Water Reducible UV Cure Allophanate Urethane Acrylates

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Summary

UV curable polyurethane dispersions (UV-PUD) are well established waterborne raw materials. These resins have found many applications industrially. Although very versatile in many different applications they have to be synthesised and delivered in roughly 50%-65% of water.

In this paper alternative concepts of water-compatible resins are presented that start from low viscosity. These resins are 100% solids and they can be incorporated into water via a simple stirring process at room temperature.

We have developed UV curable resins based on hydrophilic modified allophanates that can be directly emulsified into water leading to a stable emulsion. In addition, these resin systems can be easily diluted by any amount of water to yield a clear solution.

Typical application property deficiencies associated with highly water compatible binders were addressed and could be significantly reduced.

Introduction

Waterborne UV curable polyurethane dispersion (UV-PUD) are well established e.g. in the furniture coatings industry. UV-PUDs offer high productivity and a high environmental compatibility due to the fact that they usually do not contain any solvent without sacrificing from any of the properties. Built up from unsaturated resins like polyester acrylate polyols or polyepoxy acrylate polyols, diols, diamines, and polyisocyanates they receive their water compatibility from the presence of a hydrophilic group (Figure 1). These binders commonly have a high molecular weight which makes them solid or very viscous at 100% solids. That means that water as viscosity moderator has to be added during the synthesis process and is an intrinsic part of the raw material supply form. Typically, such dispersions have a solids content of 35-50% and it is hardly possible to increase that in a ready to use formulation.

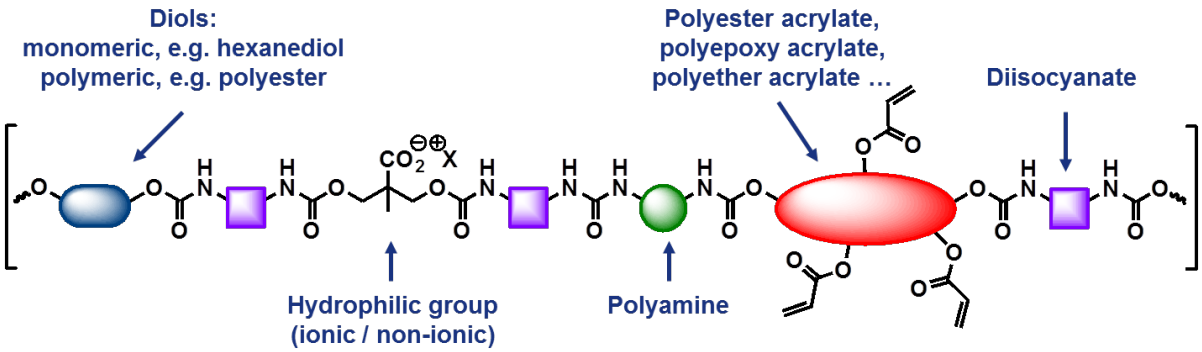

Figure 1. Schematic representation of a typical UV curable polyurethane dispersion.

Thus, applicators have to accept some limitations that come along with the high water content. The water has to be removed prior to the radiation curing. With increasing water content more time and energy will be consumed for that step and the maximum possible film thickness will decrease. For example in wood primer applications waterborne systems are preferred as they induce wood swelling that improves adhesion. However, at 35-50% solid contents there will still be a need to flash off excess water which slows down the production process. It is a characteristic of such systems that they do not show a homogeneous organic phase but are usually milk-like dispersions / emulsions in water.

On the other hand there are water dilutable systems available in the market. Such systems usually have much higher initial solids content than dispersions and appear as clear solutions. Typically, these products are based on raw materials with a lot of polyether content. The ability to be diluted with water depends on the ethylene oxide content of the polyether (Figure 2). Many polyethyleneoxide polyol containing raw materials; however, can be diluted only with a certain amount of water and are prone to phase separation upon higher dilution. Resins with high polyethyleneoxide contents can be diluted with any concentration of water. However, high contents of polyethylene oxides in the backbone of radiation curing polyurethanes tend to deteriorate key properties of the coatings such as hardness, toughness, scratch resistance, and chemical resistance. Further products based on higher molecular weight polyethylene oxides are typically solids, which means, that it is necessary to add some water during production to achieve liquid products.

