Modern use of vinyl ethers, vinyl amides and vinyl esters in UV curable applications

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Abstract

UV curing technology is rapidly becoming the technique of choice for printing and coating where high quality and environmental safety are desired. This article reviews the use of vinyl ether, vinyl amid and vinyl ester compounds in the formulation of UV-curing coatings in Graphic Arts, wood and plastic coating applications.
Styrene and monomeric acrylates are well known as reactive diluents in UV formulations. Aside from these monomers, vinyl ethers, vinyl amides and vinyl esters find use in special applications where unique properties are required. The latter reactive diluents polymerize under free radical and cationic conditions, and are well known as candidates for the substitution of acrylates due to their special performance and better toxicological profile. The paper will demonstrate the ability of vinyl compounds to significantly reduce the formulation viscosity. The copolymerization behavior of vinyl ethers with acrylates and unsaturated polyesters during cure have also been studied. Evaluations with real-time IR spectroscopy were done in order to find the optimum level of vinyl ether diluents required to satisfy the application needs and to minimize potential hydrolysis reactions. The systems reveal high reactivity and complete conversion of the vinyl ethers in optimized formulations. Application tests of coating performance will also be given in this publication.

Introduction

Vinyl ethers have been described in excellent overviews with respect to syntheses, structure and reactivity as well as photo initiated polymerization in cationic and radical UV curing systems [1-3]. The kinetics of the copolymerization of vinyl ethers with acrylates by pure free radical means, as well as the combined radical and cationic initiation method have been studied by C. Decker [2]. It has been shown that in such formulations upon radical photo initiation the acrylate radical is twice as reactive towards the acrylate double bond as towards the vinyl ether double bond.
Vinyl-amides offer high reactivity in copolymerization with acrylates. The polar amid-structure improves the adhesion of the cured film to plastic substrates and lowers the viscosity of the UV-binder resins.
New developments in the industrial production of vinyl esters now make this product group more accessible to the UV-curing industry. Performance wise vinyl esters are comparable to methacrylates and offer therefore new fields of applications.
Many different vinyl ethers are commercially available and can used for UV curable formulations with lower irritation index. The comparison of vinyl ethers with acrylate reactive diluents show the distinctive advantage afforded by vinyl ethers; we will present data to demonstrate the optimum amount for performance. As reported in the literature [4] acid catalyzed hydrolysis of vinyl ethers can take place, leading to several side reactions, including the formation of acetaldehyde.
Our investigations analyses the degree of conversion in selected formulations and demonstrates how to drive the conversion of vinyl ethers nearly to completion.

Vinyl ether monomers

Vinyl ethers are known for more than 100 years. The industrial production of vinyl ether monomers started in the 1930s based on the Reppe reaction of acetylene with alcohols. Many different vinyl-ethers are commercially available today. Low molecular weight vinyl ethers are versatile monomers for polymerization.

From the portfolio of available vinyl ethers, the higher boiling and the difunctional vinyl ethers are preferred in coatings applications. The scope of the Reppe reaction allows for the synthesis of a broad range of vinyl ethers having different functionalities and performance. The manufacturing of vinyl ethers includes a distillation step after the synthesis and allows for an assay of > 99%. This higher assay makes vinyl ethers more attractive for applications, especially where high reproducibility and little by-products are required. Beside the low viscous vinyl-ethers which are typically used as reactive diluents, vinyl-ether based oligomeric binders are also available on commercial scale. Polyester- and urethane based vinyl-ethers are also available with hydroxyl- and amino-functionalities. Those binders are used in applications where fast cure speed, low viscosity and low odor are required for flexible coatings with high gloss and adhesion.

