

Novel acrylated building blocks for UV curable polyurethane dispersions

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Abstract

Radiation curable polyurethane dispersions have recently shown increasing growth and market interest as they exhibit high technical performance together with low viscosity and low VOC without the use of solvents or irritant monomers. UV PUD's provide high performance coatings combining the benefits of 100 % UV curable resins, polyurethane chemistry and waterborne technology. In this paper a method is presented for introducing pendant acrylate groups distributed along the polyurethane chain. As a result of the high and controlled cross linking density, these coatings exhibit superior performance such as hardness, scratch and chemical resistance.

Introduction

Polyurethane dispersions (PUD's) are polyurethane polymers dispersed in water. The polyurethane contains a repetitive moiety resulting from the reaction between an isocyanate group and a hydroxyl group, and its morphology is dependent on the structure and nature of the macrodiol and the diisocyanate used. In addition the PUD contains a dihydroxy carboxylic acid, e.g. dimethylol propionic acid (Bis-MPA), to render it water dispersible. PUD's are well known for their high performance, and thanks to the urethane bonds they are both flexible and tough and can be formulated to suit a wide range of applications. However, due to lack of crosslinking, they often exhibit deficient chemical and abrasion resistance.

Conventional 100 % UV curable systems provide coatings of high hardness, good chemical resistance and high gloss as a result of the high crosslinking. On the other hand the high crosslinking density in these systems might have a negative impact of the flexibility and the coatings are tacky until cured. To obtain a low viscosity 100 % UV curable formulation there is often a need for organic solvents or low molecular weight acrylates, which can be irritating to the skin.

One way to overcome the drawbacks of the above-mentioned systems is to combine them to form a radiation curable polyurethane dispersion (abbreviated to UV PUD) by introducing chemical crosslinking, e.g. acrylate unsaturation, to the PUD. The advantages of both systems are here combined to provide a system with unique features. A UV PUD offers the benefits of the traditional PUD systems plus improved chemical resistance, hardness and abrasion resistance. Since the UV PUDs are waterborne they offer low viscosity sprayable formulations without the need for skin irritant monomers or solvents. The benefit of being tack free after water evaporation and prior to UV cure makes them ideal when difficult shaded areas are present on the substrate and in highly pigmented systems.

The UV curable polyurethane dispersions (UV PUD) provide a high performance coating combining the benefits of 100 % UV curable resins, polyurethane chemistry and waterborne technology. UV PUD's offer properties such as:

- Excellent hardness/flexibility balance
- High gloss
- Very good chemical resistance
- Very good film forming properties
- Tack-free before cure
- Low VOC
- Low viscosity without the use of solvents or irritating monomers
- Sprayable
- Wide variety of raw material available

There are several possible methods of rendering PUD's radiation curable:

- End-capping of the isocyanate terminated polyurethane prepolymer with a monofunctional acrylate, e.g. 2-hydroxyethyl acrylate or pentaerythritol triacrylate
- Introduction of reactive diluents, i.e. acrylate monomers/oligomers, to a conventional PUD
- Incorporation of acrylate groups along the polyurethane backbone using a polyhydroxyl acrylate

One major drawback with acrylate end capped UV PUD's is the problem of obtaining a high concentration of unsaturation while maintaining a high molecular weight of the polymer. In linear polyurethane polymers the possibility of chain extending the dispersed isocyanate terminated urethane polymer is lost when using monohydroxyl functional acrylates, since they act as chain stoppers. These polymers also display very poor coating properties prior to UV cure due to the lack of high molecular weight segments. The problem with the lower molecular weight polymers can of course be counteracted if branched polyurethanes are synthesized by adding trimethylolpropane or a polyisocyanate, for example. However, the problem of low acrylate concentrations still remains. An additional drawback is the toxicity of 2-hydroxyethyl acrylate and skin irritation of pentaerythritol triacrylate.

