



Hybrid polymers with double nature acrylic and urethanic for leather finishing

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1. Abstract

This type of hybrid polymers can be defined as a kind of composites with a shell-core structure. The polyurethane is the matrix and the polyacrylate grows inside it. Traditionally, pure mixes polyacrylate/polyurethane have been done in order to combine properties. Those mixes show an interesting balance of properties, but some disadvantages can be underlined:

- Sediment formation due to the sensivity of the PUD to the presence of carboxilic acid in the acrylic chain.
- Incompatibility of the PUD with the surfactants of the acrylic emulsion.

What advantages can be obtained from the hybrid structure?

- To avoid incompatibility problems between the two polymeric chains. Effects:
 - Very low level of sediments
 - No separation phase
- Excelent difusion of the acrylic chains into the urethanic chains. This homogeneity has consequences:
 - Chemical properties: equal to or better than those of pure mixes
 - Mechanical properties: better than pure mixes

The last generations of acrylic-urethanic hybrids have been designed for getting real environmentally friendly products by removing solvent and volatile amines from the PUD structure.

The result is a group of products that can be classified as low-VOC or even VOC-free with performances close to those of pure PUD, when the application requires that level.

This work analyzes the singular structure of the acrylic-urethanic hybrid polymer, the different generations, the basic industrial process, the main properties on leather and the differences in front of the pure products (pure polyurethane, pure polyacrylate).

2. Introduction

The first time you hear the word “hybrid”, or, more specifically, the expresion “acrylic-urethanic hybrid polymer”, maybe little more than a polymers mixture comes into your mind. In fact, physical mixtures PUD-Acrylic emulsions have been very useful to adjust hardness, tackiness and reduce cost.

Hybrids of Stahl were thought initially like a way to overcome typical problems of those physical mixtures between waterborne polyurethanes and emulsions of polyacrylates:



- Unstability and sediment formation due to contrast of pH
- Lack of transparency in the product and in the film
- Migration of surfactants
- Lack of thermal stability and coagulation

But, what about properties?

Mixtures relied on, mainly, the properties coming from the polyurethane. The polyacrylate was chosen taking into account not to reduce significantly the mechanical advantages of the PUD. As a consequence, the acrylic part of the hybrid was designed according to this requirement. The polyacrylate had to be a “good servant” of the polyurethane. But hybrids have evolved. Their structure, chemistry and properties are now singular. The contact between the two natures gives benefits further than a mixture of polymers.

3. Structure of an acrylic-urethanic hybrid polymer

The term composite can be used to explain the hybrid structure: the polyurethane working as a matrix and the polyacrylate as the element dispersed into the matrix.

The polyurethane is made by this waterborne process:

- **Solvent step:** polycondensation reactions between diisocyanates and hydroxylated components (one of them, with pendant carboxyl group). Final product: a prepolymer, with relatively small molecular weight, and functionalized with NCO active groups at the end of the chains.
- **Neutralization of the prepolymer:** a suitable tertiary amine neutralizes the carboxyl groups.
- **Aqueous step:** the neutralized prepolymer is feeded into water and simultaneous solvation and dispersion or self-emulsification are carried out. Chain extension is made by reaction with a diamine: during or after the feed process. Final product: a polyurethane-polyurea copolymer with high molecular weight and all the required properties.
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Prepolymer from the solvent step:

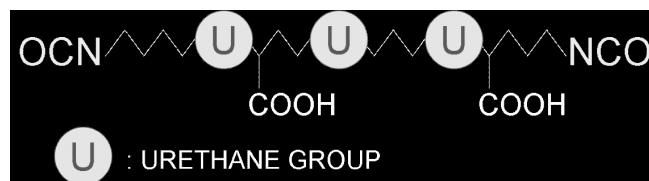


Fig.1: Structure of the NCO functionalized PU prepolymer at the end of the solvent step

Neutralization:

