UV Coatings can do it for Plastics

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Introduction

Due to the increasing use of plastics as construction materials in automotive, electronic and telecommunication fields, the coatability of plastics is becoming very important. Finding a universal coating for all types of plastics is still a utopia. Due to the low surface energies, the sensitivity to temperature and solvent, many plastics are difficult to coat. The number of different materials consisting of homopolymers or blends of different polymers is enormous and mostly requires tailor-made solutions for each plastic. Moreover, due to different intrinsic properties within a polymer family (e.g. PP), different properties are targeted. Optimization and fine-tuning of well-known materials by blending or additive approach to obtain better properties requires simultaneous adjustment of the coating properties. The drive towards cheaper polymers, replacing existing polymers, is determined mostly by their coatability to obtain the surface aesthetics of the latter.

With UV-technology, one is no longer limited to coat plastics with solvent-based products only. The high VOC-emissions, the thermal drying requiring long drying tunnels and much space as well as the limited curing speed by using solvent based products have been the key drivers to look for alternative products and technologies in the past. Although UV-technology has already proven to overcome these obstacles, other advantages as the ability to coat heat sensitive substrates, the performance improvement like scratch and stain resistance are becoming more and more important as well.

Although UV-resins are well established for surface protection and decoration in many applications like furniture, wood flooring, construction, graphic arts and electronics their use on plastic substrates is still limited. This paper gives an overview of building blocks that have shown their value on a range of typical plastic substrates.

UV Curing Technology

Despite the advantages of the UV technology equipment manufacturer, formulator and raw material supplier are faced with new challenges to introduce this technology further into the field of plastic coatings.

The UV curing technology consists of drying a coating through exposure to UV-light, leading to polymerisation between the components of the formulation. The chemistry used in UV polymerisation is almost entirely based on acrylate functionalised materials.

A UV formulation always contains the following ingredients:

- Diluting acrylates and acrylated oligomers, which are reactive materials forming the backbone of the coating after drying.
- Photoinitiators, which under exposure to UV light form radicals that initiate a radical polymerisation reaction between diluting acrylates and acrylated oligomers.
- Fillers and additives, which mostly do not participate in the polymerisation reaction and thus remain as such in the cured network.

Diluting Acrylates

As an UV-coating should be free of solvent, which actually contributes to the adhesion to the substrate, one has to compensate for this lack of adhesion. The adhesion to a plastic substrate is mostly difficult due to the inherent polymerisation process of the UV-resins. When exposed to UV light the photoinitiator start a chain reaction leading to polymerisation of the liquid coating accompanied by a decrease in volume and thus shrinkage. The liquid coating consists mainly of high viscous oligomers and low viscous monomers. The purpose of the diluting acrylates or monomers is the reduction of the viscosity of the total UV formulation. They typically play the role of “reactive” solvents by analogy with conventional formulations. But as they react in the final polymer, they influence the final properties as well. Low viscous acrylates with high functionality and low molecular weight will give high reactivity, high crosslink density but also high shrinkage and thus decrease the adhesion of an UV-coating. Low viscous acrylates with low functionality will give low reactivity, low crosslink density and thus a high flexibility. Due to the very fast UV-polymerisation process internal stress is developed in the coating which plays less a role in conventional thermal drying processes. The shrinkage of some diluting acrylates is shown in table 1. The shrinkage is expressed as the change in density during curing of a formulation containing 100 % resin and 5 % photoinitiator. Although these values give a good indication of the intrinsic properties of a diluting acrylates, the behavior in a final formulation depends on the other components as well.

Diluting acrylate	**Molecular weight**	**Shrinkage %**
Isobornyl acrylate (IBOA)	208	5.2
Oxyethylated phenol acrylate (OEPA)	236	6.8
Octadecyl acrylate (ODA)	200	8.3
Tricyclodecane diol diacrylate (TCDA)	304	5.9
Propoxylated neopentyl glycol diacrylate (NPGPODA)	328	9.0
Dipropylene glycol diacrylate (DPGDA)	242	13.0
Tripropylene glycol diacrylate (TPGDA)	300	18.1
Hexane diol diacrylate (HDDA)	226	19.0
Trimethylolpropane ethoxy triacrylate (TMPEOTA)	428	14.1
Propoxylated glycerol triacrylate (OTA 480)	480	15.1
Trimethylolpropane triacrylate (TMPTA)	296	25.1
Alkoxylated pentaerythritol tetraacrylate (OPETIA)	571	8.7
Ditrimethylol propane tetraacrylate (DiTMPTA)	438	10.0

Table 1. Shrinkage of diluting acrylates

Apart from their role to reduce the viscosity, diluting acrylates should be carfully chosen for each plastic substrate.

