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Advanced Polyols and Dendritic Polymers for Radiation Curing:

Allying Improved Performances with Safety and Environmental Compliance

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Abstract

Low viscous components in a radiation curing formulation are essential to allow a high versatility in combining different oligomers and/or surface modifiers like matting agents in order to reach the desired coating properties and appearance.

Today, a wide range of acrylate monomers exists, based on polyols like alkoxyated trimethylolpropane, pentaerythritol and neopentyl glycol with significantly lower irritancy than TPGDA or HDDA while keeping a good dilution power. The right combination with low viscous highly performant oligomers like dendritic polymers makes possible the preparation of suitable formulations for parquet flooring where exceptionally good wear properties as well as reactivity can be obtained.

This paper presents low viscous UV curable formulations based on these technologies exhibiting higher reactivity, higher toughness, chemical resistance and abrasion resistance than conventional formulations (i.e. comprising irritating diluents like TPGDA or HDDA).

Introduction

The radiation curing technology has encountered a number of innovations during the past 20 years and a strong development for a larger acceptance and for broader market penetrations are still under progress. One example is the development of higher molecular weight monomers as replacement to highly irritating low molecular weight acrylates like TPGDA or HDDA for better safety and health compliance with today's regulations. More than only improving SHE compliance, these acrylate monomers based on alkoxyated polyols like neopentylglycol (NEO), butylethylpropane diol (BEPD), trimethylolpropane (TMP) or pentaerythritol (PENTA) offer a wide range of properties, thus enlarging considerably the possibilities of the formulators for reaching today's most difficult technical challenges.

Today, the dendritic acrylates can be considered as a step forward in making acrylates with even higher molecular weight while maintaining extremely low viscosity. The globular shape of these polymers provides a unique combination between molecular weight, functionality and viscosity resulting in improved overall performances of the coating, like a higher reactivity, better toughness, wear resistance and low extractables compared to conventional formulations.

The monomers are more than just "reactive diluents"

A typical acrylate formulation for radiation curing consists of an acrylate oligomer that will mostly govern the end properties and the performances of the coating, some monomers to adjust the viscosity for an adequate processing, some photoinitiator and additives package. The monomers are commonly regarded as detrimental for the coating properties together with bad safety and health compliance due to their low molecular weight.

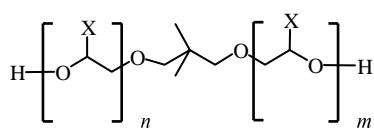
This is true for the first generation of monomers like trimethylolpropane triacrylate or hexandiol diacrylate but today, relatively recent development lead to monomers being more than just reactive diluents and they may highly participate to the coating performance together with significantly better safety and health compliance.

In a formulation, the origin of the major drawbacks of the monomers for a coating properties and performances are coming from their low molecular weight and following problems may arise:

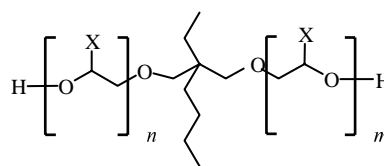
- hazards regarding handling of the products (skin and eye irritation)
- important shrinkage, resulting in a bad adhesion and formation of strong residual stresses affecting the longevity of the coating
- low reactivity due to their low molecular weight
- high amount of extractables (uncured monomers in the coating)

Neopentyl glycol (NEO), butyl ethyl propane diol (BEPD), trimethylol propane (TMP) and pentaerythritol (PENTA) based monomers

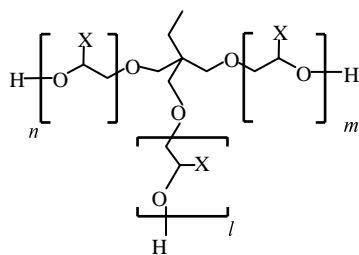
In order to decrease the negative impacts of the very low molecular weight monomers, a new generation of acrylate monomers appeared, principally based on alkoxyated polyols like trimethylolpropane, pentaerythritol and neopentylglycol showing significantly improvement compared to the first generation of monomers like TMPTA, PETA, HDDA or TPGDA.