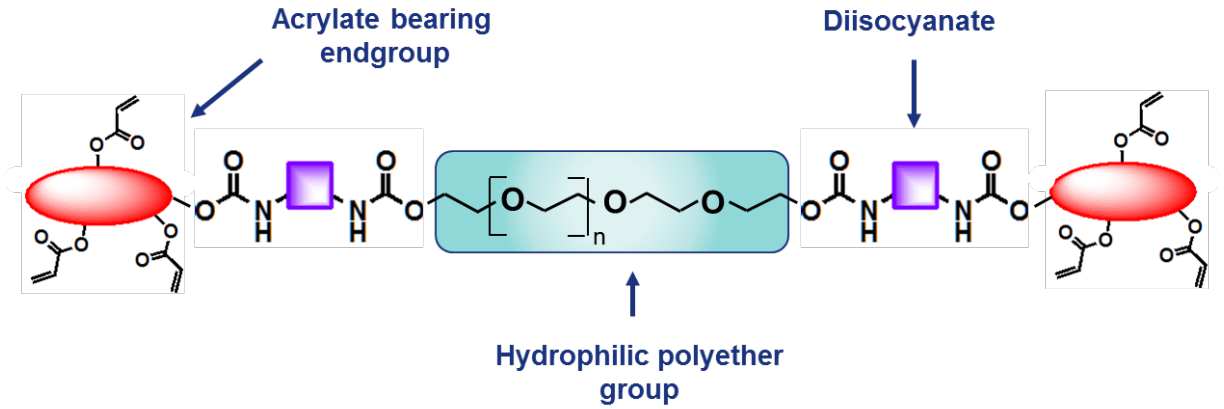

Figure 2. Schematic representation of a typical water thinnable UV curable polyurethane resin.

Allophanate technology as means for low viscosity modification of polyurethanes

As reported earlier[1], it is possible to significantly reduce the viscosity of radiation curing polyurethane resins with allophanate technology. The direct approach (Figure 3) leads to a product that is an order of a magnitude lower in viscosity than the corresponding isocyanurate based technologies.

When the synthesis is performed with a hydroxyl group bearing acrylate as allophanate-alcohol the functionality can be equally high compared to an isocyanurate. This leads to similar performance data such as scratch resistance, hardness, and chemical resistance.

It could be shown that by incorporation of different building blocks the properties can be pushed towards more hardness and scratch resistance or on the other hand to a softer and more elastic material. As long as the molecular weight build up is not significant, modifications like this will lead to a reduced viscosity as the hydrogen bond density is reduced. An overview over typical viscosities for different kinds of resins is given in Table 1.