It has been reported earlier that the solubility parameters of both polymeric substrate and formulation give an indication of whether adhesion is expected to be difficult or not. Generally, a diluting acrylate which can attack or swell a substrate will form an interpenetrating polymer network between substrate and coating, leading to an excellent adhesion. Diluting acrylates such as oxyethylated phenol acrylate, DPGDA or HDDA are able to attack and swell polycarbonate.

Another important parameter to consider is the surface tension of the substrate. It has been shown in literature that good adhesion is obtained when the surface tension of the substrate is higher than this of the coating giving an optimal wetting of the substrate. The surface tension of typical diluting acrylates and typical plastic substrates are shown in table 2 and table 3.

Diluting Acrylate	Surface Tension (mN/m)
Isobornyl acrylate (IBOA)	32
Oxyethylated phenol acrylate (OEPA)	39
Octadecyl acrylate (ODA)	30
Urethane monoacrylate (UMA) Mw: 215	33
Tricyclodecane diol diacrylate (TCDA)	40
Propoxylated neopentyl glycol diacrylate (NPGPODA)	31
Dipropylene glycol diacrylate (DPGDA)	35
Tripropylene glycol diacrylate (TPGDA)	34
Hexane diol diacrylate (HDDA)	36
Trimethylolpropane ethoxy triacrylate (TMPEOTA)	39
Propoxylated glycerol triacrylate (OTA 480)	36
Trimethylolpropane triacrylate (TMPTA)	38
Alkoxylated pentaerythritol tetraacrylate (OPETIA)	40
Ditrimethylol propane tetraacrylate (DiTMPTA)	38

Table 2. Surface tension of diluting acrylates at 25 °C

Substrate	Surface Tension (mN/m)
Polypropylene	29
Polyethylene	30
Polystyrene	33
PVC (plasticized)	33
Polycarbonate	38
PMMA	39
PET	41

Table 3. Typical values of surface tension of common plastic substrates

The wide range of surface tensions of certain substrates is explained by the different treatments of their surfaces. For example, untreated polypropylene may have 28 mN/m whereas the surface tension of corona treated PP can go up to 40 mN/m. A surface treatment with corona or flame results in the formation of polar groups on the substrate.

The described parameters (shrinkage during UV-polymerisation, solubility and surface tension of substrate and diluting acrylates) should be considered when selecting diluting acrylates in a formulation. As a formulation mostly contains different diluting acrylates in low to high concentration, these parameters are taking into account only a part of the reality and must be used complementary with the experimental work. It its known that a formulation leading to a good adhesion on a particular plastic may not deliver good performance on another type of the same plastic family. The ability of several diluting acrylates to serve as an adhesion promoter in a coating is shown in figure 1. In the blue region one can find the preferred diluting acrylates, whereas the products in the green region are optional in balance with other properties such as diluting power and reactivity. Due to its capacity to swell the plastic surface, HDDA is an interesting adhesion promoter. In the case of PC or impact resistant PS, only a small amount of HDDA is needed in a formulation whereas for harder PS higher quantities are necessary. Due to its low surface tension, ODA is a very interesting diluting acrylate for PP and PE. ODA is mostly used in small amounts due to its incompatibility with many acrylated oligomers at high concentration. UMA is prefered above OEPA when a higher flexibility is required. TCDA is an interesting difunctional diluting acrylate for rigid SMC/BMC as it has a low shrinkage combined with an excellent hardness.