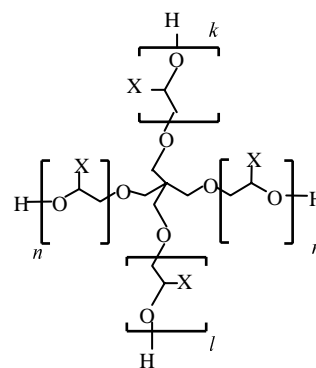
a. NEO (difunctional)



b. BEPD difunctional)



c. TMP (Trifunctional)



d. PENTA (Tetrafunctional)

Figure 1. Chemical structure of the alkoxyated NEO, BEPD, TMP and PENTA (X:CH₃ Propoxyated; X:H, ethoxyated)

In case n , m , k or $l \geq 3$, the product will be a polymer according to the OECD definition and these products do not require extensive notification efforts.

These polyols can be acrylated through a conventional esterification of acrylic acid, using inhibitors like hydroquinones and acid catalysts like methane sulfonic acid. In table 1 are given some examples of the characteristics of these acrylates and the improvement in classification compared to the first generation of reactive diluents.

		Funct.	Nominal Mw (g/mol)	Viscosity (mPas, 25°C)	Acrylate concentration (mmol/g)	Symbol/Risk ¹	PII Draize value*
First generation of reactive diluent	NEOA	2	212	10	9.4	T, R24+36/38+43	5-8
	HDDA	2	226	10	8.8	Xi, R36/38+43	3-5
	TPGDA	2	300	15	6.6	Xi, N, R36/37/38+ 43+ 51/53	3-5
	TMPTA	3	296	120	10.1	Xi, R36/38+43	3.7-4.5
	PENTAA	4	352	1400	13.4	Xi, R36/38+43	4.3-5
Second generation of reactive diluent	NEOA (2PO)	2	328	30	6.1	Xi +R36/38	0.8-2.4
	BEPDGA (3PO)	2	384	35	5.2	Xi +R36/38	0.3
	TMPTA (3EO)	3	428	90	7.0	Xi +R36	0.2-0.6
	PENTA A(5EO)	4	572	140	7.0	Xi +R36	<0.1
	PENTA A (5PO)	4	642	650	6.2	Xi +R36	0.6

*the PII number is given as a range since discrepancy is observed depending the source

Table 1. Comparison of the characteristics and hazards of some acrylated polyols

Increasing the functionality (from NEO diacrylate to PENTA tetraacrylate) generally has a positive impact on increasing the chemical resistance, the glass transition temperature and the reactivity due to the higher crosslinking density but to the detriment of viscosity (table 1) and flexibility of the coating.

More than simply increasing the molecular weight of the base core molecule and improving safety and health compliance, the alkoxylation is a unique way to tailor the end properties of the coatings. The type (ethoxylation vs propoxylation) and the degree of alkoxylation has a strong influence on the viscosity, reactivity, chemical resistance and the thermomechanical properties of a UV cured film, covering from hard to soft coating based on the same core molecule.

Common trends of the effects of increasing the alkoxylation degree are observed whatever the core molecule (NEO, BEPD etc...). Anyhow, it results in a compromise between viscosity, wear resistance and thermomechanical properties of a cured film.

As a function of the degree of alkoxylation, the viscosity generally follows a pattern showing firstly a decrease in viscosity thanks to a more flexible structure and secondly by an increase in viscosity due to the apparition of chain entanglements when the degree of alkoxylation is important. The case of ethoxylated and propoxylated TMP acrylate is presented in figure 1 where a minimum viscosity is observed for an alkoxylation of 2 to 6 alkylene oxide segments.

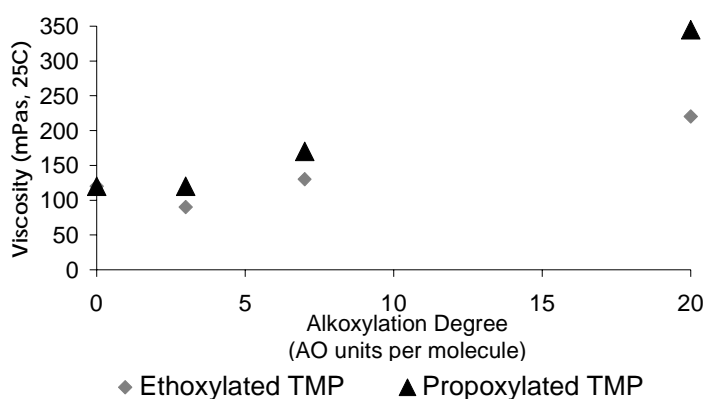


Figure 2. Comparison of the viscosity vs the degree of alkoxylation of triacrylated TMP

The combination of increasing the inherent flexibility of the backbone of the molecule thanks to the flexible alkylene oxide segments with an increase in the molecular weight between crosslinks creates a synergetic effect in strongly decreasing the Tg of the coating (and thus the hardness) to the benefit of flexibility.

