-NV005) will also be studied in greater detail due to the absence of solvent in the process of obtaining said resin.

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