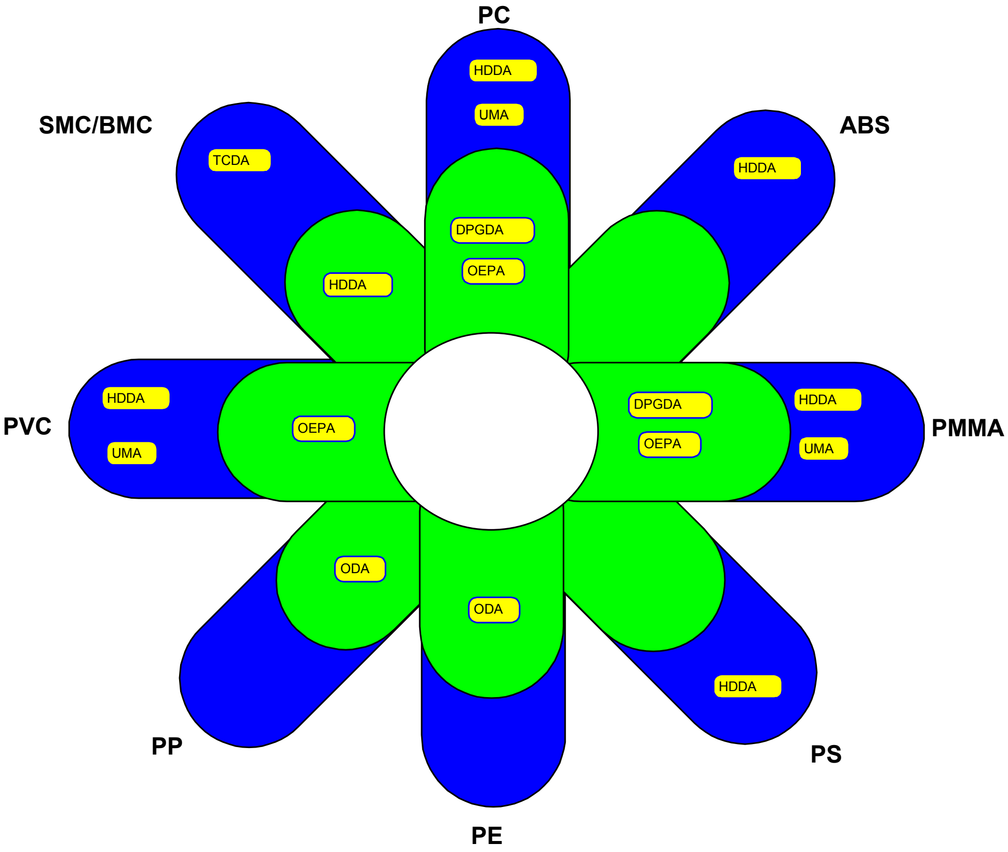

Figure 1. Effect of diluting acrylates on adhesion to several substrates.
Blue regions: highly preferred. Green regions: optional in balance with other properties

UV adhesion promoters

As diluting acrylates in an UV formulation are used to reduce the viscosity and to increase the adhesion on several plastic substrates, their main drawback is the reduction of the high performance of an UV coating. In order to limit the percentage of diluting acrylates in an UV formulation one can switch from a one layer to a multi layer approach with primer, basecoat and topcoat. As the primer is necessary for the adhesion to the substrate, both basecoat and topcoat may contain less diluting oligomers. Almost all-automotive paints use the primer/basecoat/clearcoat buildup in order to fulfill the high quality requirements. The basecoat is a pigmented coat responsible for the color of the paint, while the topcoat will give the resistance to scratches etcetera. With the multi-layer approach one has the possibility to easily switch from one color to another without changing the primer and topcoat. Looking at the different plastics used in automotive, one realizes that the use of one UV-primer for several plastic parts could simplify the coating process already much.

We have found out that several of our UV resins (table 4) can provide a good adhesion towards different plastic substrates. Although these resins are used in the plastic field, and as a plastic can vary from one supplier to another, can be filled or non-filled, can be a blend of two miscible or compatibilised polymers, their value has to be evaluated with experimental work on each plastic.

Resin	Description	Hoppler Viscosity mPa.s (T in °C)
ACRYLIC 1	Acrylic oligomer in TPGDA	8500 (60)
ACRYLIC 2	Acrylic oligomer in IBOA	8500 (60)
ACRYLIC 3	Acrylic oligomer in blend TPGDA/HDDA	20000 (25)
VINYLIC 1	Polymeric Resin in HDDA	900 (20)
PE 1	Chlorinated polyester resin in TMPTA	1500 (60)
PE 2	Chlorinated polyester resin in OTA 480	1500 (60)
PE 3	Chlorinated polyester resin in HDDA	2000 (25)
ADDITIVE 1	Amine functional acrylate	1200 (25)
ADDITIVE 2	Methacrylated acidic derivative	1350 (25)
ADDITIVE 3	Acrylated acidic derivative	3000 (25)

Table 4. UV resins for adhesion on plastic substrates

The ability to serve as an adhesion promoter in a primer and/or in a coating is shown in figure 2. As the adhesion of UV resins towards PC, PVC and PMMA is mostly obtained with a small amount of diluting acrylate, no adhesion promoter is required. Surface treatments as corona, flame, plasma or IPA cleaning are advised to activate the surface but also to remove processing additives and contamination. The figure 2, composed out of three regions (blue, green, white), should serve as a guideline to coat several plastic substrates. The resins in the blue region represent the major component in a formulation, which can be diluted with one of the diluting acrylates from the white region. Acrylic 1, 2 and 3 are acrylic acrylates which give good adhesion towards many plastics mainly due to their low functionality and thus shrinkage. Vinylic 1 is a polymeric resin diluted in HDDA that shows good adhesion in combination with acrylic acrylates. PE 1, 2 and 3 are chlorinated polyester resins respectively diluted in TMPTA, OTA 480 and HDDA. They have a good reactivity combined with a very low shrinkage (< 4 %).