Vinyl ether monomers for radiation curing

Vinyl ether oligomers for radiation curing
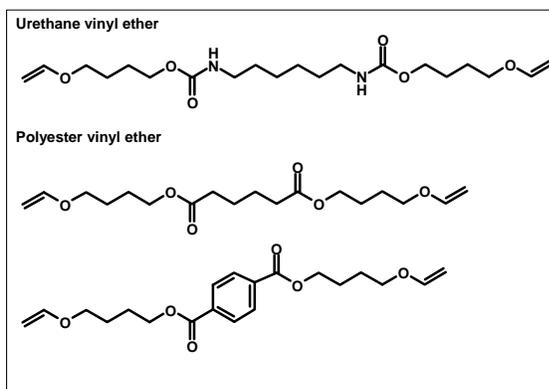
Figure 1: Selection of vinyl ether monomers   Figure 2: oligomeric vinyl binders

Materials and Equipment

Where as the low molecular weight mono-functional vinyl ethers are mainly used as industrial monomers for the production of poly vinyl ethers, the difunctional vinyl ethers are used as cross-linking agents or reactive diluents in UV-curable applications. One attractive compound in this respect is triethylene glycol divinylether (DVE-3 from BASF), which has been registered in ELINCS, is TSCA and MITI listed, and needs no further classification or labeling.

Thus, we have compared its properties with an ethoxylated trimethylolpropane triacrylate (Laromer LR 8863 from BASF) and a classical reactive diluent tripropylene glycol diacrylate (Laromer[®] TPGDA from BASF), which however is labeled Xi (table 1).

Data	TPGDA	DVE-3	Polyether acrylate
Viscosity (mPas)	11	2.6	100
Boiling point (°C)	109 at 0,3 mbar	242	> 250°C
Labeling / Classification	X_i , R 36/38/43	- none -	X_i , R 36/38
% diluent for epoxy acrylate*	20 %	8 %	28 %
% diluent for PE acrylate **	20 %	9 %	40 %

* Epoxy acrylate LR 8986 (4500 mPas) containing the given amounts of reactive diluent to get 1000 mPas viscosity

** Polyetheracrylate PO 84 F (700 mPas) containing the given amounts of reactive diluent to get 200 mPas (for spray application)

Table 1:   Comparison of reactive diluents

The following resins were used in this study: standard epoxy acrylates (Bisphenol-A-diglycidyl ether reacted with acrylic acid) and Laromer LR 8986, an unsaturated polyester (UPE based on fumaric acid and ethylene glycol) synthesized in the lab and an amine modified polyether acrylate (Laromer PO 84F, BASF).

As photo initiators hydroxy alkyl phenyl ketones (Iragacure® 184 and Irgarocure® 1173, Ciba) and a sulfonium salt (Chivacure® 1176, DBC) were used.

The UV exposure equipment from IST contains two Hg quartz tubes with a total power of 120 W/cm². The energy applied was determined by the speed of a conveyor belt moving the samples below the lamps.

The real time infrared spectroscopy (RT-IR) measurements were done with a Bruker IFS-66 with rapid scan.

Photo induced radical copolymerization

Mixtures of DVE-3 with the resins UPE and epoxy acrylate will exemplify the radical copolymerization behavior of vinyl ether monomers with unsaturated polyesters and acrylates, respectively.

The copolymerization behavior can be described by the equations shown in figure 3. From these values it can be estimated, that the copolymerization of unsaturated polyesters with vinyl ethers tends towards an alternating copolymerization, since the vinyl ether undergoes no homo polymerization. In the copolymerization with the acrylate, the sequences of acrylates will dominate, as depicted in figure 4.