The case of ethoxylated TMPTA is presented figure 3 and it clearly shows the strong impact of the ethoxylation degree in decreasing the hardness to the benefit of the flexibility in a formulation containing only 25% of the alkoxyated TMPTA.

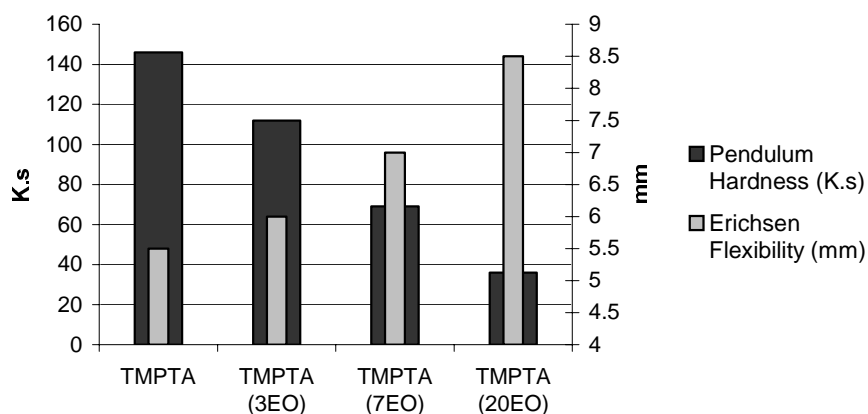


Figure 3. Comparison of hardness and flexibility of a formulation containing either TMPTA, TMPTA (3EO), TMPTA (7EO) and TMPTA (20EO).
 Formulation: LR8799 (BASF, Germany):TPGDA:TMPTA (x) 50:25:25
 Curing conditions: total UV dose of app. 1500mj/cm² using 4% of Darocur 1173 (CIBA, Switzerland)

The decrease in crosslinking density and the hydrophilicity of the ethylene oxide groups makes the coating more sensitive to swelling by polar chemicals and particularly water. For a same degree of alkoxylation, the propoxylation will have generally a higher viscosity than the ethoxylated one (see table 1 comparing PENTA [5EO] tetraacrylate and PENTA [5PO] tetraacrylate and figure 2 presenting the case of TMPTA PO or EO). Furthermore, a slightly lower glass transition temperature is observed compared its ethoxylated counterparts due to the pendant methyl group and the lower acrylate to molecular weight ratio resulting in a lower crosslinking density.

Nevertheless, a positive effect of the propoxylation is a lower water sensitivity of the propoxylated homologue due to the lower hydrophilicity of the propylene oxide segment compared to the ethylene oxide segment as shown on figure 4. The high octanol water partitioning value of BEPDA is maintained by increasing the degree of propoxylation whereas the ethoxylation has for consequence to decrease this factor showing the higher sensitivity of ethoxylated TMPTA to polar substances ².

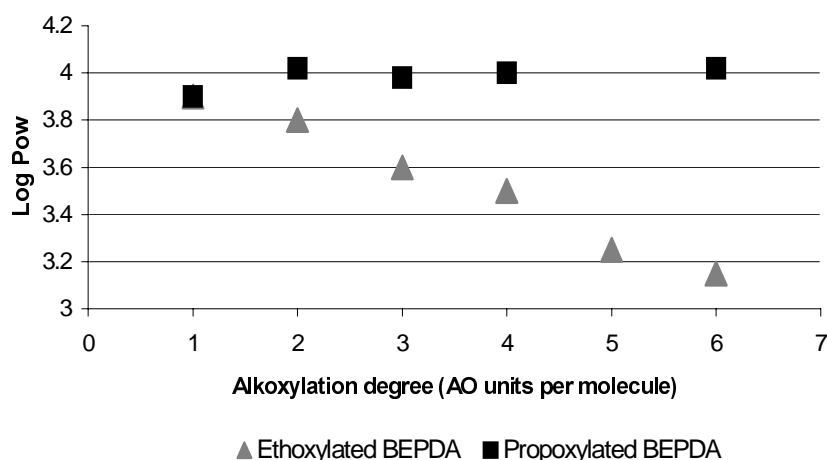


Figure 4. Octanol-water partitioning coefficient Pow with various levels of alkylene oxide modification on BEPD

Furthermore, a higher degree of ethoxylation has a positive impact on reactivity since the two carbons adjacent to the oxygen atom in the ethylene oxide segment are primary and provide a source of abstractable hydrogen susceptible to participate for the initiation of free radicals in combination with ketone type photoinitiator. In case of propoxylation, only one primary carbon is present resulting in a lower reactivity than the ethoxylated homologue³.