The amount of diluting acrylate must be chosen depending on the required viscosity, but also the rigidity of the substrate. To increase the reactivity one can take a higher functional diluting acrylate, or one can add additive 1, which is a low viscous amine functional acrylate. Additives 2 and 3 are methacrylated or acrylated acidic components which are able to etch the surface of a filled plastic. By diffusion of the coating through the surface heterogeneities followed by polymerisation, the coating becomes strongly attached to the substrate, a mechanical entrapment. They can be used in small quantities (5, 10 %) if the adhesion with the other components is not sufficient. The efficacy of the UV resins to adhere to a plastic depends on the application process and the contact and drying time. It is not our intention to explain the adhesion phenomena of the mentioned resins by the different theoretical approaches such as the adsorption, electrostatic, diffusion or chemical interaction theories. As mentioned before, the best evaluation is done by industrial trials.

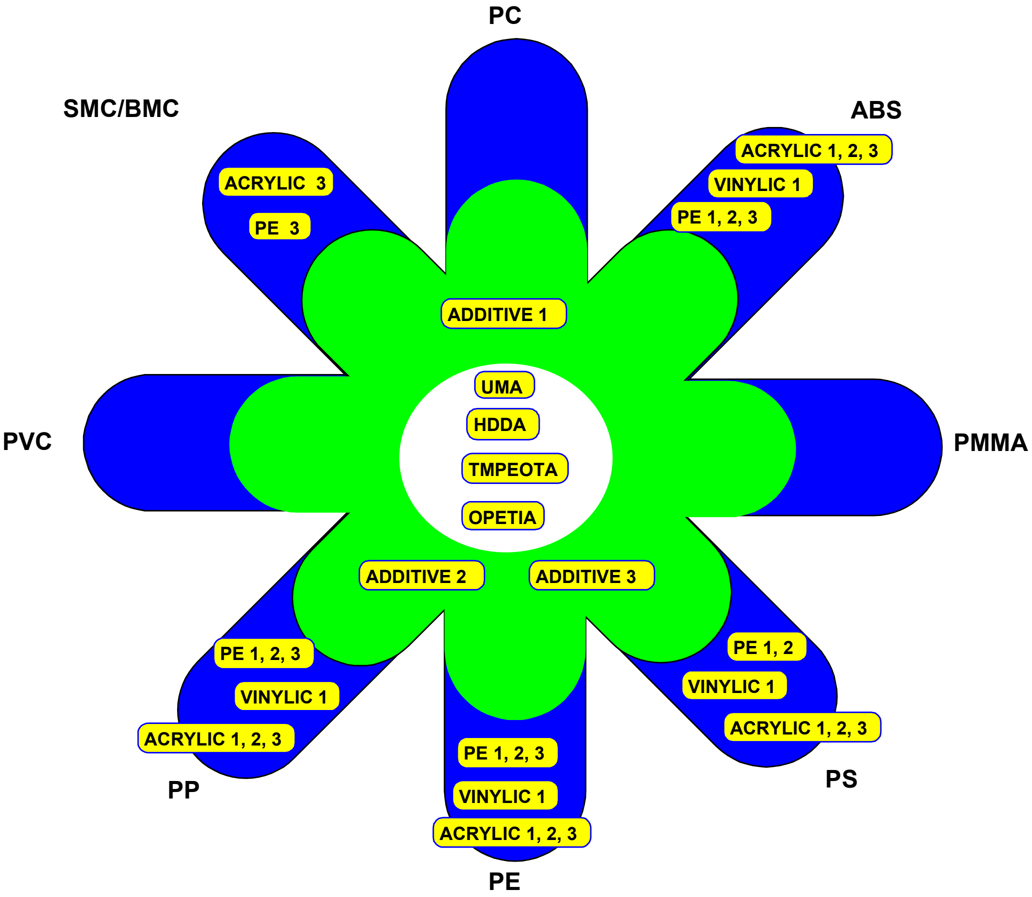

Figure 2. UV adhesion promoters for plastics. Blue regions: main component; green regions: optional additive; white region: optional diluting acrylate

Low viscous, high performance UV resins

The design of low viscous, high performance resins useful for spray application to coat 3-dimensional objects has lead to a new generation of binders, radiation curable polyurethane dispersions (PUD-UV).

