ACRYLIC-URETHANE HYBRID POLYMERS: MATERIALS WITH HIGH POTENTIAL IN LEATHER FINISHING*

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ABSTRACT

Hybrid materials based on polyurethanes and polyacrylics are a very interesting class of materials combining unique properties with cost advantages over traditional polyurethanes. Untill now the use of these materials for leather finish applications is still limited and the materials have not yet been used at their full potential. Beside the technical advantages of combining the properties of acrylics and urethanes in one material, the hybrid concept has significant advantages when it comes to environmental issues such as co-solvent-free and even VOC-free. In this paper the concept of these hybrid materials will be explained and both the technical and environmental opportunities will be discussed.

RESUMEN

Materiales híbridos basados en poliuretanos y poliacrílicos conforman una clase muy interesante de materiales por su combinación de propiedades únicas con ventajas de costos inferiores comparados con los de poliuretanos tradicionales. Hasta ahora el uso de esos materiales para aplicaciones en acabados para el cuero sigue limitado y los materiales no han sido utilizados a su pleno potencial. Fuera de las ventajas técnicas en combinar las propiedades de acrílicos y uretanos en un solo material, el concepto de hibridación tiene ventajas significativas en relación a asuntos medioambientales tales cómo exención de co-solventes y aun libres de compuestos orgánicos volátiles. En esta obra los conceptos detrás de estos materiales híbridos serán explicados y las oportunidades tanto técnicas como ambientales serán discutidas.

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INTRODUCTION

Polyurethanes are very well appreciated in leather finish because of their excellent balance of mechanical properties and chemical resistance. This superior combination of physical and chemical properties have been linked to both the molecular structure and the domain morphology consisting of hard (urethane) and soft (diol) segments.[1,2] For environmental reasons coating systems with low levels of VOC are preferred. Therefore waterborne Polyurethane dispersions or PUDs have become increasingly popular as the choice for the binder system in leather finishing.

There are a number of ways to make PUDs including the "acetone process", the "melt-dispersion process" and the "pre-polymer mixing process". The polyurethane polymers or the polyurethane part of the hybrids described in this article have been prepared via the "pre-polymer mixing process". Making polyurethanes in this way avoids the use of large amounts of solvents. The pre-polymer is prepared by reacting an excess of diisocyanate with a (mixture of) polyol(s). When using for example DMPA (dimethylolpropionicacid) as one of the diol components a hydrophilically modified NCO-terminated PU pre-polymer is formed. This reaction is carried out in the presence of a relatively small amount of a water-miscible co-solvent. This co-solvent is added to control the viscosity of the pre-polymer, which is important for successful dispersion of the pre-polymer in water. After neutralization of the acid groups with an amine and dispersing of the pre-polymer, chain extension inside the dispersed particles takes place using a diamine like hydrazine. The amount of the DMPA acid-diol is crucial in controlling the dispersibility and the resulting particle size of the PUD.

PUD can be prepared using both aromatic and aliphatic isocyanates. Aromatic versions provide better hardness and chemical resistance than the aliphatic types. However, they also tend to show significant yellowing which is unacceptable for most types of leather finish. For this reason aliphatic versions are the most preferred in finishing systems. Unfortunately, one of the main disadvantages of an aliphatic PUD is the rather high price of the NCO raw material. A popular way to reduce the cost of a PU-based finishing system is to mix the PUD with an acrylic polymer emulsion. As acrylic emulsions are typically significantly lower in price compared to polyurethanes, they significantly reduce the price of the system. On the other hand the physical and chemical performance of the acrylic polymers are substantially lower leading in general to a reduction in the overall performance of the finish. This reduction in performance is often even stronger then what can be expected based on a linear interpolation of the properties of the individual components.[3,4] An explanation for this behavior is often found in the possible incompatibility of the two types of polymers resulting in phase-separation during the film formation.

What is a Hybrid?

