Water-Based Radiation Curable Polyurethane Dispersions as Performant Coatings for Challenging Applications

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PRA's second international conference dedicated to:
Waterborne & High Solids Coatings
"Reducing Environmental Impact"
Brussels, 11-12 March 2008

Abstract

Radiation curable polyurethane dispersions (called UV-PUD) have benefited over the last years from a continuous growth as high-end and innovative performance materials for several markets. These products combine the advantages of (i) polyurethane chemistry (ii) radiation curing technology and (iii) aqueous colloidal dispersions. Such a combination allows obtaining high-performance environment-friendly coatings on various types of substrates with simple formulation work and almost no viscosity limitations. Modifications of the polyurethane backbone can address challenging requirements of the different market segments: wood, PVC resilient flooring, concrete flooring, paper upgrading, plastics and even outdoor applications.

1. Introduction

Low viscosity, high performance water-based UV-resins

The coating technologies having a lower chemical impact on environment and health are gradually dominating the market with, as a consequence, the development of innovative waterborne polymers with good standards of performance for many industries. Further, the design of low viscous, high performance resins for spray application to coat three-dimensional objects has led to a new generation of binders, radiation curable polyurethane dispersions (UV-PUD) [1–3]. The high molar mass of UV-PUDs induces limited shrinkage after curing, resulting in an excellent adhesion to many substrates. The combination of this property together with their low viscosity and the advantages of UV-technology (i.e. the ability to coat heat-sensitive substrates like plastics and wood as well as superior scratch and stain resistance and absence of VOC) make these aqueous dispersions of acrylated polyurethane oligomers very suitable for either primer or topcoat with high end performance and strong potential [4].

UVPUD chemistry, structure and properties

UV-PUDs are synthesized in a multi-step process (see figure 1):

1) preparation of a polyurethane pre-polymer by reaction of a diol (long and short chain and containing carboxylic functions) with a diisocyanate in solvent.
2) capping of the isocyanate terminated polyurethane with a hydroxylated acrylate molecule.
3) dispersion in water and neutralization of the carboxylic functions.
4) stripping of solvent.

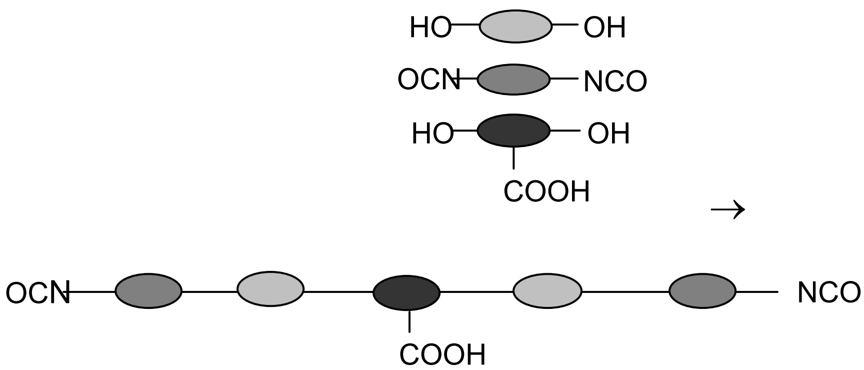

Figure 1. Schematic representation of a UVPUD synthesis

The resulting UV-PUDs are low viscosity colloidal dispersions (< 200 mPa.s) characterized by a solid content between 35% and 45%, a pH value between 7 and 8 and an average particle size below 100 nm. Figure 2 gives the schematic structure of the UVPUD oligomer. Thanks to the broad variety of raw materials, a lot of different UV-PUD structures can be synthesized in order to fit the requirements of various applications.

