Dual functionality monomers for photo-crosslinking open up new opportunities

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Introduction

Dual cure systems based on 2 pack isocyanate coatings (2 K) and UV formulations open up new horizons for formulators since these systems circumvent some of the drawback of 100% UV curing systems such as poor flexibility or lack of adhesion[1, 2] and improve the productivity of 2K systems thanks to the immediate UV processing. We present in this paper dual functionality monomers and oligomers bearing hydroxyl and acrylate groups (partially acrylated polyols) allowing the formation and crosslinking of interpenetrating polymer network (IPN´s) between the acrylates and the polyurethane networks. To the opposite of simple blends of conventional acrylates monomers/oligomers and 2 pack isocyanate formulations, even non-UV exposed areas are crosslinked and film forming using these dual functionality monomers and oligomers. Compared to highly viscous partial acrylate isocyanates, these partial acrylated polyols have lower viscosity and allow the formulation of high solid formulations suitable for spray application.

These new high solid systems can address the severe technical demands for new applications of the radiation curing technology such as exterior and interior applications for various end uses in original equipment manufacturer (OEM), car refinishes, plastic coatings or coatings for 3D and complex shapes with shadow areas (non UV exposed). Accelerated weathering evaluation (QUV-A) was performed for these UV dual cured coatings and compared to conventional solvent borne 2 pack isocyanate coatings.

Acrylated polyols characteristics

The multifunctional polyols used in this study were the tetrafunctional Di-Trimethylolpropane (Di-TMP[3]) and an aliphatic dendritic polyester polyol [4] with 16 primary hydroxyl groups, both available from Perstorp Specialty Chemicals AB. These polyols are partially acrylated according to conventional methods of esterification with acrylic acid by quenching the esterification to the desired residual hydroxyl number. Table 1 lists some nominal and typical characteristics of the acrylated polyols used in this study.

Table 1. Typical and nominal characteristics of the partially acrylated polyols

	Mw (nom.)	Acrylate concentration (nominal)	OH number (mg/KOH/g)	Acrylate Funct. (average)	Hydroxyl funct. (average)	Viscosity	Shrinkage
	g/mol	mmol/g				Pas @25°C	%
Di-Trimethylolpropane Di-acrylate (Di-TMPDA)	358	5,2-5,5	300-350	1,5-2,5	1,5-2,5	2-4	10-15
Dendritic polyester polyol, 70% acrylate	2345	4,5-4,7	100-150	10-11	5-6	120-180	5-10

Formulation suitable for outdoor application

Formulations

UV cured formulations for outdoor applications require a right selection of photoinitiators and light stabilizer package for long term durability. All coatings evaluated in this study contained light stabilizer (Tinuvin 400, CIBA) and hindered amine light stabilizer (HALS such as Tinuvin 292, CIBA) in order to provide the sufficient protection against UV degradation[5, 6]. Table 2 and 3 present the formulations used in this study.

Table 2. 2K reference formulation

	2K ref
Acrylic polyol (A 870 BA, BAYER)	65.9
HDI trimer (N 3390, BAYER)	17.1
IPDI (Z 4470 BA, BAYER)	14.1
DBTL	0.01
Tinuvin 292 (CIBA)	1.2
Tinuvin 400 (CIBA)	1.0
BYK 333 (Byk Chemie)	0.5
Viscosity mPas, 23°C	55
Solid content wt % (in BuAc)	58

Table 3. UV formulations (100% acrylate, dual cure based on simple blends of acrylate monomers and isocyanates or partial acrylates)

Formulation	1 (100% UV)	2 (Dual cure, physical blend)	3 (Dual cure, physical blend and IPN)	4 (Dual cure, IPN)	5 (Dual cure, IPN)
HDDA	40	30	24		
TMPTA	20	20	9,5		
Di-TMPDA				44	
Aliphatic urethane acrylate (CN963B80, Sartomer)	33.7	21			
Dendritic polyol, 70% Acrylate			45		71
Acrylic polyol (Acryflow M100, Lyondell)		13,3			
Acrylic polyol (Acryflow P120, Lyondell)		4,2			
HDI trimer (DESMODUR N3600, BAYER)		16,4	15,2	50	23,6
DBTL		0,01	0,01	0,01	0,01
Iracure 184 (CIBA)	4	4	4	4	4
Irgacure 819 (CIBA)	0,5	0,5	0,5	0,5	0,5
Tinuvin 292 (CIBA)	1,2	1,2	1,2	1,2	1,2
Tinuvin 400 (CIBA)	1	1	1	1	1
BYK 333 (Byk Chemie)	0,5	0,5	0,5	0,5	0,5
Viscosity mPas, 23°C	100	55	55	55	55
Solid content wt % (in BuAc)	100	89	90	93	67