In order to achieve the best combination of properties provided by the use of acrylics (weatherability, hardness and pigmentability) and polyurethane (toughness, abrasion resistance and flexibility) special acrylic-urethane dispersion systems have been developed which are called "hybrids". The hybrids incorporate both the polyurethane and the polyacrylics into the same dispersion. In general there are several ways of making a hybrid of the urethane and the acrylic all resulting in different types of material with different properties. Graft copolymerization where the urethane is polymerized onto an acrylic backbone is a popular route for making hybrid polymers. Polyurethane Interpenetrating Networks (IPN's) are unique blends of cross-linked polymers containing essentially no covalent bonds or grafts between the two types of polymers. Permanent entanglements formed by cross-linking of the components networks hold them together. Typically, the two polymers types are combined by polymerizing and cross-linking one in the presence of the other.

A third route towards urethane/acrylic hybrids is by sequential polymerization. In this technique an addition polymer (the acrylic) is formed by the free radical initiation of a monomer that is added to a pre-polymerized water-dispersed polyurethane. Preparing the hybrid in this way actually leads to a material which is also sometimes referred to in the literature as the "type 1" hybrid.[5] This type of hybrid material is more similar to a blend of an acrylic and a polyurethane. This is reflected both in the structure as in the properties of the material. Materials with advanced properties can be obtained by added the acrylic monomers to the urethane pre-polymer and disperse the mixture in water. Both the chain extension and the acrylic polymerization are carried out simultaneously. In this way the acrylic polymer become a part of the PUD particles resulting in improved molecular compatibility versus simple blending. Hybrids made in this way are also referred to as "type 2."

The Structure of a Hybrid

Hybrids materials prepared according to type 1 appear to have more similarities with a blend of an acrylic and a urethane. When the acrylic monomer is added to the PUD it will result in the formation of a separate acrylic dispersion and only a minor amount will penetrate into the PU particles to form the real hybrid. This type of hybrids often shows incompatibility issues and sedimentation of the acrylic part during storage. The type 2 hybrid system represents actually the "real" hybrid materials where the acrylic and the polyurethane part are strongly entangled. The acrylic monomer reacts inside the PU particle forming strong entanglements in the core of the particle. In this way the hybrid could be described, as a complex polymer in which the PU works as the container while the acrylic is the content. This is illustrated in Figure 1. The polyurethane particles are stabilized via the neutralization of the carboxylic acid through an amine. Since the acrylic polymer is completely inside the PU particle no separate stabilization is necessary. Actually the polyurethane particle serves as the "dispersing agent" and stabilizer of the acrylic core of the particle.

The fact that the type 2 hybrid has a structure that is quite close to a core-shell structure can also be made visible with Transmission Electron Microscopy (TEM). Figure 2 shows a TEM picture of a typical type 2 hybrid material. Inside the three circles particles can be seen where the core-shell structure is clearly visible. A close look reveals that there is a light grey area around a whitish core. The white core of the particle has been identified as being the acrylic. The light grey area around the core is actually the shell material formed by the polyurethane. From the TEM picture quite a number of particles can be distinguished showing this typical morphology. Obviously the acrylic monomers penetrate into the PU particles where the polymerization takes place to form the core which is heavily entangles with the polymer chains of the PU. The particle size of the hybrid particles is typically in the range of 50–120 nm. The size is, to a large extent, controlled by the amount of DMPA (dimethylolpropionicacid) used in the synthesis of the Polyurethane. However, compared to PUDs the particle size is larger and the dispersions are typically milky white.

The molecular weight and molecular weight distribution of the hybrids has been measured by using GPC (Gel Permeation Chromatography). The hybrid material has been dissolved in DMF, which is a strong solvent and dissolves both the acrylic and PU part. A typical example of such a chromatogram is shown in Figure 3. The top part of the picture shows the chromatogram of the original PU dispersion. The average molecular weight has been determined to be about 150.000. After polymerization of the acrylic the hybrid is formed. The molecular weight distribution is shown in the lower part of and the shows a molecular weight distribution with two clearly distinguishable peaks. The first peak is the high molecular weight part of the acrylic with an average of about 930.000, while the second part of the distribution is the original PU with an average as mentioned above of about 150.000.