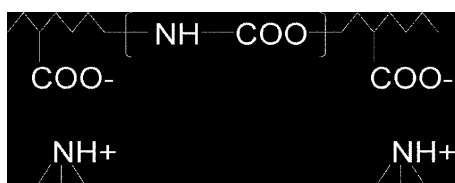


Fig.2: Neutralization of the carboxylic groups with tertiary amine



Dispersion/self-emulsification in water:

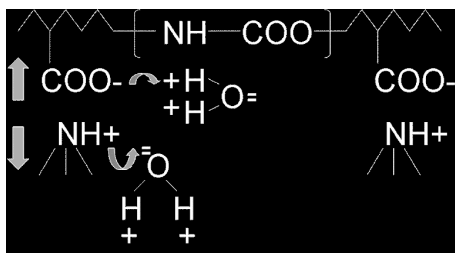


Fig.3: Solvation, counter-ion separation by water and dispersion of the prepolymer

Chain extension and final polyurethane:

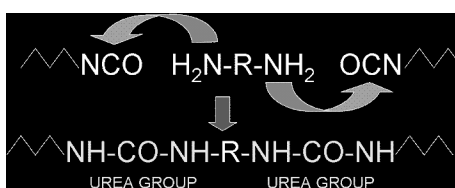


Fig.4: Reaction with diamine, chain extension and final structure of PUD

The most hydrophilic regions –those with high content of carboxylic groups- are the outer part of the polymer and they are in contact with water. Those areas support an electrical double layer ($-\text{COO}^-$, $+\text{HNR}_3$) that stabilize the polymer in the aqueous media and determine the semi-esferical geometry typical of emulsion particles. This structure has been confirmed by SANS (small angle neutron scattering) and luminiscence experiments¹.

The polyurethane is stable and it is able to stabilize another polymer (surfactant ability). It is prepared to allow the polymerization of a polyacrylate inside by means of this process:

- **Absortion of acrylic monomers:** certain amount of monomers are dispersed into the PUD until an homogeneous preemulsion is obtained. The droplets of acrylic monomer are gradually stabilized by the PUD particles. This step needs time and mixing, although no special flow is requiered.
- **Acrylic polymerization:** the acrylic monomers are polymerized by radical chain mechanism. Usually, a chemical pair of oxidizing and reducing agents are used to generate free radicals. A partially water soluble peroxide is preferred to be for the acrylic growth inside the PUD. The following steps are those common to any poliaddition:
 - Initiation: first radicals are generated in the initiators and open the first double bonds
 - Propagation: every chain with radicals react with free monomer
 - Termination: two growing chains react and the radicals dissapear

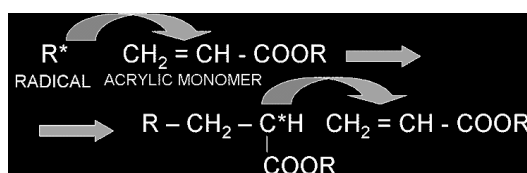


Fig. 5: Radical chain polymerization of the acrylic part

The final product can be identified as a shell-core structure, in which the PUD most hydrophilic areas PUD formed the *shell* and the PUD hydrophobic regions along with the polyacrylate are the *core*.

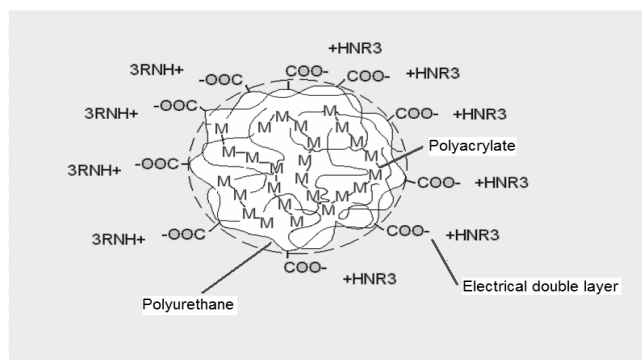


Fig. 6: Schematic final structure of a hybrid particle. *M*: acrylic chain

According to the process described, there is no covalent bond urethane-acrylate. But the polyacrylate has grown in permanent contact with the polyurethane chains. A new kind of structure has been obtained: a *semi interpenetrating polymeric network* (SIPN)².