UV PUD's prepared by mixing a conventional PUD with acrylate oligomers/monomers is one of the easiest methods of producing radiation curable polyurethane dispersions. The desired acrylates can be charged at the beginning of PUD synthesis, together with the macro diol, dispersing agent and isocyanates, or prior to the water dispersion step. The acrylate monomers/oligomers can act as a reactive diluent during the prepolymer synthesis and especially if a low viscous acrylate is chosen, solvents which often are used in the prepolymer route to lower the viscosity of the prepolymer can be avoided. The possibility of selecting different acrylates and concentrations renders it possible to tailor the properties of the UV PUD and the coatings thereof quite easily. For instance, by adding a high functional acrylate a hard, fast curing and resistant coating is obtained whereas acrylates of lower functionality will yield a coating with higher flexibility, for example. When UV cured these types of UV PUDs do not form a cross linked network between the polyurethane and the acrylates since the polyurethane backbone itself is not acrylate functionalized. This can have a negative affect on the chemical resistance of the coatings, for example. Another drawback of these PUD/acrylate blends is the plasticizing effect of the acrylates resulting in poorer performance of the coatings before they have been subjected to UV/EB cure.

To further improve the properties of the UV PUD's, e.g. the chemical resistance, and to avoid the plasticizing effect of added acrylates in non UV cured UV PUD coatings, and still be able to obtain high acrylate concentrations in the UV PUD, acrylates could be incorporated within the polyurethane backbone of the polymer. By functionalizing the polyurethane backbone along the polymer chain instead of just on the chain ends as described above, a higher double bond concentration and more uniform distribution of the acrylate groups can be achieved. Following UV/EB curing these pendant acrylate groups in the polymer backbone will form a highly cross linked network to provide coatings with very high chemical and abrasion resistance. The acrylate concentration in these systems can be further increased by the addition of reactive diluents e.g. di, tri or tetra functional acrylate monomers. When reactive diluents are utilized together with acrylate functionalized polyurethane an fully cross linked network will be formed, unlike in the above described blends of non-functionalized PUD and acrylate monomers. There are several possibilities of introducing pendant acrylates into polyurethane dispersions available, e.g. the reaction between a monohydroxyl functional acrylate and a polyisocyanate (trimer), an allophanate with a pendant acrylate group [1], epoxy acrylates based on hydrogenated bis-phenol A [2], pentaerythritol diacrylate [3], partially acrylated polyols [4] or other hydroxyl functional oligomer acrylates [5]. To circumvent or minimize the skin irritation of pentaerythritol diacrylate, an alkoxyated pentaerythritol diacrylate could be utilized, for example, to incorporate unsaturation in the polymer backbone.

In this paper the pendant acrylate groups have been introduced to the polymer backbone by using TMP monoacrylate (TMP MA). The benefits of utilizing acrylates incorporated in the polymer backbone compared to blends of a PUD and acrylate diluents is demonstrated with respect to basic coating properties such as hardness, scratch and chemical resistance.

Experimental

Aqueous anionic polyurethane dispersions were prepared according to Table 1 by the prepolymer mixing process using a five-necked glass reactor equipped with a thermometer, anchor agitator, condenser and nitrogen inlet. When a constant NCO value was obtained, as determined by the NCO standard back titration method, the carboxylic acid groups in the prepolymer were neutralized by the addition of triethyl amine to render it water dispersible. The NCO terminated polymer chains were then dispersed in water and chain extended with 1,2-ethylene diamine. Formulation 1 is a conventional PUD without any acrylate functionality. In formulation 2 pendant acrylate groups were introduced along polymer backbone by utilizing TMP MA. In formulation 3 the acrylate concentration of formulation 2 was further increased by the addition of Di-TMP TA prior to the water dispersion step. The acrylate concentration could naturally be further increased by additional TMP MA, as a result of which the increased amount of diisocyanate to be utilized would also contribute to improved coating properties. The last UV PUD, formulation 4, is a blend of a conventional PUD and Di-TMP TA.

The final polyurethane dispersions were characterized with respect to pH and viscosity, non volatile content and mean particle size, see Table 2.