High solid sprayable formulations were easily achieved using UV dual cure coating systems. A 100% UV formulation prepared from an aliphatic urethane acrylate oligomer and acrylate monomers was used as a UV reference (formulation 1). All dual cure systems were formulated with NCO/OH 1,05 ratio. The polyol or partial acrylated polyol or acrylate monomers (containing the photoinitiator and additive package) were mixed with the HDI trimer prior to application.

- The formulation 2 was a simple physical blend of a 2 pack isocyanate formulation based on acrylic polyols and HDI trimer with the same components as the UV reference formulation 1. UV curing was necessary for film forming. With UV curing an IPN is obtained but without crosslinking between the two polymeric networks.
- The formulation 3 was based on a partial acrylated dendritic polyol and acrylic monomers together with HDI trimer. Both physical blend and interpenetrating polymer network are formed and thermal curing only is not possible.
- The formulation 4 was only based on a partial acrylate of Di-Trimethylolpropane and the HDI trimer, allowing thermal curing only for obtaining a coating since the acrylates bearing at least 2 hydroxyl groups condensate with the HDI trimer to form a polyurethane network.
- The formulation 5 is only based on a partial acrylated dendritic polyol and the HDI trimer, allowing thermal curing only as for the formulation 4.

Pot life, curing conditions and conversions

The pot life of the 2 pack reference and the UV dual cure formulations were evaluated at room temperature. The dual cure systems were better than the 2 pack reference, with pot life exceeding 6 to 8 hours as shown in table 4.

Table 4. Pot life of the dual cure and 2 K formulations

Formulation	2 K reference	Form. 2 (Dual cure, physical blend)	Form. 3 (Dual cure, physical blend and IPN)	Form- 4 (Dual cure, IPN)	Form. 5 (Dual cure, IPN)
Pot life	1,5 hours	>8 hours	>8 hours	2 hours	2 hours

After flash off at 80°C for 5 minutes for BuAc containing UV formulations, all the UV coatings were cured under air using a H bulb from Fusion (F600, 240W/cm) at 5 m/min (4 pass) which corresponded to a total UV dose of 2000 mJ/cm². All the UV dual cure coatings were tack free after UV exposure, hence not requiring any thermal treatment despite an eventual thermal curing stage can be beneficial to accelerate the polyurethane network formation. The 2K reference coating was air force dried at 80°C for 30 minutes. 36µm ± 2µm thick coatings were applied. The conversions of the coatings (C=C conversion 24 hours after UV exposure and NCO conversion as function of time at room temperature after exposure) were measured by FTIR-ATR and the results presented in figure 1.

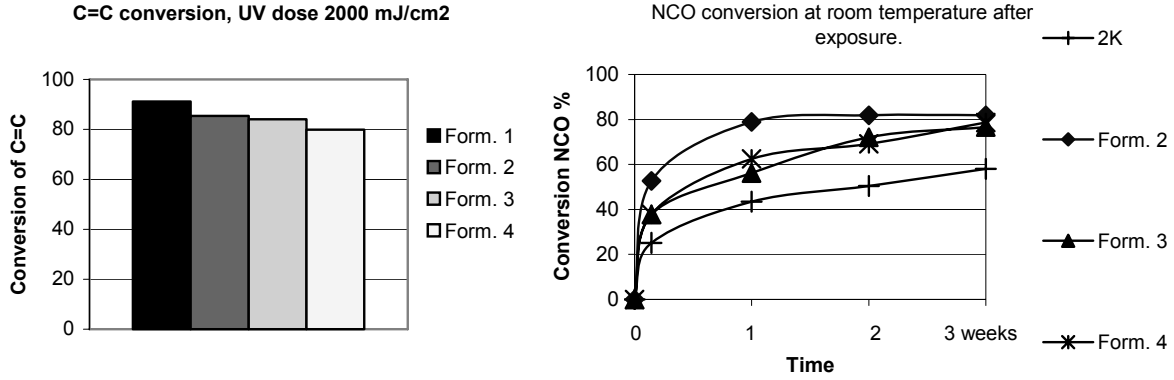

Figure 1. C=C Conversion for a total UV exposure of 2000 mJ/cm² and NCO conversion at room temperature