The alkoxylation may participate in the reduction of shrinkage since the crosslinking density is decreased. Furthermore, a reduction in residual stresses upon photocuring thanks to the decrease of the Tg and better flexibility of the coating can be expected⁴. These effects are essential for a good adhesion and the longevity of the coating.

A very high degree of ethoxylation may render the monomer suitable for water-reducible systems since the acrylate monomer become fully or partially water-soluble as shown in the case of TMPTA 20EO and PENTA 15EO triacrylate in the following figure.

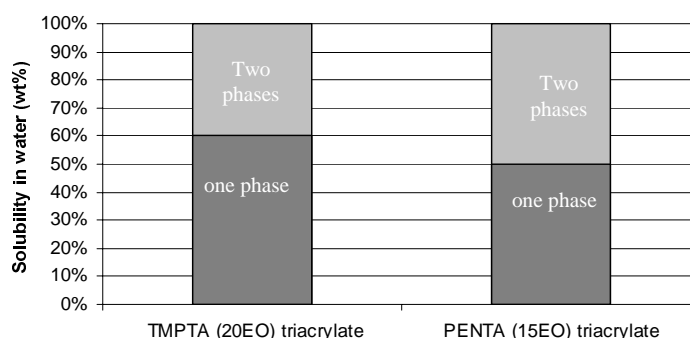


Figure 5. Water solubility of TMPTA (20EO) triacrylate and PENTA (15EO) triacrylate

The water sensitivity of the coating and its very low Tg making the coating very soft maybe overcome by an addition of high functional monomers like Di-TMP tetraacrylate for example and by mixing them prior to the water addition.

Di-trimethylpropane (tetrafunctional) and Di-pentaerythritol (hexafunctional)

Di-TMP and Di-PENTA acrylate should not really be seen as diluents since their viscosity is relatively high. Furthermore, they have a strong impact on end coating properties due to the very high crosslinking density they provide: it results in a high chemical resistance, a high hardness and scratch resistance and a very good reactivity even a low addition level.

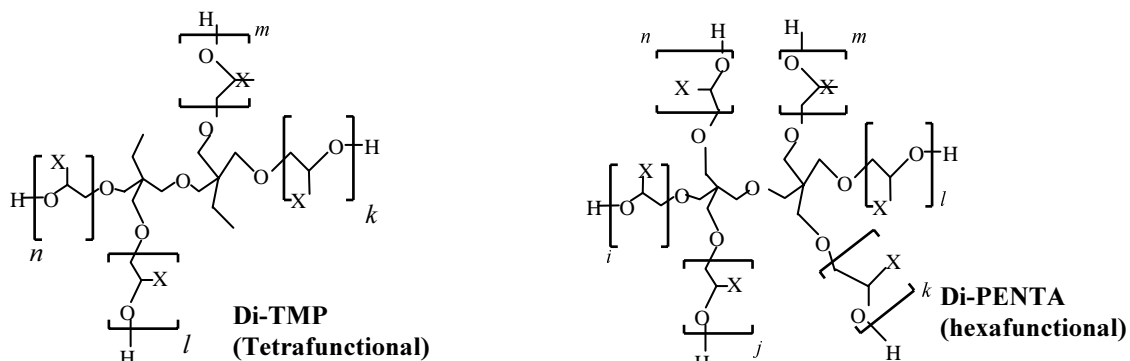


Figure 5. Chemical structure of di-trimethylolpropane and di-pentaerythritol

Di-TMP tetraacrylate can be a good replacement to PENTA tetraacrylate when labelling issues are critical, since they have similar viscosity and they result in similar coating properties, but Di-TMP tetraacrylate has significantly lower risks as shown in the following table.

	Funct.	Nominal Mw (g/mol)	Viscosity (mPas, 25°C)	Acrylate concentration (mmol/g)	Symbol/Risk	PII Draize value
TMPTA	3	296	120	10.1	Xi, R36/38+43	3.7-4.5
PENTAA	4	352	1400	13.4	Xi, R36/38+43	4.3-5
Di-TMPTA	4	466	1450	8.6	Xi +R36	0.5
Di-PENTAA	6	578	11200	10.4	Xi +R36	0.3

Table 2. Comparison of the characteristics and hazards of high functional acrylated polyols

Further development are under way to develop new alkoxyated polyols on these technologies with improved low impurities levels in order to obtain very low extractables (glycol free) and by fine tuning the level of alkoxylation for the best match of properties.