Table 1. Composition of the PUD's.

Materials	Formulation			
	1	2	3	4
Poly(hexanediol adipate) ¹	18.1	14.1	11.4	14.5
Dimethylolpropionic acid (Bis-MPA)	2.4	1.9	1.5	1.9
Dibutyltin dilaurate (DBTL)	0.018	0.014	0.011	0.014
Isophorone diisocyanate (IPDI)	12.0	14.1	11.3	9.7
Dipropylene glycol dimethyl ether (DPGDME)	7.2	7.6	7.3	7.2
Trimethylol propane mono acrylate (TMP MA)	-	2.6	2.1	-
Di-trimethylolpropane tetra acrylate (Di-TMP TA)	-	-	6.8	6.9
Polymerization inhibitor	-	0.001	0.004	0.004
Triethyl amine	1.5	1.1	0.9	1.2
Water	57.8	57.4	57.7	57.7
Ethylene diamine	1.0	1.1	0.9	0.8
Total charge:	100	100	100	100

¹ OH No. = 112 mg KOH/g

The acrylate concentration of the UV PUD's was theoretically calculated taking both the acrylate derived from the TMP MA and Di-TMP TA into account. The non volatile content was evaluated by drying the sample for 3 h at 105 °C and comparing the difference in weight before and after drying. Mean particle size was determined using a Microtac UPA 150. The viscosity of the synthesized dispersions was determined using a Stresstech Rheometer with a 20 mm plate and plate system at a shear rate of 100 s⁻¹ at 23 °C.

Table 2. Properties of PUDs

(UV) PUD's	1	2	3	4
C=C content on solid, meq/g	-	0.4	2.0	1.8
Non-volatile content m/m %	33.2	34.5	33.7	33.1
Mean particle size, nm	25	90	90	90
pH	9.2	8.3	7.4	7.4
Viscosity, mPas	460.0	70.0	20.0	30

To the UV PUD's 4% by weight of Irgacure 500, based on solid content, was added and the formulations were applied to glass and aluminum substrates using a 100 µm K-wire bar applicator. After application the water was flashed off for 30 mins. at 80 °C. Two separate panels of each formulation and substrate were prepared, one of which was stored in a constant climate chamber (23 °C and 50 % RH) after water flash-off, while the second one was UV cured with 2 passes at 5 m/min beneath an H-bulb of 160 W/cm (Fusion F600), equivalent to a UV dose of approximately 1000

mJ/cm². Clear coatings with a thickness of approximately 20 µm were obtained by this means. After cure, all coatings were stored at 23 °C and 50 % RH for 1 week before evaluation.

The hardness of both non UV cured and UV cured coatings was evaluated using a pendulum hardness tester (according to DIN EN ISO 1552) and pencil hardness tester (according to ISO 15184), with pencils ranging from 9B (softest) to 9H (hardest). The flexibility was determined with Erichsen testing equipment (according to ISO 1520) and the chemical resistance by chemical spot tests (according to ISO 4211). In the spot test method a cotton pad soaked in the liquid to be tested was placed on the coating and covered by a cup for the desired exposure time. After the test, the cup and cotton pad were removed and the surface gently wiped with a paper tissue and left to recover for 24 h in a constant climate chamber before evaluation. The result was graded on a scale of 1 to 5, where 5 equals no visible change in the coating surface and 1 equals a distinct mark with an altered surface.

MEK double rubs were performed by soaking a cotton stick in methyl ethyl ketone (MEK), which was rubbed against the coating surface. The number of double rubs before the coating was dissolved and penetrated by the cotton stick was recorded.

Results and discussions

When comparing Formulation 1 of the conventional PUD to the UV PUD's, the advantages of using UV curable polyurethane dispersions is clearly seen in terms of coating properties. In formulation 4, where a similar PUD was mixed with Di-TMP TA, the benefit of simply adding acrylates to a PUD is demonstrated. Formulation 2 is a pure polyurethane with pendant acrylate groups along the polyurethane backbone with no other acrylates added. In formulation 3 the acrylate concentration of formulation 2 was further increased by the addition of Di-TMP TA. The pendant acrylate groups, together with the Di-TMP TA will, upon curing, form a fully cross linked network resulting in very high overall performance. By comparing formulation 3 and formulation 4 the impact of using a functionalized backbone is demonstrated since the formulations contained similar acrylate concentrations.