Evolution of the Hybrid Technology

The concept of polyurethane/acrylic hybrids exists already for somewhat more than 15 years. During this time several major technological improvements have been realized through intensive research and development. In this section these technological improvements will be described and the impact on leather finishing will be highlighted. Every major improvement actually marks the start of a new generation. This is also how the hybrids are classified in the next sections. The first generation of hybrids is actually similar to what has been referred to before as the "type 1". The hybrid is based on an existing PUD (including co-solvent like NMP) to where the acrylic monomers are added. Surfactants are used for

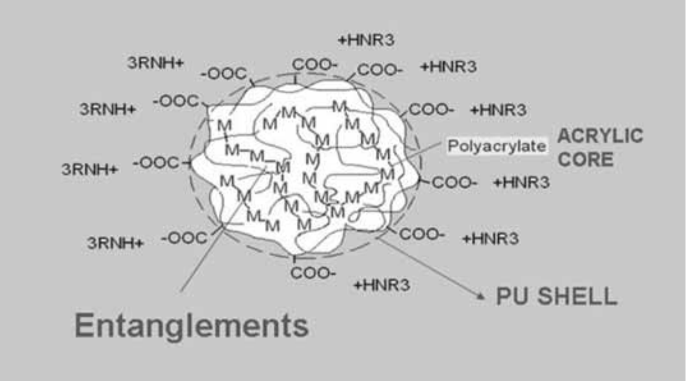


Figure 1. Schematic representation of the core-shell type of structure which is typically observed for the type 2 hybrid materials.

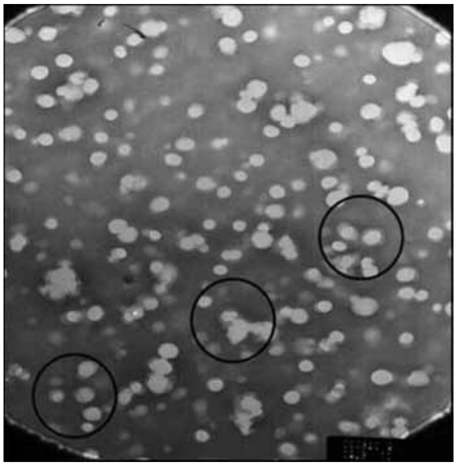


Figure 2. Transmission Eelectron Microscope (TEM) picture of a Urethane/Acrylic hybrid. The sample has been treated with a special chemical containing a heavy element to improve the contrast between the urethane and the acrylic part.

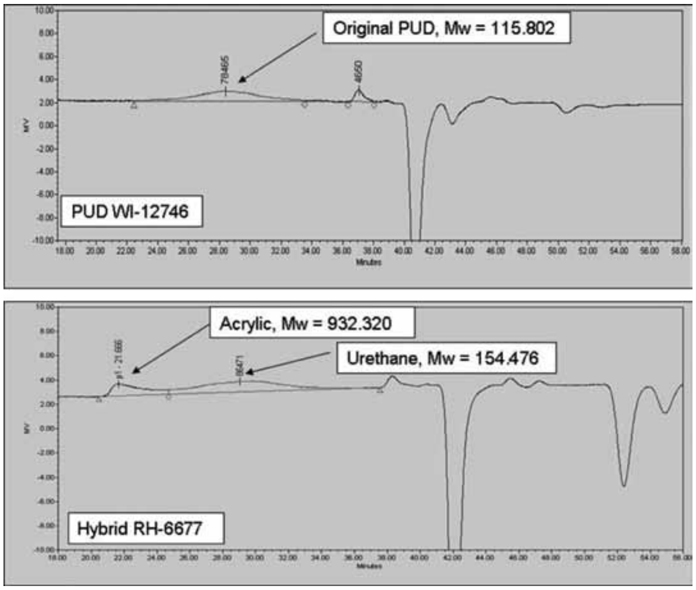


Figure 3. Molecular weight distribution of both the original PUD and the hybrid material as measured by GPC. The polymers have been dissolved in DMF prior to the measurement.