A schematic presentation of a PUD-UV is shown in figure 3. The reaction of diisocyanates (blue color) with different polyols (polyester, polyether, polycarbonate) results in a polyurethane which forms the basic chemistry of a PUD-UV.

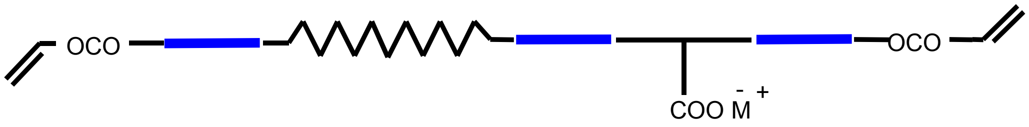

Figure 3.

Due to their relatively high equivalent molecular weight they show almost no shrinkage after curing, resulting in an excellent adhesion towards many substrates. The combination of this property together with the very low viscosity and the advantages of UV technology make these structures very suitable as well as primer, or as topcoat.

A few of the radiation curable aliphatic polyurethane dispersions that are tack free after water evaporation and before cure are shown in table 5.

Dispersions	**Maximum Viscosity at 25 °C (B, mPa.s)**	**% of solid**	**Maximum Particle size (nm)**	**pH**	**Reactivity**	**Hardness**	**Flexibility**	**Stain Resistance**	**Adhesion**
PUD-UV 1	200	35	80	7.5	3	3	3	3	4
PUD-UV 2	200	40	100	7.5	3	4	1	4	4
PUD-UV 3	200	35	100	7.5	3	1	4	2	4
PUD-UV 4	250	35	80	7.5	3	4	1	4	4
PUD-UV 5	200	35	100	7.5	3	1	4	2	4

Table 5. Few examples of PUD-UV products. Different properties are evaluated (1 = low, 4 = high).

Such products are environmentally friendly and contribute to VOC reduction, as they are solvent free. Moreover the urethane technology provides versatile solutions combining different chain structures, as described in figure 4. Such polymers combine HARD SEGMENTS which could be urethane, urea, allophanates and SOFT SEGMENTS such as polyester, polyether, polycarbonate.

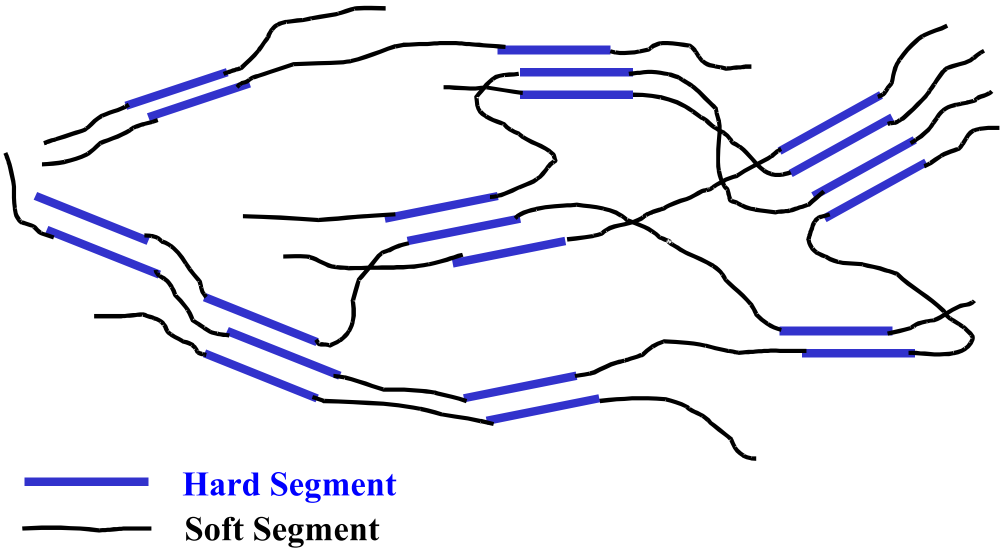

Figure 4. Schematic presentation of the hard and soft segments in a PUD-UV

If compared to traditional 100% UV systems, the PUD-UV's morphology could be adjusted depending of the crosslinking degree needed and the desired stiffness (figure 5).