The few examples presented here highlight the higher versatility of available monomers covering a wide range of properties. It is important to select the right monomer for a formulation, not only based on its inherent viscosity, but considering which oligomer it is used with in order to obtain the best coating performances. It has already been reported that when formulating a complex matting formulation, the rheological behaviour of the complete formulation may differ significantly and independently of the inherent viscosity of the monomers used⁵.

Dendritic polymers

One of the major innovation in the polymer chemistry for the past 20 years is the emergence onto the market of the dendritic polymers. Thanks to their globular shape, a higher molecular weight for a similar or lower viscosity while having a high number of functionality is a unique combination compared to conventional polymers. For the past 10 years, Perstorp has developed a number of hydroxyl functional dendritic polyesters based on bismethylolpropionic acid⁶ and more recently newly hydroxyl functional polyethers having trimethylolpropane as the branching unit⁷. These dendritic polymers find a number of applications in the paint and coating industries as well as in commodity and engineering plastics^{8,9,10,11}.

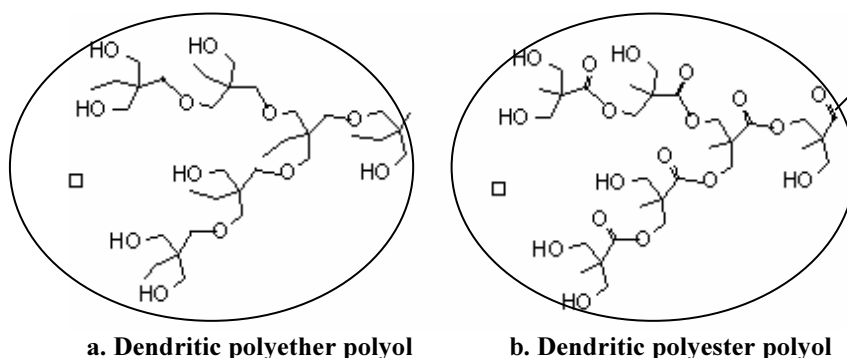


Figure 6. Illustration of a branch of the dendritic polyether (a) and the dendritic polyester (b)

Recently, a dendritic polyester/ether polyol has been specially designed for radiation curing. The acrylated polyol can reach a unique combination of viscosity to molecular weight ratio ($M_w=2280\text{g/mol}$ with a viscosity of $290\text{mPa}\cdot\text{s}@25^\circ\text{C}$) as shown by its characteristics in table 3.

Table 3. Characteristics of the dendritic polyester/ether acrylate used in this study

	Molecular weight		Acrylate conc.	Acid number	Non VOC	Viscosity	Tg*
	Mw (SEC, g/mol)	polydispersity.	mmol/g	mgKOH/g	%	Cone & plate (mPa.s, 25°C , 30s^{-1})	$^\circ\text{C}$
Dendritic acrylate	2281	2.85	5.2	2.0	>99	290	60

*The Tg was obtained from a $40\ \mu\text{m}$ thick fully UV cured film (>95% of C=C conversion according to FTIR measurement) and measured by DMA in tensile/tensile mode. The Tg is taken as the temperature of maximum of $\text{Tan } \delta$.

This dendritic acrylate is compliant to the OECD's polymer definition and it has a PII value less than 0.1. A simple comparison of viscosity as a function of molecular weight for 5 types of conventional acrylate oligomers used in radiation curing is given in figure 7.