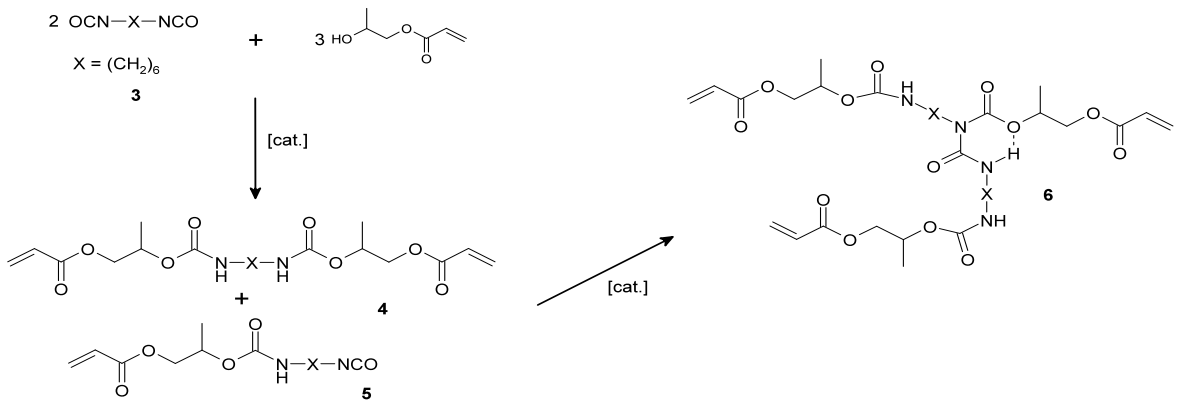

Figure 3. Direct allophanatisation without distillation step.

These allophanate based resins are outdoor resistant and suitable for many applications such as plastics and metal coatings[2].

Table 1. Viscosity range of HDI-based urethane acrylates.

UV Cure resin (100% Solids)	Viscosity at 23 °C
Isocyanurate based	>500,000 mPas
Allophanate	75,000 mPas
Allophanate, optimized	38,500 mPas
Allophanate, scratch resistant	16,500 mPas
Allophanate, elastified	7,500 mPas

Water dispersible allophanate urethane acrylates

Although already very low in viscosity many coating applications need a further dilution of such resins either in solvent or in reactive thinner. As a logical step the already low viscous allophanate scaffold was modified with water-compatible building blocks to receive resins that can easily be dispersed in water (Figure 4).

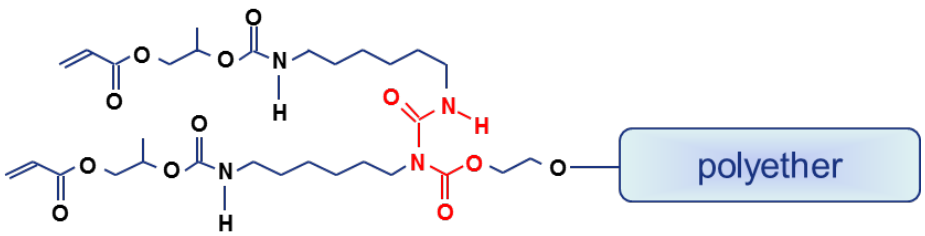

Figure 4. Water compatible allophanate based urethane acrylate.

It was a developmental goal to achieve a resin with a moderate to low viscosity that can easily be dispersed in water by a simple stirring process. Two types of products exemplify the options towards different properties. Allophanate A has a comparatively high polyether

content leading to a lower viscosity, a lower hardness and a slightly worse chemical resistance. Allophanate B has a reduced polyether content which results in a significantly higher hardness and a higher viscosity in supply form. After dilution with water, however, the viscosity turns out to be much lower compared to allophanate A.

Table 2. Property profiles of two different hydrophilic modified allophanate urethane acrylates.

Properties	Allophanate A	Allophanate B
Viscosity at 100% Solids	18,500 mPas	34,000 mPas
Zone Cup Viscosity at 50% Solids	102 s	21s
Re-emulsification	Immediate	Immediate
Grain wetting (Oak)	Very good	Very good
Pendulum hardness, after UV cure	50 seconds	122 seconds
Chemical Resistance		
Water	Very good	Very good
Red Wine	Moderate	Moderate
48% Ethanol	Moderate	Good
96% Ethanol	Good	Good

When closely looking at the process of water addition to the 100%-solids systems, a clear solution is visible at very high solids content. The viscosity is reduced at this point. On further dilution the solution gets turbid and the viscosity increases. At this point a water-in-oil emulsion is being formed. Continuing dilution causes increasing viscosities up to the point where the phase inversion to an oil-in-water emulsion takes place. From that point on, the viscosity decreases continuously with increasing water content.

Currently, a major disadvantage of the water dispersible allophanates is the fact that they perform very well at higher dilutions but are quite instable at very high solids contents. In particular the water–in-oil emulsion is very unstable and not really suitable for industrial processes. Solids contents close to the phase inversion point are prohibitive due to the high viscosity and for stability reasons.