Copolymerization behaviour

.. $-M_1^* + M_1 \xrightarrow{k_{11}}$ .. $- M_1 - M_1^*$

.. $-M_1^* + M_2 \xrightarrow{k_{12}}$ .. $- M_1 - M_2^*$ $r_1 = k_{11}/k_{12}$

.. $-M_2^* + M_1 \xrightarrow{k_{21}}$ .. $- M_2 - M_1^*$ $r_2 = k_{22}/k_{21}$

.. $-M_2^* + M_2 \xrightarrow{k_{22}}$ .. $- M_2 - M_2^*$

$r \sim 1$:	statistic distribution of M1 and M2
$r > 1$:	preferred addition of the same monomer
$r < 1$:	preferred addition of the other monomer

Fumaric acid butylene glycol polyester	Ethyl vinyl ether
$r_1 = 1.6$	$r_2 = 0$
Acrylic acid methyl ester	Ethyl vinyl ether
$r_1 = 3.3$	$r_2 = 0$
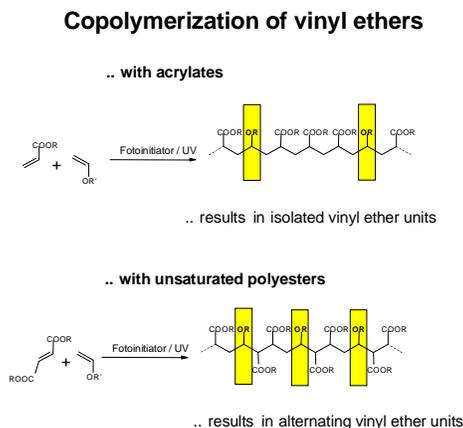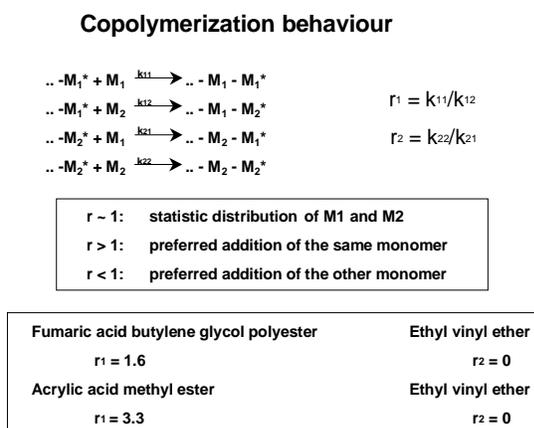
Figure 3: Copolymerization equations

Copolymerization of vinyl ethers

.. with acrylates

.. results in isolated vinyl ether units

.. with unsaturated polyesters

.. results in alternating vinyl ether units

Figure 4: Copolymerization scheme

From these considerations it can be concluded that the vinyl ether content in unsaturated polyesters should not exceed the molar ratio of fumaric groups in order to avoid unrelated residual vinyl ether monomers or monomer units.

Reactivity and conversion studies

Using RT-IR spectroscopy we evaluated the copolymerization behavior of vinyl ether (DVE-3) with an acrylate oligomer and unsaturated polyester, respectively. The structure of the resins is given below:

Epoxy acrylate (EA)

UPE

In figure 5 the conversion of acrylate (1407 cm^{-1}) and vinyl ether groups (1618 cm^{-1}) are plotted as a function of vinyl ether content. It is remarkable that only 10% addition of DVE-3 increases the conversion of the acrylate from about 55% to nearly 100%. The vinyl ether conversion decreases with increasing content. The formulation with 10% DVE-3 had the highest consumption of vinyl ether and no residual monomer could be detected. Thus, all divinyl ether must have been polymerized with at least one vinyl ether group. The polymerization rate (figure 6) of the pure radical reaction shows that the epoxy acrylates react faster than DVE-3 and the network formation is on the same time scale, whereas in combined radical/cationic photo initiated systems (super-imposed curve from [2])

a consecutive reaction of a fast acrylate polymerization (incorporation of some vinyl ether) and a following cationic polymerization leads to interpenetrating networks.