Hardness

As seen in Figure 1 all the UV PUD's exceeded the conventional PUD in hardness, with formulation 3 exhibiting the highest hardness. The high hardness of formulation 2 can partially be explained by the increased amount of urethane linkages due to the incorporated acrylate diol. Comparing formulation 1 and the non UV cured coating of formulation 2, the impact of additional isocyanates is seen. The plasticizing effect of the Di-TMP TA in the non UV cured coatings is clearly observed when comparing formulation 2 with formulation 3 and 4 in the pendulum hardness test. As a result of the relatively high hardness of formulation 2 prior to UV cure, this could make it ideal for use when coatings for hard to cure substrates, e.g. 3 dimensional objects or in highly pigmented systems. Despite the high acrylate concentration of formulation 4 this formulation displayed the lowest hardness except for the conventional PUD, formulation 1.

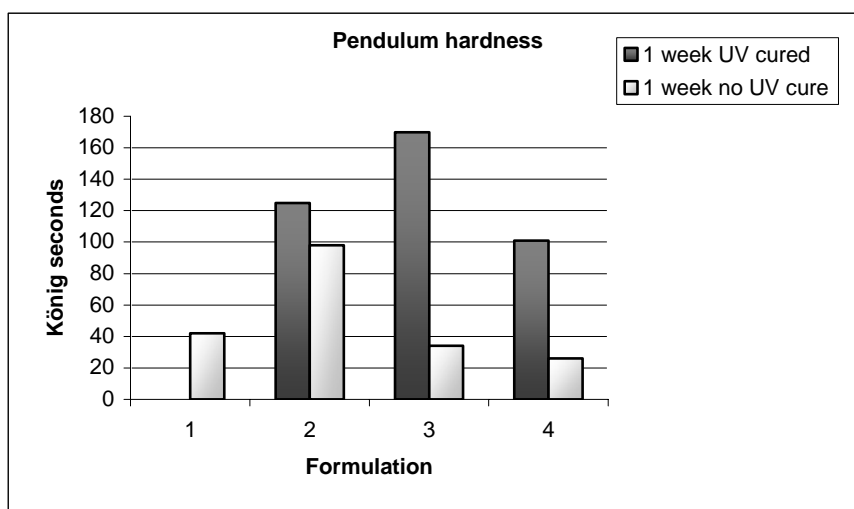


Figure 1. The pendulum hardness of both UV cured and only forced dried coatings.

The pencil hardness of the formulations, listed in Table 3, are all in the upper range except for the conventional PUD. The best pencil hardness was observed for formulation 3, the one of the two with the highest double bond concentration. Once again a clear difference could be observed between formulation 3 and formulation 4. Looking at the pencil hardness of the non UV cured coatings, formulation 2, which previously displayed very good performance in the pendulum hardness evaluation, shows rather good pencil hardness not much softer than the UV cured counterpart. The non UV cured coatings of formulation 3 and 4 did not display this property because of the reactive acrylate diluents.

Table 3. Pencil hardness of both UV and non UV cured coatings.

Pencil hardness	1	2	3	4
Pencil hardness UV	-	F/H	3H/4H	F/H
Pencil hardness No UV	4B/3B	B/HB	9B	9B

Flexibility

In Table 4 the flexibility, as measured by the Erichsen flexibility, of the different coatings is reported. In addition to the high pendulum hardness all the UV PUD's displayed very high flexibility even after UV cure. The aluminum substrates break at approximately 6-7 mm. Therefore higher values could not be measured. Despite the high crosslinking in the coatings the UV cured formulations display a flexibility equal to the non cross linked formulation 1.