All coatings unsaturation conversions reached high values, typically from 80% to 90%. The NCO conversion was quite fast at room temperature with conversion of approximately 50 to 80% reached after 1 week. The formulations 1 (100% UV) and 2 (physical blend) were not able to form any film without UV exposure. The formulation 3 (physical blend and IPN) gave tack free films without exposure but rather poor integrity (poor scratch resistance) since it contains some unreacted acrylate monomers. Only the formulations 4 and 5 exhibited good film properties without UV exposure.

Coating properties

The UV formulations were evaluated for pencil hardness after 24 hours and 2 weeks. The minimum number of pass at 5 m/min under the 240W/cm lamp for obtaining a nail scratch free film was considered as a measurement of reactivity and the corresponding UV dose reported. All of the coatings were conditioned in 50 % relative humidity and 23 °C and the results presented in table 5.

Table 5. UV dual cure coating properties and reference 2 K isocyanate coating properties after 24 hours and 2 weeks (36 µm thick coatings, substrate: glass plate, conditioned in constant room)

Formulation	2 K reference	Form. 1 (100 % UV reference)	Form. 2 (Dual cure, physical blend)	Form. 3 (Dual cure, physical blend and IPN)	Form. 4 (Dual cure, IPN)	Form 5 (Dual cure, IPN)	Form. 4 (Dual cure, IPN)	Form. 5 (Dual cure, IPN)
Curing conditions	Air Forced dried, 30 minutes at 80°C	Under air, H bulb 240 W/cm, 4 pass at 5 m/min (2000 mJ/cm^2)					Air Forced dried, 30 minutes at 80°C	
Number of passes for nail scratch free (240W/cm, 5 m/min)	-	3	4	1	4	3	-	-
UV dose (mJ/cm^2)		1500	2000	500	2000	1500		
Pencil hardness 24 hours	HB/F	H/2H	F/H	2H/3H	H/2H	F/H	HB/F	F/H
Pencil hardness 2 weeks	F/H	H/2H	F/H	5H/6H	2H/3H	H/2H	F/H	F/H
Erichsen Flexibility mm, 24 hrs	6,0	0,7	1,0	1,2	4,4	2,0	>6	>6
Erichsen Flexibility mm, 2 weeks	6,0	0,7	0,8	0,8	2,5	1,8	>6	>6
MEK double rubs 24 hrs	36	>200	>200	>200	>200	>200	85	15
MEK dble rubs 48 hrs	85	>200	>200	>200	>200	>200	190	100

The dual cure physical blend formulation 2 was rather poorly performing compared to the IPN based coatings as based on formulations 3, 4 and 5 and compared to the 100% UV formulation.

The formulation 3 based on the 70% acrylated dendritic polyester exhibited the fastest UV cure and the highest pencil hardness. Furthermore a clear improvement of the properties after UV exposure can be noticed thanks to the crosslinked IPN formation which leads to high crosslinking density, hence an increased pencil hardness.

The formulations 4 and 5 exhibited good coating properties even without UV exposure. The properties are in a similar range as for the 2K reference coating while having a much better scratch resistance as seen in figure 2. With UV exposure, these formulations were largely better than the 2K reference in terms of chemical resistance and pencil hardness.

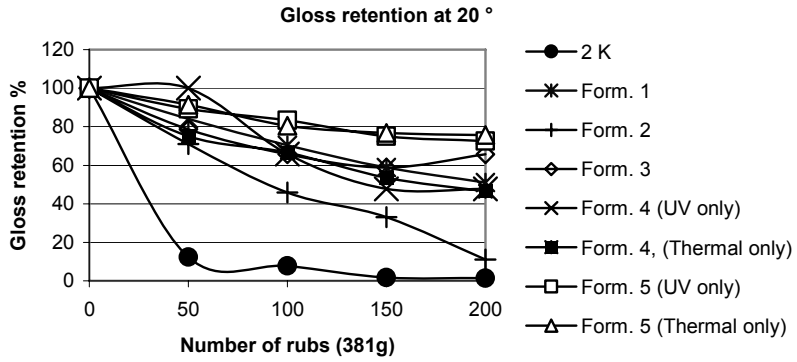

Figure 2. Scratch resistance (scrub test with 381 grs load) of the 2K isocyanate coating and the UV coatings (UV dose 2000 mJ/cm^2 for all the UV coating and only by air force dried for formulation 4 and 5 and the 2K reference)