Conversion of Acrylate and Vinyl ether

UV curing with 3% I 184, 1800 mJ/cm^2

Figure 5: Conversion

Figure 6: Polymerization rate

In figure 5 the conversion of acrylate (1407 cm^{-1}) and vinyl ether groups (1618 cm^{-1}) are plotted as a function of vinyl ether content. It is remarkable that only 10% addition of DVE-3 increases the conversion of the acrylate from about 55% to nearly 100%. The vinyl ether conversion decreases with increasing content. The formulation with 10% DVE-3 had the highest consumption of vinyl ether and no residual monomer could be detected. Thus, all divinyl ether must have been polymerized with at least one vinyl ether group. The polymerization rate (figure 6) of the pure radical reaction shows that the epoxy acrylates react faster than DVE-3 and the network formation is on the same time scale, whereas in combined radical/cationic photo initiated systems (super-imposed curve from [2]) a consecutive reaction of a fast acrylate polymerization (incorporation of some vinyl ether) and a following cationic polymerization leads to interpenetrating networks.

The results of the mechanistic studies of the copolymerization of unsaturated polyesters with vinyl ethers clearly show that high conversions are obtained at equimolar concentrations of vinyl ether to fumarate. With lower content of vinyl ether the conversion increases, whereas it decreases when the molar concentration of DVE-3 exceeds the molar ratio of fumarate. Higher temperature generally increases conversion. The reactivity was similar for all three ratios of UPE and DVE-3, but fastest in the case of the highest DVE-3 content. In systems, where a radical photo initiator was combined with a cationic one, the conversion of the vinyl ether groups can be increased to completion (figure 8).

Conversion of UPE and vinyl ether
UV curing with different ratio of UPE to DVE-3
(4% Irgacure 184, 1800 mJ/cm^2)
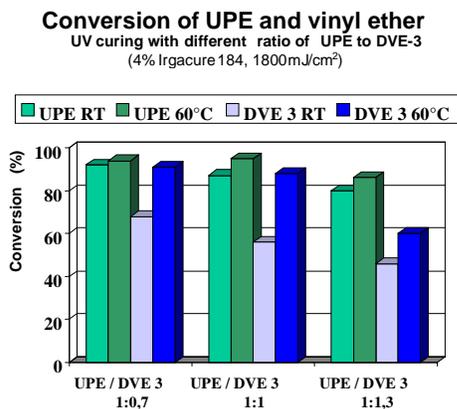
Figure 7: Conversion as function of UPE/VE ratio

Conversion of UPE and vinyl ether

UV curing with radical, radical/cationic and cationic photoinitiators
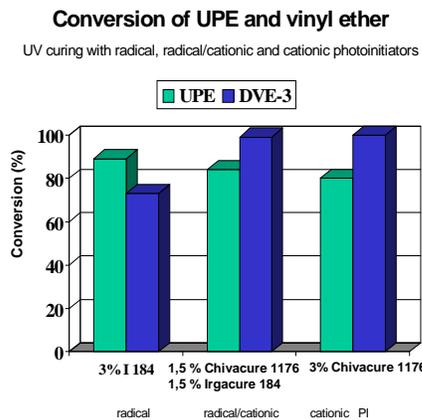
Figure 8: Radical and cationic initiation

Performance data

The performance of coatings containing vinyl ethers as reactive diluents, exemplified by mixtures of an epoxy acrylate resin (Laromer LR 8986) with DVE-3, is compared to the mixtures containing TPGDA.
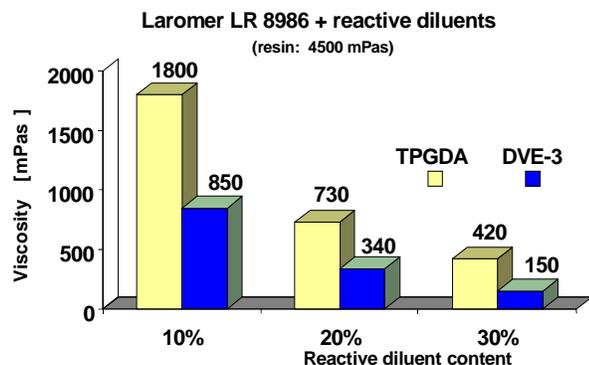
Figure 9:   **Viscosity reduction**
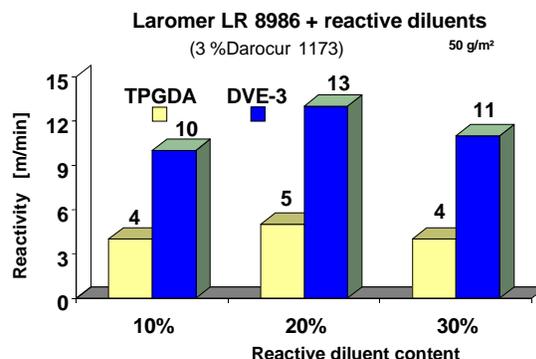
Figure 10:   **Reactivity**