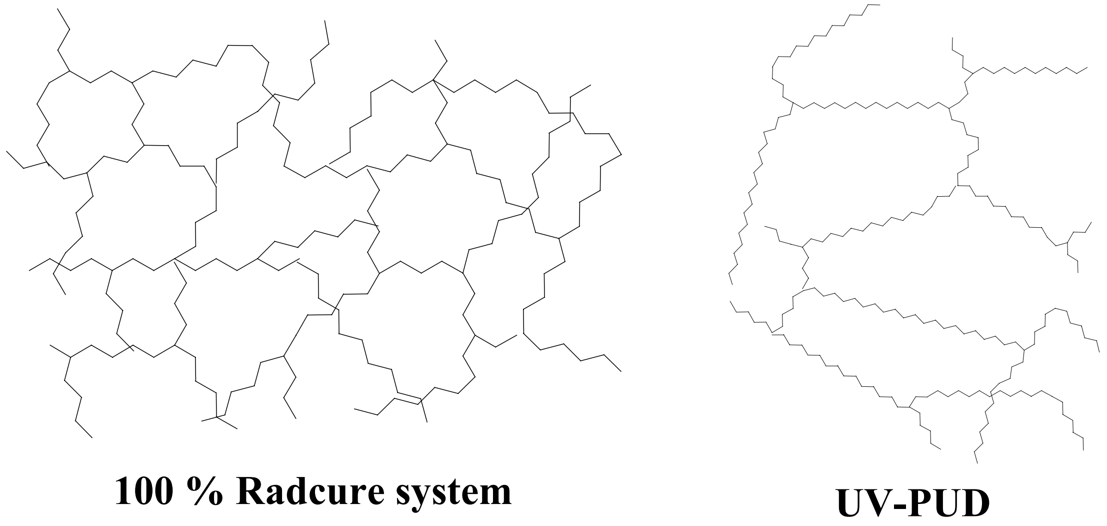

Figure 5. Comparison of the crosslink density of a 100 % radiation curable formulation and a PUD-UV

The adhesion of different radiation curable PUD's on different substrates has been tested. 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 (*A*cetone *D*ouble *R*ubs of a 12 µm film on PC) in shown in table 6.

Dispersions	Persoz Hardness (s)	Solvent Resist. (ADR) 12 µm on PC	Flexibility (impact cm)	PVC	PC	PP (corana)
PUD-UV 1	311	> 100	> 100	5B	5B	0B
PUD-UV 2	352	> 100	< 20	5B	5B	5B
PUD-UV 3	295	50	> 100	5B	5B	0B
PUD-UV 4	312	>100	< 20	5B	5B	5B
PUD-UV 5	263	30	> 100	5B	5B	0B

Table 6. Adhesion performance of some PUD-UV's. 5B = perfect adhesion

Good adhesion could be achieved on a number of different substrates. Formulating such products could provide further the desired balanced properties for the targeted end-use application.

UV resins for exterior applications

Damage of common plastics on exposure to solar radiation depends on the susceptibility of the polymer type to solar UV wavelength as well as the complexity of the weathering environment to which it is exposed. The magnitude of the damage can be controlled using stabilizers in the plastic composition. A further growth of radiation cured coatings on plastics used in exterior applications depends on the development of binders which combine excellent weathering performance with other more and more stringent requirements. Accelerated weathering tests are widely used to assess the weatherability of polymers. The most important difference between the various equipments is the nature of the light source employed. The short-wavelength emission of UV-B lamps can cause unnatural acceleration or degradation whereas UV-A lamps have no output below the normal solar cut-off of 295 nm and may alllow enhanced correlation with actual outdoor weathering. With appropriate filters, the Xenon arc spectral light distribution approximates well the sunlight in both UV and visible range. This makes the Xenon test together with the humidity control feature the most widely accepted standard.

The specific correlation of accelerated testing with actual outdoor exposure results depends both on the chemistry and the application under evaluation and should ideally be investigated for each system separately. Even correlation with natural exposure can be questionable as such because of the variable conditions found outdoors. Nevertheless, accelerated tests offer the opportunity to compare different samples and give an indication about long-term performance.

At Surface Specialties UCB, extensive test experience is gained with different types of accelerated tests and cycling conditions. In this paper we will only concentrate on the Xenon test, using a Xenon WeatherOMeter, according to ASTM G26 method: Florida simulation program

- Irradiance: 0.55W/m^2 – 340 nm
- Borosilicate inner- and outerfilters
- 90 min UV - 30 min UV + front spray
- Black Panel Temperature: 75°C
- Chamber Temperature: 50°C
- Relative Humidity: 50°C

Due to the huge variety of plastics, we have decided to test the UV clearcoats on weather stable white thermoset polymer coated panels at 20 µm coating thickness. A visual evaluation was carried out along with colour and gloss monitoring during the tests. Aliphatic urethane acrylates in general, outperform other oligomer types in both accelerated and natural weathering tests. Aromatic polymers in general are inherently not stable to light and tend to yellow and degrade rapidly. Also conventional polyether and polyester acrylates are more sensitive to degradation.

