What's an Acrylic-Urethane Hybrid polymers?

by

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Hybrid materials based on polyurethanes and polyacrylics are a very interesting class of materials combining unique properties with cost advantages over traditional polyurethanes. Till 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 like co-solvent-free and even VOC-free

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. They are held together by permanent entanglements formed by cross-linking of the components networks. Typically, the two polymers types are combined by polymerizing and cross-linking one in the presence of the other.

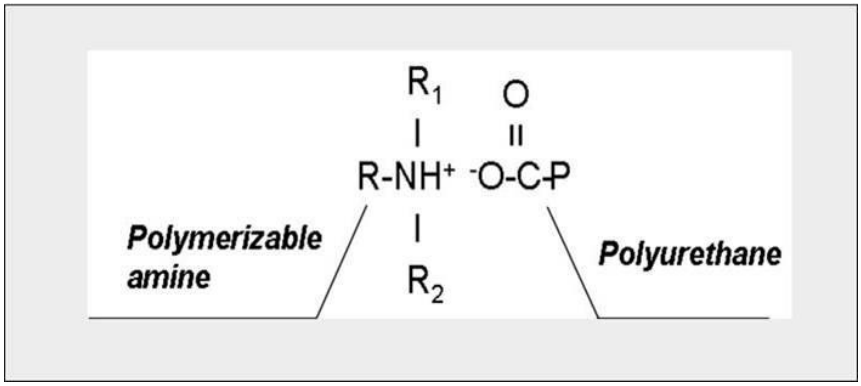
A third route towards urethane/acrylic hybrids is by sequential polymerization. In this technique an addition polymer (the acrylic) is formed by the free radical initiation of a monomer that is added to a pre-polymerized water-dispersed polyurethane. Preparing the hybrid in this way actually leads to a material which is also sometimes referred to in the literature as the "type 1" hybrid. 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 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.
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 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.

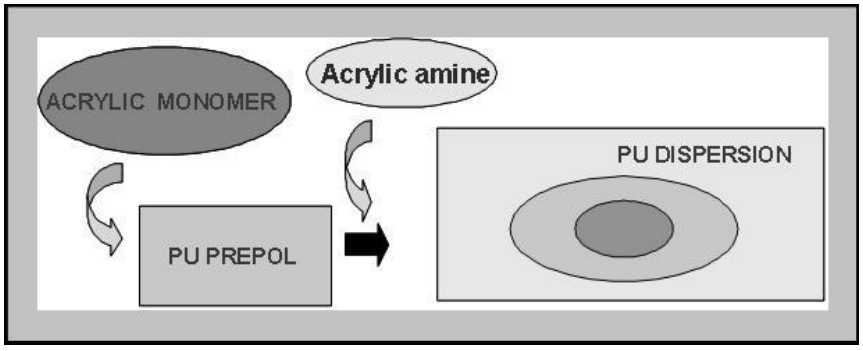
The next milestone in the development is reached with generation 3. The drive for reducing free amines in the dispersions raised the question whether it is possible to find a neutralizing agent which can be polymerized while holding its protonated form as well as its stabilizing function. The answer 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.



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.



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 250ºC. 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 use of the base coat application and is also being developed now for topcoat application.

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