IPN and SIPN are a practical way to compatibilize polymers with different natures³. Strictly speaking, the formation of an SIPN requires the following steps:

- First: synthesis of a crosslinked polymer.
- Second: synthesis of a linear polymer that grows into the rings of the initial chains.

The link between the two structures is not chemical but it is strong enough to hold them together and avoid phase separation. It is based on permanent entanglements⁴.

Strictly speaking, a hybrid should be made from a previous crosslinked PUD in order to get efficiently those entanglements. In practice, we have:

- Hybrids with linear PUD and linear polyacrylate
- Hybrids with crosslinked PUD and linear polyacrylate
- Hybrids with linear PUD and crosslinked polyacrylate
- Real IPN: crosslinked PUD and crosslinked polyacrylate

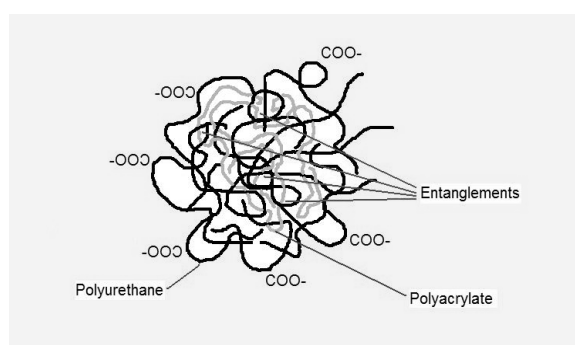


Fig. 7: Schematic representation of SIPN in the hybrid particle

The SIPN is not merely a kind of interconnection between the two polymers. It is the key to get the specific properties of a hybrid that differentiates it from a physical mixture:

A report by R.A. Brown et al.⁵ analyzes the amount of PU and polyacrylate in the interphase of the two polymers - the common domain for both polymers- and determines the following results:



Product	%Polyurethane	%Polyacrylate
Hybrid	20-30	35-50
Physical blend PU-PA	2-20	1-19

Table 1. Presence of the two polymers in the interphase

These results explain the better performances that are usually get with hybrids in comparison with physical blends. The hybrid structure is substantially more homogeneous than the blend, and, consequently, there is quite higher isotropy for the average properties. This report compares mechanical and chemical properties of hybrids and blends and shows clearly the higher level of the hybrid.

But there are acrylic-urethanic hybrid structures with real covalent bonds. These are made by reacting hydroxylated acrylic monomers with the usual components of a PU prepolymer. Two structures are possible:

- A kind of 'block' copolymer urethanic-acrylic. PU chains are end-capped with monohydroxylated acrylic monomers.
- A graft copolymer: by introduction of a unsaturated diol. An amount of double bounds remain along the PU chain.

This two structures are, actually, intermediate stages. All the double bonds are reactive points, they can be opened massively and a real hybrid network comes up. A photoinitiator is used for that purpose. Products made by this technique belong to the UV-curing subfamily of acrylic-urethanic hybrids.

The hybrid structure take advantage of the high molecular weight which is usually obtained from the acrylic radical chain polymerization. The following figures show the differences between the original PUD and the subsequent hybrid. Description of the polymers:

Polyurethane : Intermediate PUD for RH-6671

Hybrid : RH-6671

Ratio U/A: 1:1

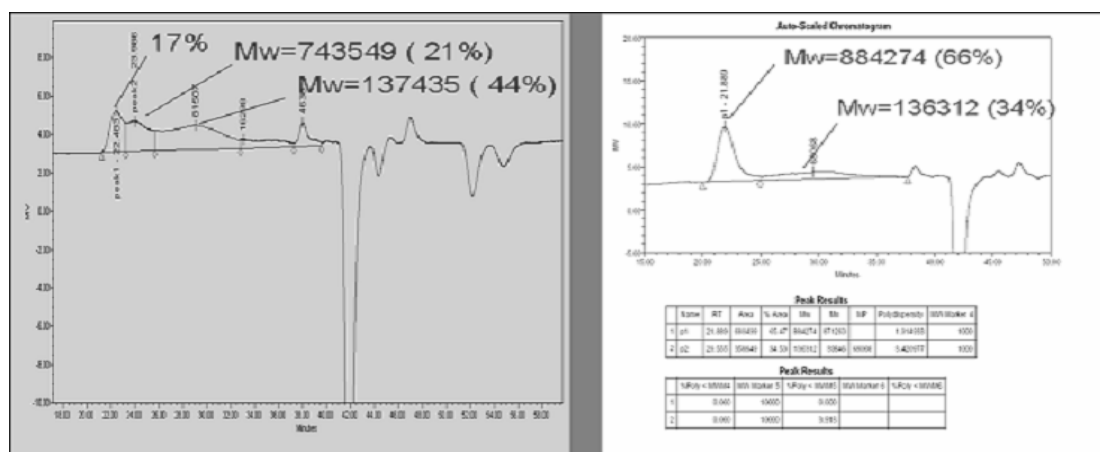


Fig. 8: Molecular weight PUD Molecular weight hybrid
Analysis by GPC technique. Polymer samples dissolved in DMF.

These molecular weight distributions shows the typical polydispersed polyurethane and the narrower polyacrylate. The high molecular weight fractions are notably increased by means of the acrylic polymerization. According to the molecular weight values reached –close to one million-, it is reasonable to accept that the radical chain polymerization is carried out without no significant



interactions of the polar polyurethane chains. This indicates good compatibility. Grafting effects are unlikely to take place by means of any chain transfer parallel process.

4. Generations of hybrids for leather finishing

Stahl has developed its hybrids through different stages. The engines that have made possible to run this race have been:

- Permanent demand of better properties
- Environmentally friendly requirements
- Feasibility and robustness to assure regular production process

1st-Generation:

Definition: Mix between a real shell-core hybrid and acrylic emulsion particles.

Features:

- Use of commercial PUD not specifically adapted for hybrid polymerization
- Use of surfactants to reinforce the stability of the system

2nd-Generation:

Definition: First real shell-core hybrid structure.

Features:

- Use of PUD with higher concentration of hydrophilic components and water miscible solvent
- Total surfactant-free system

3rd-Generation:

Definition: Volatile amine-free hybrids.

Features:

- The PUD is stabilized by means of a polymerizable tertiary amine (PTA).
- Presence of a water miscible solvent
- Copolymerization of the PTA with the acrylic monomers
- Process patented by Stahl

4th-Generation:

Definition: Volatile amine-free, solvent-free hybrids.

Features:

- The PUD is stabilized by means of a polymerizable tertiary amine (PTA).
- Total solvent-free system.
- Acrylic monomers take part in the PUD synthesis as solvents in the prepolymer step.

5th-Generation:

Definition: Volatile amine-free, no-VOC hybrids.

Features:

- The PUD is stabilized by means of a polymerizable tertiary amine (PTA).
- The solvent system of the PUD combines acrylic monomers with no-VOC solvents (boiling point, higher than 250°C)



Remarks about the 3rd-Generation:

This new family of hybrid is the result of a long research process started in 1998 to get stable waterborne hybrids by avoiding the use of toxic volatile amines. Even, those tertiary amines with high boiling points –in the border line of no-VOC- are not used at all.