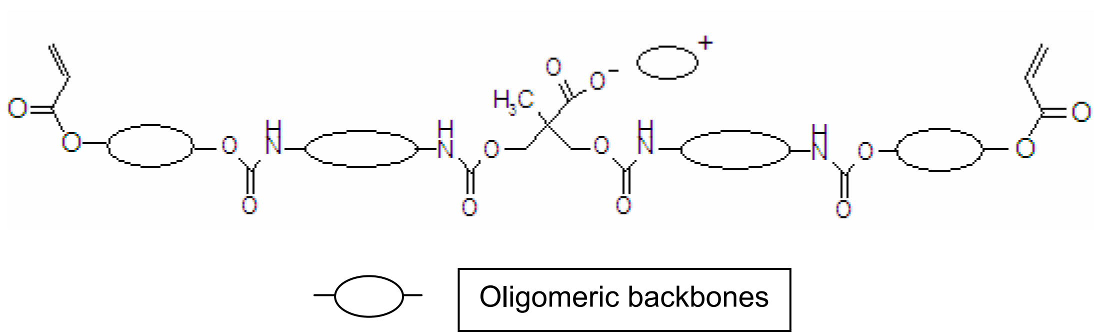

Figure 2. UVPUD oligomer structure

Physical drying, film formation and UV curing of UVPUDs

Before UV curing, the water needs to be evaporated completely to avoid blisters, whitening of the film and other defects. The minimum film formation temperature (MFFT) of these coatings is below room temperature and does not require the use of coalescing agents. The dry layer formed after particle coalescence is generally tack-free before cure, thus decreasing dust contamination, heat blocking and ensuring uniform gloss for the topcoat.

Following water evaporation upon drying and after UV curing, the hard urethane domains combined with the acrylate crosslinked network, will give the cured film its hardness and resistance while the softer domains will serve as buffer zones and account for the flexibility and impact resistance. A superior balance in chemical resistance and mechanical properties – like (cold) flexibility and impact deformation – is obtained when comparing to 100% UV systems (based on mixture of acrylated molecules), due to the lower cross-linking density and the higher molar mass between crosslinks. The influence of the cross-linking density and the molar mass between cross-linking knots on the coating performance was reported elsewhere in the case of 100% UV systems [5] and UV-PUDs [6]. Recent investigations about UVPUD chemistry and physics addressed outdoor performance [7], colloidal stability [8] as well as rheology [9].

2. Formulating and applying UVPUDs on challenging substrates

2-1. Wood substrates

Generalities

The wood substrate is a natural porous material consisting mainly of cellulosic fibers and lignin. Wood is not dimensionally stable and is very vulnerable to surface deterioration through fungal, microbial, moisture and light degradation as well as to tannin staining. As such, the wood substrate continues to present a challenge for efficient protective coatings in terms of esthetical and qualitative performance, more typically for outdoor applications.

The furniture industry needs to coat flat panels, slightly profiled pieces (for example doors) and 3-D pieces such as chairs or assembled furniture. Spray, curtain or vacuum coaters are better suited to these applications than roller coater. The flexibility, adhesion and stain resistance of UVPUD coatings as well as their low viscosity and the very low VOC makes them very attractive for such applications.

To meet the market demands, durable clear coats for wood are required that reduce photochemical degradation and moisture uptake. The coating must have a good dimensional stability to avoid film failure (cracking) and loss of adhesion (flaking, peeling, blistering) arising from mechanical solicitations (scratch), from thermal effects (freeze thaw) and from the penetration of water and its accumulation at the coating interface [10].

Coatings on wood are generally obtained using the following steps (see figure 3):

- substrate sanding
- application of an adhesion primer (optional)
- application of a sealer in order to “close” the surface and bring abrasion properties (optional).
- sanding
- application of a topcoat for providing end properties such as aspect and scratch resistance

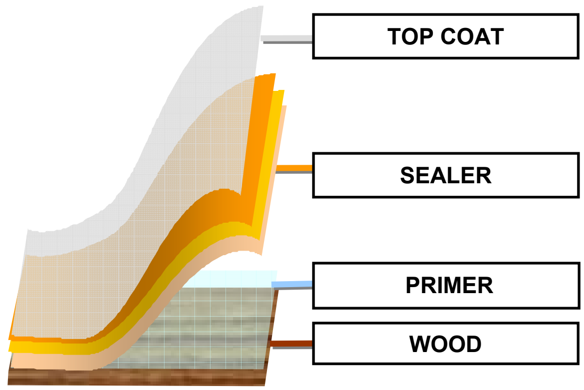

Figure 3. Schematic representation of a coating on wood

A UVPUD mat formulation for spray application on wood is given in table 1, coating weight being 60 – 70 g/m² per coat.