Therefore, the most interesting application form of this kind of resins will be in ready for use formulations with 40-55% solids. This makes the application profile quite similar to classical dispersions, with the advantage of a 100% solids delivery form and thus a very high degree of freedom of formulation.

Water dilutable urethane acrylates

To achieve resin systems that are truly water dilutable some conceptual changes are necessary.

Emulsion forming resins have a molecular design that consists of very hydrophobic moieties and of parts that are very hydrophilic, in summary, tenside-like. Products structured like this form agglomerates that separate the oil and the water phase from each other. Micelles will be formed that can grow to small drops up to roughly 200 nm in diameter for a stable dispersion.

For a water dilutable system it is necessary to have a molecular design that is dominated by hydrophilic groups to make the molecule completely water soluble. Such systems should not build separate phases at any point. That means they are completely water soluble over the whole range of water content. The viscosity of a 100%-solids system will continuously decrease upon water addition as there is no phase inversion with the corresponding viscosity maximum.

The materials of choice to achieve very high water compatibility are again the ethylene oxide based polyethers. Such polyethers are miscible with water as well as with many organic solvents or building blocks. However, large amounts of polyethers can reduce film properties regarding physical and chemical resistance. Additionally, high amounts of polyethers will reduce the double bond density of the resin resulting in a lowered reactivity and crosslink density.

As shown in Figure 5 a new molecular design with a second hydrophilic building block beneath the non-functional polyether leads to a higher hydrophilicity of the whole molecule. In addition, this hydrophilic building block contains UV-reactive sites as well to enhance the reactivity.

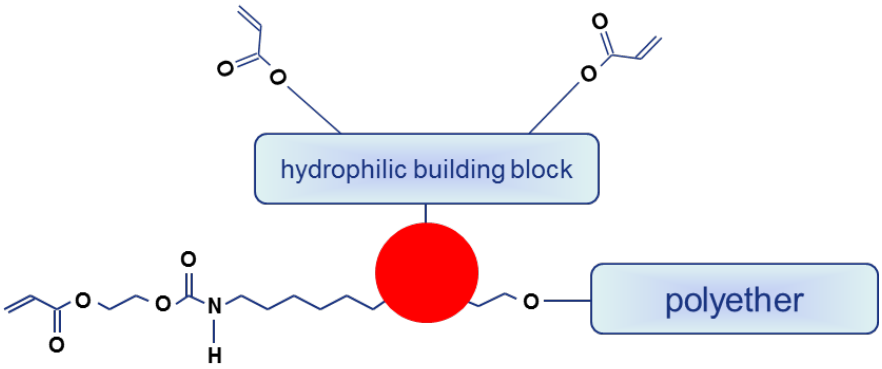

Figure 5. Water dilutable urethane acrylate

Table 3 gives an overview over the property profile of such a product called ‘urethane acrylate C’. As comparison two classical concepts were tested.

The first comparison product (urethane acrylate D) is based on the classical approach: A very long-chain polyether converted with a diisocyanate to a prepolymer and capped with a hydroxyfunctional alkyltriacrylate. The very long linear polyether leads to a solid product that can easily be dissolved in some water. It is comparatively high in viscosity at different solids contents but very stable at any concentration. It does show a small phase inversion viscosity peak. Although it is end-capped with an oligofunctional acrylate its UV-reactivity is rather poor.

The second comparison product (urethane acrylate E) is based on a branched short chain polyether that is partly esterified with acrylic acid and subsequently converted with a diisocyanate. Although not stable at low solids content it is quite low in viscosity. However, the UV-reactivity is still poor.

Urethane acrylate C overcomes most disadvantages of the comparison products. It is a low viscosity liquid that is easily dilutable with water to any concentration. It shows a very high UV-reactivity, comparatively high pendulum hardness and a good resistance against a 10%NaOH-solution.