From the point of view of the structure, the following points has to be underlined:

- After the copolymerization of the PTA, the product is perfectly stable. So, there is no distortion in the distribution of the electrical double layer.
- Specific homopolymerization of the PTA results in coagulation of the hybrid, while copolymerization conditions with other acrylates allows the desired stability.
- An ionic link between the polyurethane and the polyacrylate is established by means of the PTA.
- A narrower particle size distribution is obtained in comparison with hybrids from the previous generations, as it is shown in the following figure:

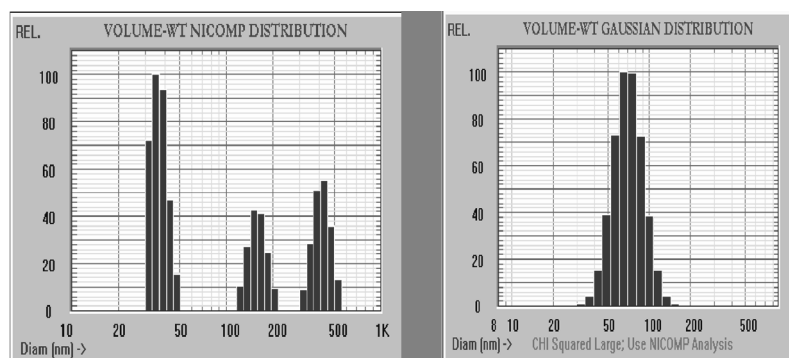


Fig.9: Particle size hybrid 2nd-G

Particle size hybrid 3rd-G

Hybrids analysed:

- Hybrid from 2nd-generation : RH-6663
- Hybrid from 3rd-generation : RH-6677

Other advantages of this generation:

- Better adhesion to different substrates
- Better pigmentability
- Lower viscosity of the intermediate PUD
- Higher degree of monomer conversion for the acrylic polymerization

Remarks about the 4th and 5th Generations:

The replacement of solvent by acrylic monomers allows to produce strictly solvent-free hybrids. This is an advantage from the environmental point of view. But there are some disadvantages from the point of view of the Application requirements:

1. More critical film formation if the MFFT is above 0°C. This is not applicable to soft products, with low MFFT and glass transition temperatures required for high flexibility.
2. Drying problems while working with Roller machine.

The purpose of 5th-Generation is overcome these issues in those products that hardness or application conditions need the presence of a cosolvent, but keeping the no-VOC label.



The following table contains a summary of the different commercial hybrids for Leather Finishing of every generation:

Product	Generation	PUD/PA nature	Application	Remarks
RH-6659	1 st	Polyether/acrylic	Basecoat	High flexes
RH-6663	2 nd	Polyether/acrylic	Basecoat/Topcoat	Balance hardness/flexes
RH-6671	2 nd	Polyether/acrylic	Basecoat	High flexes
RH-6672	2 nd	Polyether/acrylic	Topcoat	Good print retention
RH-6613	2 nd	Polyester/vinylic	Topcoat	Balance hardness/flexes
RH-6677	3 rd	Polyether/acrylic	Basecoat	Extremely flexible
RH-6678	4 th	Polyether/acrylic	Basecoat	Extremely flexible
RH-22048	4 th	Polyether/acrylic	Basecoat/Topcoat	Balance hardness/flexes
RH-22067	4 th	Polycarbonate/acrylic	Topcoat	Medium hardness
RH-22117	4 th	Polyether/acrylic	Basecoat/Topcoat	High solids
RH-6675	5 th	Polyether/acrylic	Basecoat/Topcoat	Best balance flexes/print retention

Table 2: Products and generations

5. Industrial process

The industrial production of hybrids is carried out by means of this kind of flow chart:

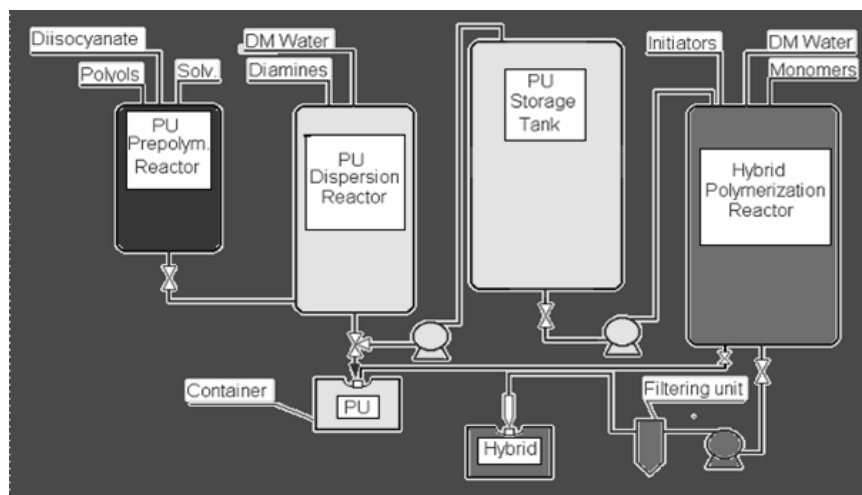


Fig. 10: Industrial process of a hybrid



6. Typical properties on leather and general comparison between hybrids, PUD, polyacrylates.

Leather finish application test waterborne polymers in order to evaluate their performances in:

- Wet rubs
- Sweat rubs
- Dry flexes
- Wet flexes
- Cold flexes
- Heat yellowing, at 105°C
- Adhesion

Average results for basecoat hybrids can be seen in the following table:

Test	Result
50 wet rubs	4/5 – 5
100 wet rubs	4 – 4/5
20 sweat rubs	4
Yellowing (105°C, 144 h)	4/5 – 5
Dry flexes: 100.000	5
Cold flexes: 15.000, at -18°C	5

Table 3: Average results hybrid basecoat. 5: no damage; 1: very bad result

The unique 5th-Generation hybrid shows the following interesting results:

Test	Result
10 wet rubs	4
20 wet rubs	3
Dry flexes	300.000
Cold flexes (-30°C)	25.000
Cold flexes (-40°C)	5.000
Yellowing (105°C, 144 h)	5
Print retention	Excellent definition, no cut-through

Table 4: Average results RH-6675

Even for more general purposes, hybrids can reached a very competitive level of properties in comparison with pure PUD. The following table shows the performances of RH-22-067 and the original PUD:

Test	Original PUD	RH-22067
Water absorption, %	2.0	3.3
MEK absorption, %	Dissolved	98.0
Ethanol absorption, %	27.3	15.6
PCE absorption, %	85.9	65.5
Softening point, °C	164	170

Table 5: Solvent resistance test on RH-22067 and its original PUD.



Hybrids have a very wide possibilities of design and performances, as well as pure PUD and pure polyacrylates. Nevertheless, the benefits of the hybrid structure in terms of general properties⁶ can be summarized by this way:

- What properties of the PUD can be improved by the presence of the Polyacrylate?
 - Yellowing (heat yellowing)
 - Outdoor resistance
 - Sensivity against ketones, alcohols
 - Pigmentability
 - Compatibility with pigments
 - VOC content (solvents, amines)
 - Cost
- What properties of the Polyacrylate can be improved by the presence of the PUD?
 - Mechanical properties: elongation, tensile strength, flexes
 - Mechanical resistances: abrasion, marring
 - Film formation
 - Need of cosolvents and plasticizers
 - Thermoplasticity: softening effect under certain thermal conditions

7. Conclusions

A significant number of papers have been written to describe the acrylic-urethanic hybrids and show them as a real step forward. These polymers are, year by year, making broader their market and application field. Leather Finish has consolidated the use of this products in many formulations. Why? Because:

- Hybrids are quite more than mixes or modified polyurethanes, in terms of:
 - Mechanical properties
 - Chemical properties
 - Overcoming traditional mixes issues
- Hybrids have answered to the environmental market questions:
 - Can we reduce or eliminate solvent content in the PUD's by a feasible industrial process?
 - Can we eliminate toxic volatile amines from the PUD's by a feasible industrial process?
 - Can we improve hard acrylics film formation without increasing coalescent?
- Hybrids offer a high potential of development not only to improve usual performances but also to explore new benefits and effects coming from the intimate contact of the two natures.

8. References

- (1) R. Satguru et al. Aqueous polyurethanes. Polymer colloids with unusual colloidal, mophological and application characteristics. Journal of Coatings Technology, March 1994.
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9. Acknowledgements

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