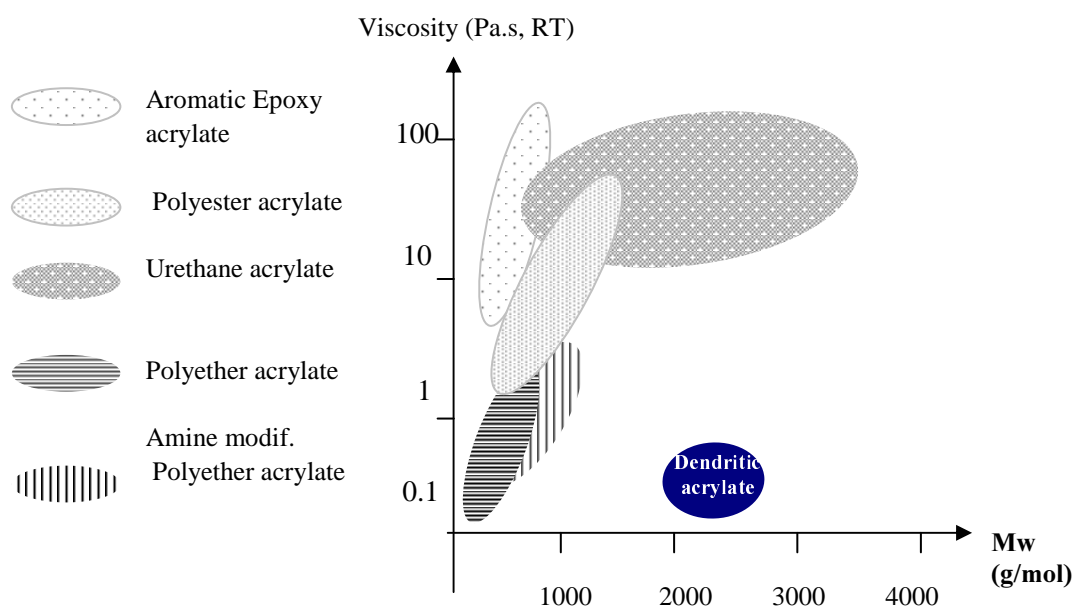


Figure 7. Comparison of molecular weight (M_w) and viscosities (Pa.s at room temperature) of conventional oligomers used in radiation curing¹²

Formulations

The dendritic acrylate was characterised and compared with 2 reference formulations based on conventional oligomers and monomers. These references were formulated in order to obtain a similar viscosity as the dendritic acrylate. Finally a formulation based on the dendritic acrylate was made together with an aromatic bisphenolA diacrylate without any monomers (100% oligomer formulation). The table 4 gives the composition of the studied formulations.

Table 4. Comparison of two conventional formulations with the dendritic acrylate and a formulation based on this dendritic acrylate

	Reference 1	Reference 2	Dendritic acrylate	Formulation 1 (based on epoxy acrylate)
Monomers				
TPGDA	25	15	-	
TMPTA (3EO)	50	50	-	
Oligomers				
Epoxy ¹	25	-	-	25
Polyester ²	-	35	-	-
Dendritic acrylate				
	-	-	100	75
Irgacure 500	3	3	3	3
Viscosity (25°C, mPas -cone and plate-)				
	210	220	250	570
1. Bisphenol A diacrylate, EB600, UCB Chemicals, Belgium			2. LR8799, BASF, Germany	

The reference 1 is composed of EB600 (UCB Chemicals, Belgium), an aromatic epoxy diacrylate known for its chemical resistance, reactivity and abrasion resistance ($\eta=3\text{Pas}@60^\circ\text{C}$). 25 parts of TPGDA have been used in order to decrease the viscosity to a similar level as the dendritic acrylate.

The reference 2 is composed of LR8799 (BASF, Germany), a polyester known for its good overall properties, especially flexibility and chemical resistance. The same monomers as for reference 1 are used. TPGDA is only used at a level of 15 parts, the viscosity of LR8799 ($\eta=2\text{-}5\text{Pas}@25^\circ\text{C}$) being much lower than EB600. This second reference should have good overall properties (toughness and chemical resistance).

Irgacure 500 (CIBA, Switzerland) is the photoinitiator used in this study and it is a combination of benzophenone and an α -hydroxyketone type of photoinitiator (Irgacure 184).

Reactivity

The reactivity of the formulations given in table 4 was evaluated by measuring the acetone double rubs resistance (max. 250) of a $12\mu\text{m}$ thick coating cured on metal plates after one pass under a UV source (lamp of $80\text{W}/\text{cm}$) in air and by varying the belt speed. The occurrence of tacky surface was as well reported in figure 7 (dashed lines).