Table 1. Spray formulation for wood

Component	parts
UVPUD	100
Matting agent	1.5
Wax	3.0
Photoinitiator	1.5
Rheology modifier	0.4

A rheology modifier is necessary, even for low viscosity spray application, to give a “cohesion” to the liquid film. This will help flow and film uniformity. The rheology modifier needs to be pre-dispersed at 50% in water before addition to the formulation.

A UVPUD formulation for curtain coater application can be derived from table 1 by increasing the rheology modifier content to 1 part, which illustrates how easy UVPUDs are to formulate. Coating weight would be in that case 80 to 100 g/m² wet per coat, 0.1 part defoamer and 0.3 part wetting agent would be advised.

Physical drying is the longest step in the wood finishing process with UV-PUD. A classical drying method is to use air at 35-40°C with a low velocity (0.5 to 1 m/s) for a few minutes in the first stage and then air at 45-50°C with high velocity (jet-dryer). This drying process is far more efficient when using dry air. One of the most efficient drying processes is to combine micro-wave water evaporation with jet-dryers. Infrared technology is suitable on closed pore wood surfaces but will induce bubbles in open pore finishing systems.

Outdoor joinery

Of the key tests which has to be passed aging is very important. The European norm EN 927 was used as a guideline for the development. For outdoor exposure, wood needs special protection, especially the wood-coating interface which is very sensitive to the combined action of UV light and humidity. The first coats need to impregnate the wood and traditional acrylic emulsions are well suited to this purpose. UV-PUD brings advantages for the topcoat: excellent weathering, chemical and physical properties and good blocking with 150 g/m² (wet) instead of 250 g/m² (wet) for a conventional topcoat.

These properties are illustrated in tables 2 & 3 which detail stain resistance and mechanical properties of UVPUDs applied on beech wood by spray. UV-PUD 2 has a better performance than UV-PUD 1 of the first generation. Chemical, scratch and blocking resistances of both UV-PUDs are superior to conventional water based acrylic. Figure 4 shows the outdoor performance of said systems (as monitored by the gloss evolution upon Xenon aging) where the superior performance (4000 h resistance) of UVPUD2 is highlighted.

Table 2. Comparative stain resistance (DIN 68 861) on beech wood
0 = unattacked, 5 = completely damaged
Acrylic industry standard = 100 + 100 + 250 g/m2 wet
UVPUD1 = 3 x 80 g/m2 wet
UVPUD2 = 3 x 75 g/m2 wet

Stain	Industry standard		UVPUD1		UVPUD2	
	1h	4h	1h	4h	1h	4h
Cleaning product	4	4	0	0	0	0
Ammonia 1%	4	4	0	0	0	0
Ammonia 5%	4	4	0	0	0	0
Ethanol 20%	0	0	0	0	0	0
Butylglycol	5	5	0	5	0	0
Water	0	0	0	0	0	0
Ketchup	0	0	0	0	0	0
Mustard	2	2	0	0	0	0
Red wine	2	2	0	0	0	0
Coffee	1	2	0	0	0	0
Bleach water 9%	2	3	0	0	0	0
Acetic acid	0	0	0	0	0	0
Eosin 2%	3	3	0	0	0	0

Table 3. Comparative mechanical properties on beech and pine wood
0 = good, 5 = bad
Acrylic industry standard = 100 + 100 + 250 g/m2 wet
UVPUD1 = 3 x 80 g/m2 wet
UVPUD2 = 3 x 75 g/m2 wet

Property	Industry standard	UVPUD1	UVPUD2
Adhesion (beech)	0	1	0
Nail scratch resistance (beech)	5	0	0
Blocking resistance (pine)	1	0	0