All products were tested for adhesion on wood. In all cases the adhesion test failed at 100% or at 90% solids. Starting from a water content of 20% the adhesion was very good in all cases, which indicates the suitability of these products for a wood primer application.

Table 3. Typical properties of Urethane Acrylate C.

Properties		Urethane Acrylate C	Urethane Acrylate D with long chain polyether	Urethane Acrylate E with branched short chain polyether
Reactivity		40 m/min	10 m/min	15 m/min
100% solids	Viscosity	19,000 mPas	Solid	830 mPas
	Pendulum Hardness	80 seconds	70 seconds	40 seconds
	Resistance to 10% NaOH in water	Good	Bad	Moderate
	Adhesion to oak	Bad	Bad	Bad
90% solids in water	Viscosity	4,400 mPas	11,000 mPas	370 mPas
	Stability (phase separation)	>40 days	>40 days	10 days
	Adhesion to oak	Bad	Bad	Bad
80% solids in water	Viscosity	2,700 mPas	5,000 mPas	330 mPas
	Stability (phase separation)	>40 days	>40 days	1 day
	Adhesion to oak	Very good	Very good	Very good
50% solids in water	Viscosity	1,900 mPas	7,000 mPas	instable
	Stability (phase separation)	>40 days	>40 days	0 days
	Adhesion to oak	Very good	Very good	-

Table 4 summarizes the properties of water dilutable urethane acrylate C. It is supplied as 100% solids form. This gives the formulator the freedom to choose between water, solvent or reactive diluent to choose form in order to adjust the formulation to applicable viscosity.

Besides wood coating applications, one other application areas of the urethane acrylate C can be for anti-fogging coatings on glass and plastic substrates. When formulated with polyethene glycol allyl (3-sulfonpropyl) diether, potassium salt (81.84 parts urethane acrylate C, 15.34 parts polyethylene glycol ally diether salt, 2.82 parts photoinitiator) it has very nice properties in terms of anti-fogging on glass and plastic substrates.

Table 4. Properties of water dilutable Urethane Acrylate C.

Form Supplied	100% Solids
Functionality	3.5
Double Bond Density	1.9 val/kg
Elongation at Break	10%
Tensile Strength	2.7 N/mm^2
Glass Trasition Temperature	-19 °C

Conclusion

Established UV-curing polyurethane dispersions with solids content of 35-50% have proven their benefit in many applications. Besides this technology, low viscous 100%-solids water-compatible binders are an alternative that provides formulators with a higher degree of formulation freedom.

Simple modification of low viscosity allophanates with a single polyether-based building block lead to tenside-like molecules that perform very well on higher dilution as they form stable oil-in-water emulsions. However, formulations with higher solids contents are hardly achievable due to the fact that the resulting water-in-oil emulsions are instable and the viscosities go up close to the phase inversion point. Many different applications are possible for products like allophanate A or allophanate B at low solids content. A major advantage is the higher freedom of formulation. As such it is possible to start formulation from the 100% solids delivery form and add additives that will remain in the oil phase after the addition of water. The resins have a significant emulsifying power which facilitates the addition of unusually high amounts of hydrophobic resins or reactive thinners to a waterborne formulation. It is further possible to enhance selected properties by co-formulating with other dispersions.

Modifications of urethane acrylates with specific additional hydrophilic building blocks lead to a structure that is completely hydrophilic and thus water dilutable in any concentration. Already the current development level leads to products with superior performance level compared to existing water dilutable products that are based on long chain polyethers.

Potential applications could be high solids spray application on wood, plastic and paper for primer, coatings and printing inks as water effectively can be seen as a solvent to be used just in the amount required by the application. In addition, latest developments on anti-fogging coating applications have shown promising results.

References

1 M. Ludewig, N. Stöckel, J. Weikard; *RadTech Europe 2005*, *Conference Proceedings Vol 1. 261-268*.

2 M. Ludewig, H. Kuczewski, W. Fischer; RadTech Europe 2007, Conference Proceedings 3.2.