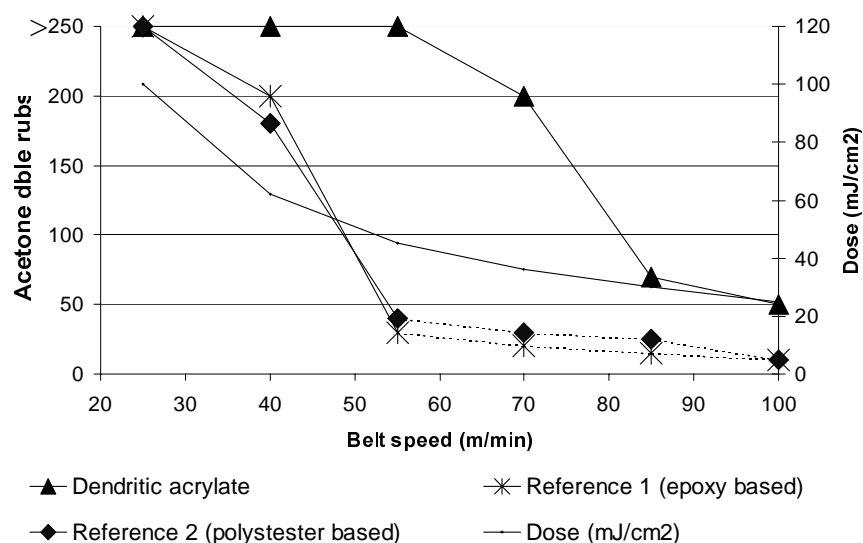


Figure 8. Reactivity of the references and the dendritic acrylate

As illustrated by figure 8, the two references have significantly lower reactivity than the dendritic acrylate. At belt speeds above 55m/min, unsatisfactory surface cure was seen for the references (a tacky surface represented by the dashed line on figure 8 and a very low acetone double rubs resistance), while the dendritic acrylate had still very good reactivity.

If the curing dose is considered (reported on figure 8), it can be evaluated that the dose required to properly cure the dendritic acrylate is two times lower than for the references at a similar viscosity and acetone double rubs resistance (for an acetone double resistance superior to 250, the required dose is 45mj/cm² and 100mj/cm² respectively).

A full cure of 12 μ m thick coatings prepared from the formulations presented in table 4 was ensured by allowing the coating samples to pass 4 times under a UV source of 240W/cm at 20m/min in air. The obtained film properties are reported in table 5.

Table 5. Characterisation of fully cured 12 μ m thick coatings

	Reference 1 (Epoxy based)	Reference 2 (Polyester based)	dendritic acrylate	Formulation 1 (epoxy based)
Curing conditions: 3% Irgacure 500, 4 passes 20 m/min in air under a 240W/cm Hg lamp (1 pass=325mJ/cm ²), 12 μ m thick samples, metal substrate				
Pendulum Hardness [K.s]	210	182	188	206
Erichsen Flexibility [mm]	2.3	3.2	3.6	3.4

Thanks to the combination of the high functionality, the hyperbranched and aliphatic structure of the dendritic acrylate, an excellent ratio hardness to flexibility was achieved, with higher values for both properties compared to the reference 2. The formulation of the dendritic acrylate with the epoxy gives even harder film while maintaining an excellent flexibility.

Abrasion resistance

The abrasion resistance was tested in accordance with ASTM 4060-84. 30 μ m thick coatings were cured on foils with 2 passes under a 240W/cm lamp in air and then laminated. The method is conducted using S33 wheels under a 500g load at a rotation speed of 60rpm. The number of cycles for 95% wear-through is reported in the following figure.

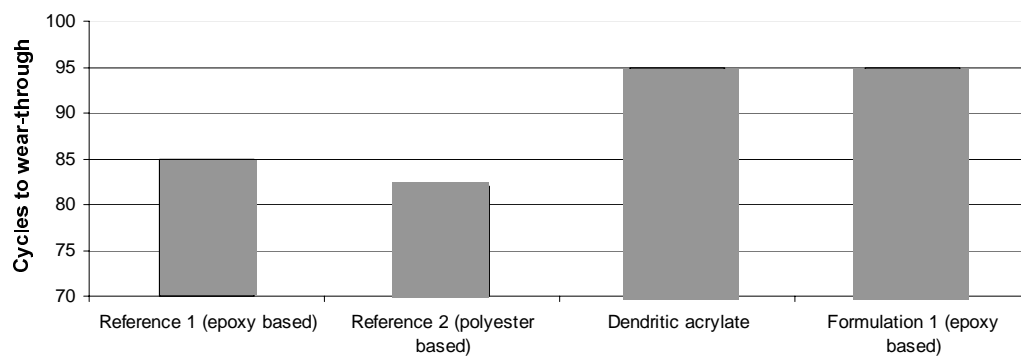


Figure 9. S33 taber, 500g load. Cycles to wear-through 95% of the coating.

The improved toughness illustrated by the characterisation of the fully cured film confirms the better abrasion resistance obtain with the dendritic acrylate compared to the references.

Chemical resistance

The chemical resistance and water sensitivity of the fully cured coating were evaluated by long time exposure to water and acetone and the results are reported in figure 10.