Table 7 reveals UV resins suitable for formulation of coatings for exterior application. These include aliphatic urethane acrylates based on chemical backbones that are stable towards degradation under influence of light and moisture. These resins have excellent color and gloss retention properties. Di- and trifunctional products result in relatively lower crosslink densities and are in general less sensitive to crack formation than higher functional products which result in more densely crosslinked systems. Nevertheless hexafunctional urethane acrylates may be indispensable to provide superior scratch resistance.

	Viscosity 25°C – mPa.s	Viscosity 60°C – mPa.s	Functionality	MW	Key Features	Reactivity	Hardness	Flexibility	Chemical Resistance	Adhesion
UA 1	-	2100	2	1200	Good exterior durability	●●	●●	●●●	●●	●●●
UA 2	-	7000	3	1500	Best stain and abrasion resistance, excellent exterior durability, good thermal stability	●●●	●●●	●●	●●●●	●●●
UA 3	-	2000	6	1000	High scratch resistance	●●●●	●●●●	●	●●●●	●
UA 4	7000	-	2	450	Good exterior durability, good impact resistance	●●●	●●●	●●	●●●	●●●●
UA 5	-	700	6	800	Combines good scratch and abrasion resistance with improved flexibility	●●●●	●●●●	●	●●●●	●●
UA 6	12500	-	2	1000	Good exterior durability and resistance to crack formation	●●	●●	●●	●●	●●●

● low ●● moderate ●●● good ●●●● very good

Table 7. Aliphatic urethane acrylates for exterior application

In a comparative study the products, except UA 3 and UA 5, have been diluted with 30% HDDA. HDDA is one of the best performing diluting acrylates for exterior use. UA 3 and UA 5 are hexafunctional urethane acrylates. They have been tested by a 20 % addition to UA 1.

Figure 6 illustrates the monitoring of the b value in the Xenon test for the 6 urethane acrylates. The colour retention is excellent, after a relaxation phase (b decreasing), b values increase only very slightly. The visual appearance of the *first* crack formation is also indicated for each product. Pictorial standards are used to note degradation with cracking (ASTM D660). It must be stated that UA 1, UA 2, UA 3 and UA 6, which are additionally tested by natural exposure in Belgium and Florida, are still free of cracks after 3 years of exposure. In general the cracking phenomena for a product are observed at an earlier stage by adding 20 % of a hexafunctional urethane acrylate. It can be explained by the higher crosslinking and corresponds with higher shrinkage values, which are an indication of the induced stress upon curing.