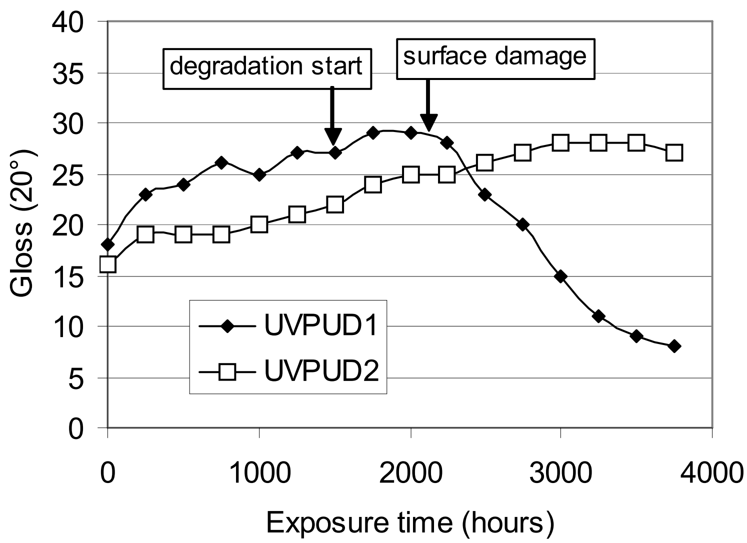

Figure 4. Comparative Xenon aging on neutral substrate

Kitchen cabinet wood furniture

A formulation for white pigmented spray coatings on melamine type panels for kitchen cabinet or bath room is given in table 3. Coating weight is between 120 and 150 gr/m² with 15 % white pigment. Drying conditions are 20 minutes exposure at 40 to 50°C.

Table 4. UVPUD white pigmented formulation for kitchen cabinet or bath room (spray)

Component	parts
UVPUD	100
White pigment	18
Photoinitiators	1.5
Rheology modifier	0.5

Table 5 details the performance of two UVPUD formulated as in table 4. Coatings were applied on white melamine paper at 110 gr/m² wet and UV cured at 5 m/min with 1 Ga and 1 Hg 80 W/cm lamps. The coating based on UVPUD4 exhibits very good scratch resistance as well as excellent chemical resistances to stains like black marker, mustard, ketchup and the like.

Table 5. Performances of UVPUD coatings for kitchen cabinet application

Performance	UVPUD3	UVPUD4
Reactivity (m/min.) * 36 microns coating applied on paper and cured under 80 W Hg lamp with 1.5 Additol BCPK	10	35
Steel wool resistance (rubs)	< 5	> 25
Stain resistance (5 = no visible stain left,1 = very strong stain)		
Tar	4	5
Shoe polish	4	5
Ketchup	4.5	5
Mustard	4	5
Sudan red colorant (SR380-WS)	4.5	5
N-70 black marker	4	5
Persoz hardness (s) 120 µ coating on glass, cured 3 x reactivity.	230	320

* maximum line speed at which the coating is touch dry

2-2. Polyvinyl chloride (PVC) resilient flooring

PVC is the main substrate used for resilient flooring and applications include transport, sport, residential use as well as social areas (hospitals, schools) and industrial applications with specific requirements for each of these. Forms of delivery will comprise rolls and tiles mainly.

Compared to conventional waterborne coatings, UVPUD coatings will exhibit superior stain and chemical resistance thanks to the crosslinked polymer network formed after UV irradiation as well as their remarkable adhesion and flexibility.

A typical mat formulation for roller coater application is given in table 6.

Table 6. UVPUD mat formulation for roller coater resilient flooring application

Component	parts
UVPUD	100
Matting agent	2.5
Leveling agent	0.4
Wax	3.0
Photoinitiator	1.5
Rheology modifier	1.4

Application will be carried out using reverse gravure as detailed in figure 5. Coating weight is 30 to 40 g/m² wet giving after drying and UV curing a dry coating of around 12 to 13 µ. Typical operating conditions are as follows:

- Line speed: 15 m/min
- Application roll: 18 m/min
- UV-curing: 200 W/cm Hg lamp
- Gloss at 60°: 8 %

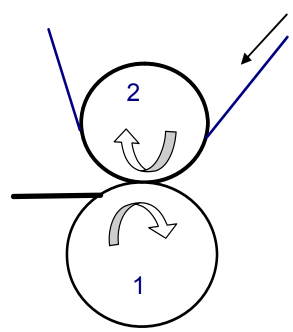

Figure 5. Schematic representation of the reverse gravure roller coater configuration for UVPUD application on PVC. Roller 1: helical engraved cylinder (40 lines/cm, volume 48 ml/m2). Roller 2: rubber press. The arrow indicates the PVC sheet direction.