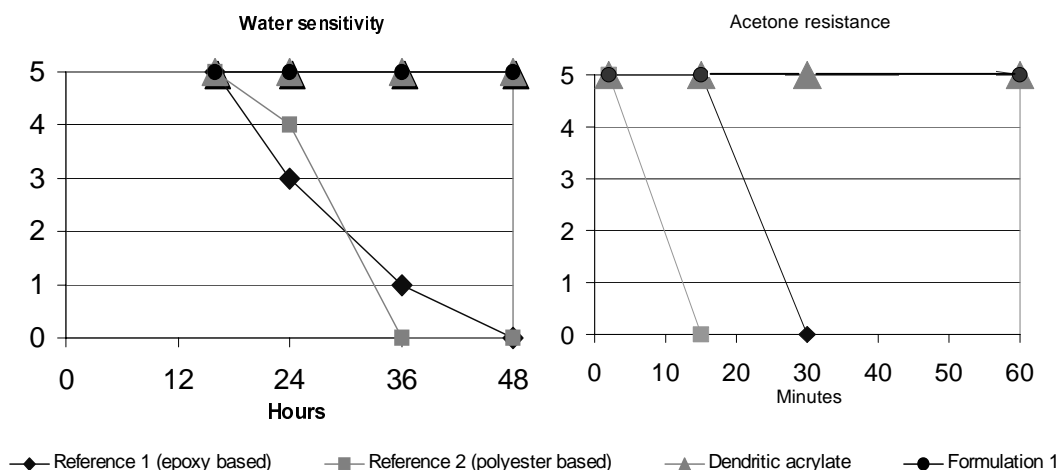


Figure 10. Water sensitivity and chemical resistance (acetone) (5: no effects, 0: complete lifting)

Thanks to the hyperbranched structure, the dendritic acrylate and its formulation with the aromatic epoxy acrylate have excellent chemical resistance and low water sensitivity since no effects have been reported after long exposure time (48 hours for water and 1 hour for acetone). The coatings made from the two references are affected by water between 16 and 24 hours and by acetone after 5 minutes in case of the polyester based formulation and after 15 minutes in case of the epoxy based coating.

Extractables

Since no diluents are used in the formulations based on the dendritic acrylate, very low extractables in a cured film are expected. The extractables were evaluated by measuring the weight loss of coatings after long time immersion in acetone (16 hours at 50°C). The coatings were cured under a 240W/cm lamp in air, 1 pass at 20/min. The coating thickness was 80µm with a total surface area of 60cm². After measuring the absorption, the coatings were dried under vacuum until a stable weight was reached and the samples weighted.

The obtained results are reported in table 6.

Table 6. Extractables from the coatings

	Reference 1 (Epoxy Based)	Reference 2 (Polyester based)	Dendritic acrylate	Formulation 1
Curing conditions: 3%Irgacure 500, 80 µm thick on metal plates, surface of 60cm ² , 1 pass 20 m/min, 240W/cm in air				
Extractables [wt%]	5.3	5.2	3.2	3.3

As shown in table 6, the coatings containing the dendritic acrylate have about 40 to 45% less extractables than the two references. Furthermore, this weight loss corresponds to the amount of photoinitiator used (3%) so that the amount of extractables from the binder is believed to be extremely low.

Conclusion

A number of acrylate monomers based on alkoxyated polyols like BEPD, NEO, TMP and PENT demonstrate higher compliance with regulations together with a greater technical versatility in obtaining coatings of different thermomechanical properties. Similar trends on properties can be observed as a function of the degree of alkoxylation whatever the core molecule and the functionality. In general, the alkoxylation has for effect to increase the molecular weight between crosslinks and flexibilise the inherent backbone, resulting in softer coating.

Ethoxylation yields higher reactivity thanks to the high number of abstractable hydrogen and a lower viscosity than propoxyated homologues but to the detriment of water resistance due to the higher hydrophilicity of the ethylene oxide groups versus the propoxyated ones.

In general, the alkoxylation provides a unique tool to cover a very wide range of properties and compromises. It offers a formulator a greater possibility of combination with oligomers and subsequently more possibilities to reach technical targets together with increased SHE considerations.

The unique combination of a high molecular weight, hyperbranched structure, high functionality and low viscosity offered by the dendritic technology exhibits a unique combination of properties. When comparing formulations of similar viscosity based on conventional monomers and oligomers, the dendritic polymer exhibited a superior reactivity, an excellent hardness to flexibility ratio, a better wear resistance (chemical resistance and abrasion resistance) and finally extremely low extractables since no monomers are present.

Acknowledgements

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