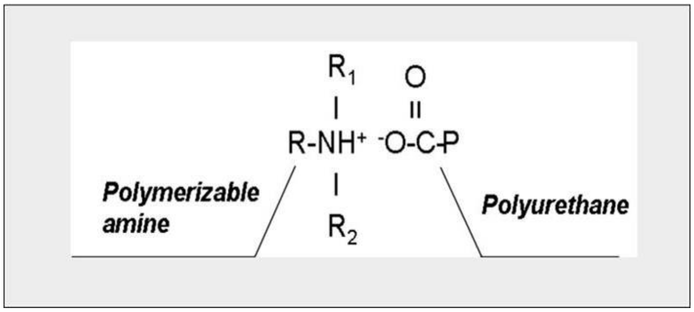
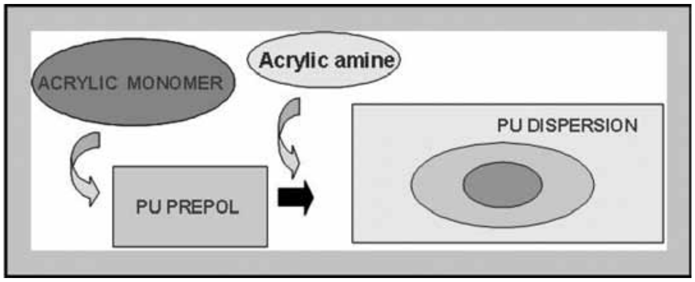


Figure 4. Schematic representation of the concept of amine free hybrid. The carboxylic acid group of the polyurethane is neutralized by a polymerizable amine that copolymerizes with the acrylic monomers.

emulsifying the monomers and improvement of the stability of the final hybrid system. These systems actually result in something that is closer to a dispersion consisting of separate polyurethane and acrylic particles, and show properties that are closer to the properties of blends of the two polymers. These hybrids often show compatibility problems and also stability issues have been observed regularly.

A significant improvement of the "type 1" has been achieved in the second generation of hybrids. These materials are characterized by the fact that they are free of surfactants. The acrylic monomers are dispersed in a PUD that is specifically designed for hybrid applications. The acrylic monomers are absorbed by the PUD particles before the polymerization take place. The resulting material has particles that consist of both polymers. The particle size of the final hybrid dispersion is controlled by the particle size of the original PUD. Because no separate acrylic phase exists compatibility and stability are significantly improved compared to the generation 1 hybrid. The next milestone in the development is reached with generation 3. The drive for reducing free amines in the dispersions raised the question whether it is possible to find a neutralizing agent which can be polymerized while holding its protonated form as well as its stabilizing function. The answer to this question was found by considering a group of materials that have a tertiary amine on one end and a polymerizable group on the other end of the molecule. This material acts both as a neutralizing agent for the PU and as a monomer for the acrylic part[6] as illustrated in Figure 4.

Materials typically used for this concept belong to the class acrylic amines. The polymerizable amine is added to the urethane pre-polymer dispersion for neutralization of the PU acid groups. After dispersion and extension of the PU the rest of the acrylic monomers are added and polymerized to obtain the final hybrid. This concept for making dispersions without free amine has proven to work very well, resulting in stable products that are very well compatible in finishing formulations. The success of the hybrids without free amine triggered the development of the next step towards "green" and environmentally friendly products. The generation 4 hybrids have been developed with the intention to make them both with free-amine and without the addition of co-solvent to the urethane pre-polymer. This is realized by using the acrylic monomers as the solvent for the pre-polymer. The urethane pre-polymer is mixed with the acrylic monomers. In this case the pre-polymer is prepared without any co-solvent and the acrylic monomers act as the solvent to control the viscosity of the mix and hence the dispersibility. The mixture is dispersed in water under the addition of the acrylic amine as neutralizing agent and subsequently the pre-polymer is extended and the acrylic monomers are polymerized. This process is schematically shown in Figure 5.



Specific properties of acrylic amine systems:

- Better compatibility with different polymer systems.
- Increase of thermal stability
- Substantial increase of adhesion to various substrates.
- Better pigmentability and dyeability.
- Lower viscosity of PU emulsions
- Volatile amine content: 0%
- Higher degree of monomer conversion
- Narrower particle size distribution
- Wider molecular weight distribution

Figure 5. Schematic representation of the process for making hybrid material without free-amines. Essential is the addition of the polymerizable acrylic amine to the PU pre-polymer prior to dispersing the pre-polymer into the water phase.