Accelerated weathering

The accelerated weathering performances of the top coats were investigated on blue metallic waterborne basecoat (the same curing conditions as in the previous section were used and the test started 2 weeks after preparation). The panels were subjected to the alternate effects of condensation (4 hours at 50°C) and the damaging effects of sunlight simulated by the fluorescent UVA lamps (4 hours at 60°C).

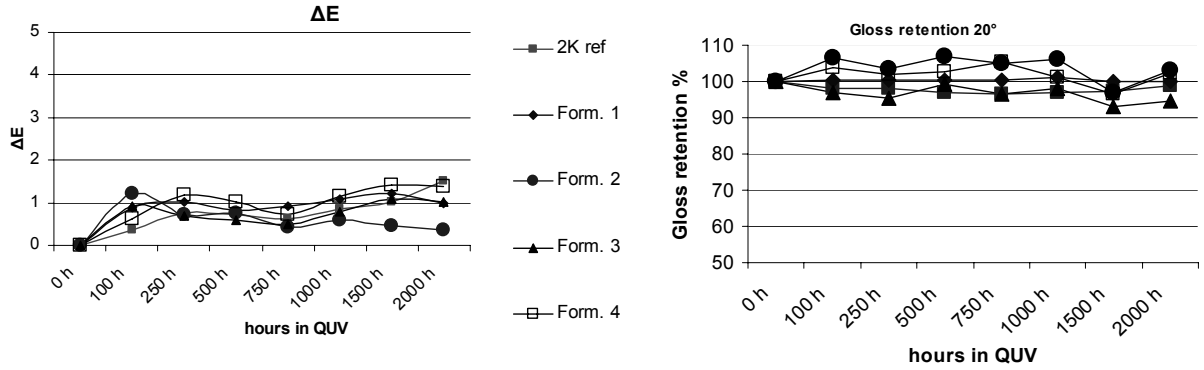

Figure 3. Delta E and gloss retention (20°) and as function of time (Cycle: 4 hours of UV-A exposure at 60°C followed by 4 hours of condensation at 50 °C)

Gloss (20°) and delta E were measured as a function of exposure time as presented in figure 3. The results show that the UV dual cure formulation perform more or less as good as the reference 2 K isocyanate based on HDI/IPDI trimers and polyacrylic polyols with a gloss retention superior to 90% and a delta E inferior to 2 after 2000 hours of accelerated weathering exposure. Long term exterior durability tests are currently running in Florida.

Conclusion

Compared to a simple mixture of acrylate monomers and conventional 2K coatings, the use of low viscous partial acrylated polyols such as Di-TMP diacrylate and the partial acrylate of a dendritic polyester polyol in dual cure thermal/UV systems with isocyanates allows the formulation of coatings able to film forming only by thermal curing. This turns to be beneficial for 3 D applications and complex shapes with shadow areas. Similar coating properties as a conventional 2K coating can be obtained with these non UV cured formulations with an enhanced scratch resistance.

When combined with UV curing, the high functionality of these acrylated polyols (both OH and C=C) provides a high crosslinking density, hence leading to coatings with excellent scratch and chemical resistance. A better flexibility than a simple dual cure mixture based on acrylates and a 2K isocyanate coating formulation or a 100% UV curing formulation is typically obtained. This better flexibility is believed to be obtained thanks to the crosslinked IPN´s and therefore the balance of crosslinked hard (acrylates) and soft (isocyanate) segments.

A Delta E inferior to 2 and a gloss 20° retention superior to 90% for all UV dual cure formulations after 2000 hrs of accelerated weathering (QUV-A) is achieved which is similar to a conventional 2K aliphatic isocyanate/acrylic polyol coating.

Beside the productivity benefit of the UV process and environmental advantages of the high solid sprayable dual cure formulations based on partial acrylated polyols, the coatings obtained by dual curing provide superior scratch and chemical resistance than conventional 2K systems.

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