Table 4. Flexibility measured on aluminum substrates

Flexibility	1	2	3	4
Ericsen flexibility (mm) UV	-	> 6.0	> 6.0	> 6.0
Ericsen flexibility (mm) No UV	> 6.0	> 6.0	> 6.0	> 6.0

Chemical resistance

Both UV cured and non UV cured coatings were evaluated for their chemical resistance. In Table 5 the chemical resistance of the UV cured coatings is indicated and Table 6 indicates the coatings which have only been forced dried. In general a very good chemical resistance was observed for the UV cured coatings. Formulation 4, which only contained reactive diluents, showed a much lower resistance towards both acetone and ethanol. One possible explanation for this could be the lack of crosslinking between the acrylates and the polyurethane backbone, in contrast to formulation 2 and 3, where the polyurethane polymers are bound together thanks to the pendant acrylate groups, resulting in a denser network and thereby increasing the chemical resistance. When comparing the chemical resistance of the UV cured formulations with the conventional PUD, distinct differences were observed with respect to the UV PUD's, demonstrating a much higher resistance, especially formulations 2 and 3.

Table 5. Chemical resistance of UV cured coatings (formulation 1 excluded)

Chemical resistance UV cured coatings ¹	Formulation			
	1	2	3	4
Acetone, 2 min	-	5	3	2
Ethanol (48 v/v%), 6 h	-	4	4	1
Water, 24 h	-	5	5	5
NaOH (aq, 5 m/m%), 30 min	-	4	5	4
Total		18	17	12

¹ 5 = No visible change, 1 = severely damaged coating

Since formulation 2 did not contain any reactive diluents, i.e. additional acrylate monomers/oligomers, very high chemical resistance was also observed for this coating prior to UV cure. The increased amount of cyclo aliphatic diisocyanate in the polymer backbone, due to the incorporated acrylate, could explain why the non UV cured formulation 2 showed a much higher resistance than formulation 1, as seen in Table 6.

Table 6. Chemical resistance of non UV cured coatings

Chemical resistance Non UV cured coatings ¹	Formulation			
	1	2	3	4
Acetone, 2 min	2	5	3	2
Ethanol (48 v/v%), 6 h	1	3	3	1
Water, 24 h	2	5	3	1
NaOH (aq, 5 m/m%), 30 min	3	3	4	3
Sum	8	16	13	7

¹ 5 = No visible change, 1 = severely damaged coating

The MEK double rubs, which can also be used to determine chemical resistance of coatings, are listed in Table 7. A dramatic increase in MEK double rubs was observed between formulation 2 and 3 due to the increased acrylate concentration. Comparing formulation 3 and 4, the impact of a having the polyurethane chains incorporated in the cross linked network was again observed, with formulation 3 displaying significantly higher MEK double rubs despite similar acrylate concentrations.

Table 7. Number of MEK double rubs on both UV and non UV cured coatings

MEK double rubs	Formulation			
	1	2	3	4
Number of double rubs UV cured	-	25	143	60
Number of double rubs no UV	7	14	10	5

Conclusions

In this paper UV PUD's were synthesized by incorporating acrylate functionality along the polyurethane backbone and by adding reactive diluents i.e. acrylate monomers to a conventional PUD and a combination thereof, and were then evaluated for basic coating properties such as hardness, scratch resistance, flexibility and chemical resistance. The differences between a UV PUD rendered radiation curable by functionalizing the polymer backbone instead of by simply adding acrylate monomers were clearly seen in the different evaluations, the latter displaying poorer coating performance. The best overall performing UV PUD was found to be the one containing both an acrylate functionalized backbone and reactive diluents.

References

- [1] WO2006/089935
- [2] EP1328565
- [3] Bai C. Y. et al, Process in Org. Coatings 55, 2006, pp 291-295
- [4] Couvret D. et al, Eur. Polymer J. Vol 27, No. 2, 1991, pp. 193-197
- [5] Sommar S. et al, The Nürnberg congress, 2007, Paper XVI.5