Table 7 details the stain resistance of different mat UVPUD systems with various rigidity on homogeneous PVC substrate. Cross hatched adhesion to PVC is in all cases 100%.

Table 7. Performances of UVPUD coatings for PVC resilient flooring

Property	Uncoated PVC	UVPUD 5	UVPUD 6	UVPUD 7	UVPUD 8
Stain resistance (5 = no visible stain left,1 = very strong stain)					
N-70 black marker	3	5	5	5	5
tar	1	4	4	3	5
KIWI black shoe polish	1	5	5	5	5
yellow colorant (SG146-WS)	1	5	5	5	5
sudan red colorant (SR380-WS)	1	5	5	5	5
blue colorant (BB750 H_2O)	5	5	5	5	5
eosin	4	3	4	3	4-5
iso-betadine	2	4	4	5	5
Coating rigidity*	-	medium	rigid	flexible	very rigid

* evaluated by bending the coated PVC and checking for cracks

It follows that UVPUDs show good (UVPUD5, 6 & 7) to excellent stain resistance (UVPUD8) while displaying different rigidities which allows to fit the application.

2-3. Other Plastic substrates

The development of telecommunication, electronic and automotive industry has led to a growing demand for high performance, high efficiency and value added coatings on various plastic substrates used as structural materials. The challenge in developing coatings for plastics lies in their low surface energies and sensitivity to temperature and solvent. The use of solvent borne coatings is increasingly prohibited due their high VOC-emissions, the space consuming, long thermal drying tunnels required and their limited curing speed.

Comparatively, UV-technology not only overcomes these problems but it also offers other advantages such as the ability to coat heat-sensitive substrates like plastics and wood as well as a performance improvement e.g. in scratch and stain resistance, which are becoming increasingly important. The low shrinkage of UV-PUDs results in an excellent adhesion to many polymer substrates. The combination of this property together with the very low viscosity and the advantages of UV-technology make these structures very suitable for either primer or topcoat on plastics.

The adhesion of different UVPUDs on different substrates has been evaluated. In addition to adhesion (12 μm dry coating), the Persoz hardness (50 μm dry film on glass), flexibility (impact resistance of a 12 μm film on aluminium) and solvent resistance (ADR = acetone double rubs of a 12 μm film on PC) are shown in Table 8.

Table 8. Performances of UVPUDs for plastics (5B = perfect adhesion)

UVPUD	Persoz hardness (s)	Solvent resistance (ADR), 12 μm on PC	Flexibility (impact, cm)	Adhesion on PVC	Adhesion on polycarbonate (PC)	Adhesion on corona-treated polypropylene (PP)
UVPUD9	311	> 100	> 100	5B	5B	0B
UVPUD10	352	> 100	<20	5B	5B	5B
UVPUD11	295	50	> 100	5B	5B	0B
UVPUD12	312	> 100	< 20	5B	5B	5B
UVPUD13	263	30	> 100	5B	5B	0B

Results show that UVPUDs can combine high hardness, solvent resistance and flexibility together with excellent adhesion, even on polypropylene.

3. Conclusions & perspectives

Radiation curable polyurethane dispersions (UVPUDs) combine the advantages of UV-technology i.e. the ability to coat heat-sensitive substrates as well as superior scratch and stain resistance, with low viscosity and absence of VOC. Further, their relatively high molar mass results in low shrinkage after curing, giving excellent adhesion on many different substrates. These benefits make these structures especially suitable for coatings for different applications on various challenging substrates like wood and plastics, including PVC for resilient flooring.

Future developments of UVPUD aim at investigating specific performances such as high gloss with mirror effect, soft feel and pigmented systems as well as targeting other challenging substrates such as metal and glass.

4. References

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Acknowledgements

The contribution of the following individuals to this paper is hereby acknowledged: Michel Tielemans, Jean-Pierre Bleus, Marc Decaux, Marc Heylen Matteo Vasconi, Stefan Peeters and Stefan Smeets. The technical support of the Radcure TS&D Industrial Coatings Europe team is also acknowledged.