The development of the generation 4 hybrids appeared to be a major step forward. The materials have a lot of positive features when compared with other polymer systems. Both with respect to formulation and performance in the final finishing system on the leather the hybrids show distinct advantages as shown in the frame.

Finally another important development on the hybrids has been achieved recently which is indicated as the generation 5 product. The additional feature compared to the generation 4 products is the use of no VOC solvents. These are "solvents" with a boiling point above 250°C. The use of these materials in the hybrid makes them suitable for specific applications in leather finishing. An important advantage is that the generation 5 products can be used for application by roller coater. This type of application equipment is very common for

TABLE I

Overview of hybrid materials for various generations. For each material the ratio of the urethane and acrylic part (Ratio U/A) and the main application area is given. The last column includes some specific information about the hybrid material.

Product ID.	Gen.	Ratio U/A	Application	Remarks
H59	1st	50/50	Base coat	Use of anionic and nonionic surfactants; PE-urethane
H63	2nd	50/50	Base + top coat	No surfactant, PE urethane, high DMPA, small particle size
H71	2nd	50/50	Base coat	No surfactant, PE urethane, high DMPA, small particle size
H13	2nd	70/30	Top coat	Polyester urethane
H72	2nd	50/50	Base coat	Improved print retention wrt H71
H77	3rd	50/50	Base coat	No free amine, PE-urethane
H78	4th	50/50	Base coat	4th Gen of H78 (NMP and amine free), PE-urethane
H048	4th	50/50	Base + top coat	4th Gen of H63 (NMP and amine free), PE-urethane
H067	4th	78/22	Top coat	Polycarbonate urethane
H117	4th	58/42	Base + top coat	High solids (45%), PE-urethane
H75	5th	70/30	Base coat	Amine free, VOC free, Excellent print retention, roller coating

use of the base coat application and is also being developed now for topcoat application.

Application and Properties

Materials used in leather finishing have to meet a lot of requirements. Depending on the specific application area this can vary from subjective requirements like feel and aesthetics, to objective requirements like physicals (rubs, flexes, abrasion), UV and heat resistance and hydrolysis resistance. Especially for high performance finishes like in automotive the number of requirements that have to be met is very high.

In this paragraph it will be shown that urethane/acrylic hybrids can be designed in such a way that they will meet these highly demanding requirements. The parameters that are available for the design of the hybrids are plenty. Depending on the specific application of the hybrid, e.g. basecoat or topcoat application, one can tune the mechanical properties like modulus and elasticity, the thermoplastic properties for printability, the chemical composition for UV resistance and hydrolysis resistance, etc.

Table I shows on overview of commercial hybrid materials based on the technology of the various generations as discussed in the previous section. For each hybrid it is indicated what the main area of application is. Additionally the ratio of the urethane part and the acrylic part (ratio U/A) in the material is given. Hybrids have been developed for both application in basecoat and topcoat. In general one can see that for basecoat applications the ratio U/A is about 50/50 while for topcoat applications the amount of urethane increases even up to 80/20. The basecoat hybrids are typically based on Polyether-urethanes (PE). The topcoat hybrids are generally based on Polycarbonate-urethanes (PC) to meet the high performance requirements as specified for automotive.

The mechanical properties as derived from tensile measurements are given in Table II. Modulus at 100% elongation, stress at break and elongation at break can be varied from low to high depending on the specific purpose of the hybrid. For basecoat applications the hybrid is more designed towards softness and flexibility to provide optimum printability and flexes while for topcoat

TABLE II

Overview of the mechanical properties of the hybrids from the various generations. The data have been collected via tensile measurements. The parameters that have been measured are the modulus (at 100% elongation), the stress at break (UTS) and the elongation at break (max elongation).

Product ID.	Application	MOD 100% (MPa)	UTS (MPa)	Max Elong. (%)
H59	Base coat	1.3	3.2	390
H63	Base + top coat	5.84	11.85	671
H71	Base coat	2.32	6.76	780
H13	Top coat	5.83	25.44	812
H72	Base coat	4.83	6.01	495
H77	Base coat	1.84	5.80	837
H78	Base coat	1.84	5.80	837
H048	Base + top coat	4.98	10.49	685
H067	Top coat	1.59	12.99	712
H117	Base + top coat	6.04	12.05	384
H75	Base coat	8.59	14.44	289

applications the hybrid tends to be harder and less flexible and is more designed towards chemical resistance and abrasion properties.