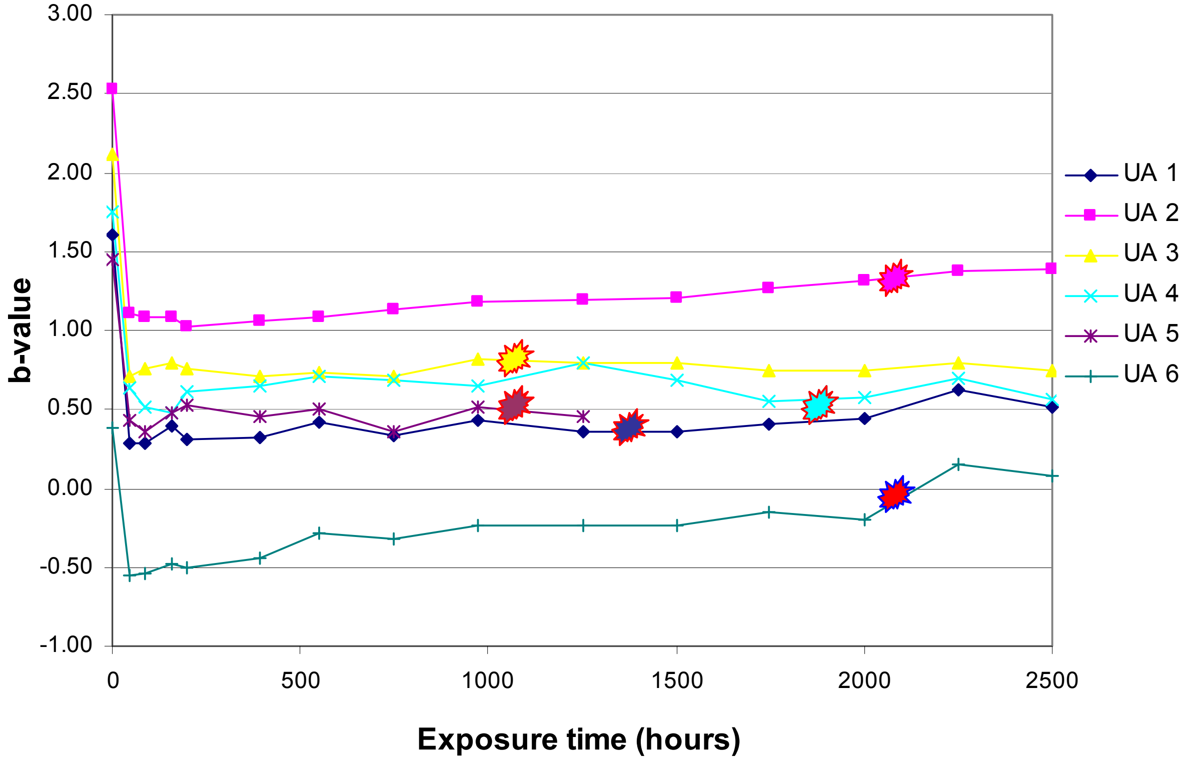

Figure 6. Monitoring of b values in Xenon. Appearance of first crack.

Figure 7 illustrates the monitoring of the gloss in the Xenon test. In general the gloss retention is excellent up to 2000h of Xenon exposure. Upon prolonged exposure the gloss decreases

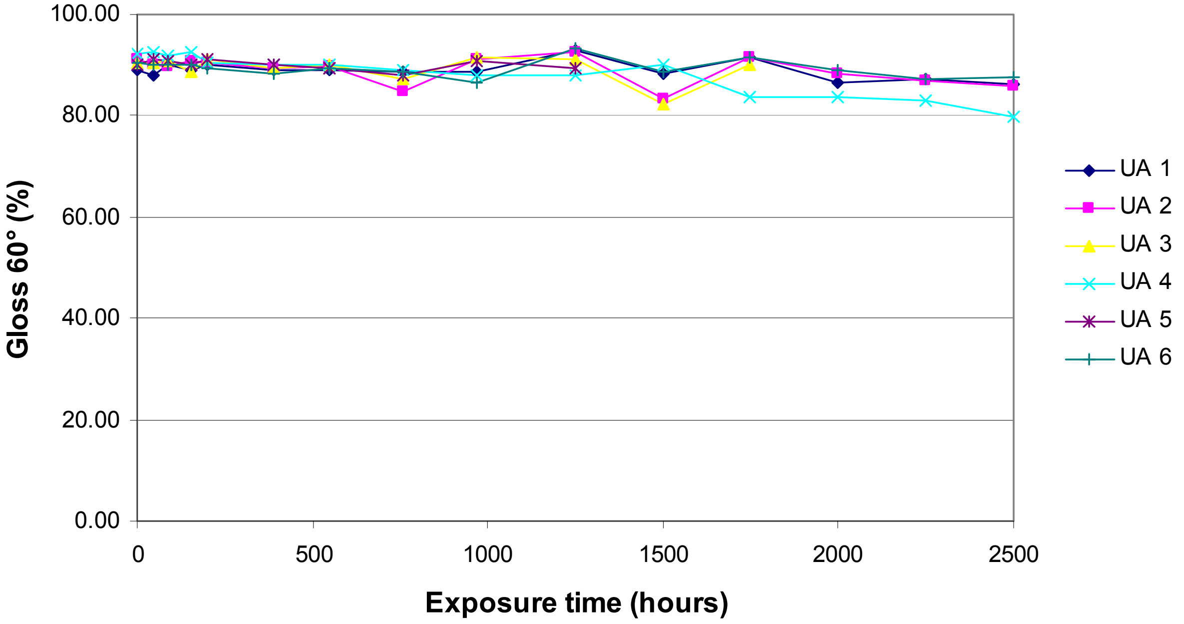

Figure 7. Gloss monitoring in Xenon

Conclusions

UV curing technology for industrial coatings has been established for decades. The advantages in terms of processing (high speed, smaller equipment), performance (scratch resistance, stain resistance, …) and environmental friendliness are well known. The use of UV technology for coating plastics has been limited. However, the translation of the advantages of UV technology into the field of plastic coatings has lead to an optimization of existing UV resins as well as the development of new UV binders. In this paper we described different UV resins that can be used as diluting agent, as adhesion promoter, as main binder with various properties, like outdoor performance, on many plastic substrates suitable for different application techniques.