Typical test parameters for leather finish are dry, wet and sweat rubs (using Veslic rub test), flexes (using Bally flex, up to 100.00 cycles) and heat yellowing (at 105°C for 144 hrs). These parameters have been measured for various hybrid materials in a typical leather finish. The average results of these measurements have been summarized in table 3. All parameters are measured using a scale from 1-5. In this scale a 1 means a very poor result while a 5 means excellent performance. The selected hybrid materials typically reach a score of 4/5 to 5 for the various parameters as illustrated in table III. The Bally flex test after 100.000 times typically shows a score of 5 while for a hybrid like the H75 even up to 300.000 flexes can be achieved with a score of 5. Also the cold flexes of these materials show excellent results which are often difficult to achieve with the more traditional polyurethanes. This H75 hybrid material has also proven to provide excellent printability and print retention properties when applied in basecoat formulations.

In high performance leather finishes, like in automotive, hydrolysis resistance is an important parameter that has to be met. Many traditional polyurethane polymers tend to fail in this test resulting in poor properties of the finish. Hybrids designed for these high performance applications have proven to meet these high quality standards. The H78 shows excellent hydrolysis resistance when tested against corresponding high performance polyurethanes, making this material very suitable for application in highly demanding automotive leather finish.

The examples of the performance of hybrid materials as described above illustrate that hybrids can meet to moist stringent requirements in leather finishing. Excellent performance can be achieved for a combination of relevant leather finish parameters. This performance level is in many cases difficult or sometimes even impossible to achieve with the traditional polyurethane materials.

TABLE III

Results for some important leather finish properties, measured on hybrid materials in a typical finish application. These parameters are all measured using a scale of 1-5. A score 1 means very poor while a score of 5 means an excellent result.

Property	Result 1: v.bad/ 5: exc.
50 wet rubs	4/5–5
100 wet rubs	4–4/5
20 sweat rubs	4
Heat yellowing 105°C	4/5–5
100.000 flexes	5
15.000 flexes—18°C	5

CONCLUSIONS

In the previous sections it has been tried to show that waterborne, urethane-acrylic hybrid polymer dispersions have high potential in leather finishing. Over the last years many technical developments have taken place to continuously improve the properties of the hybrid materials. This has resulted in materials that can meet all the stringent requirements for high performance finishes as needed for automotive upholstery. The special chemistry that has been developed for the preparation of these materials results in a structure and morphology that leads to excellent and in some case even unique properties that cannot be met by traditional polyurethanes or blend of polyurethanes and acrylics.

Additional to the technical advantages of hybrid materials also environmental aspects have to be considered. The hybrids can be considered as truly "green" and environmentally friendly materials. Step by step improvement of the preparation technology has finally resulted in waterborne dispersion binders that are surfactant-free co-solvent-free, amine-free and finally also free from VOC-solvents. Considering also the cost advantage over traditional PUD it is obvious the hybrids are a special class of materials with high potential for leather finishing.

REFERENCES

1. G. Satguru et al, *Proceedings of the Waterborne, High-Solids, and Powder Coatings Symposium,* New Orleans, February, 1993
2. W.P. Yang, *Proceedings of the American Chemical Society National Meeting,* San Francisco, April 5–10, p. 216, 1995
3. R. Derby et al, *American Ink Maker* **56**, June 1995
4. C.R. Hegedus and K.A. Kloiber, *Journal of Coatings Techology* **68** (860), 39, 1996
5. E.C. Galcogi et al, *Proceedings of the Society of the Plastics Industry,* Toronto, April 1–3, 2001.
6. J. Oller, M. Jimenez, M. Pous; *Process for the preparation of anionic aqueous polymer dispersions containing no volatile tertiary amine, obtained dispersion and coating resulting from said dispersion*; PCT Int. Appl. WO.01/27178 A1, 2001