The data in figure 9 demonstrate that the diluting property of DVE-3 is superior to TPGDA and already a content of 10% decreases the viscosity significantly below 1 Pas. The very strong cutting power of vinyl ether makes them attractive for application where low viscosity is required. Vinyl ethers are used in the formulation UV-ink jet inks which have viscosities in the range of 10 mPas. Unsaturated polyesters and urethane acrylates have high viscosities; even small amounts of vinyl ethers reduce the viscosity for application without diluting the performance of the binder. The viscosity reduction is of the difunctional DVE-3 is even better than mono-functional acrylates. The reactivity is more than doubled (figure 10), probably due to the lower viscosity and a less pronounced oxygen inhibition effect.
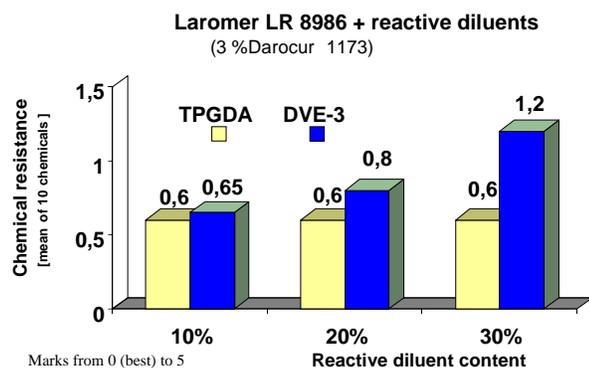
Figure 11:   **Chemical resistance**
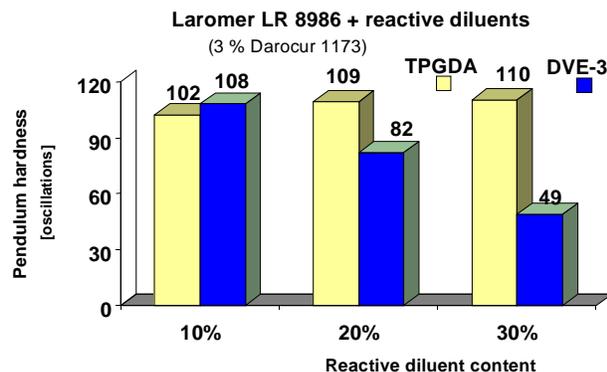
Figure 12:   **Pendulum hardness**

The chemical resistance (average mark of 10 household chemicals) of the DVE-3 formulations is comparable up to a content of around 10 % to the TPGDA mixtures (figure 11). At higher concentrations the chemical resistance of the DVE-3 formulations decreases. The pendulum hardness measurements with the 10% reactive diluent content gave nearly the same hardness, whereas the 20% and 30% addition of DVE-3 results in a significant decrease in hardness. In order to explain this behavior we assumed that unreacted vinyl ether might be present in the coating, acting as a softening agent. Thus, we evaluated the residual monomer content in extraction experiments of the cured coating (1-hour extraction with CH_2Cl_2).

Laromer LR 8986 + reactive diluents

(3 % Darocur 1173)   Extraction conditions:
CH$_2$Cl$_2$, 1h 40℃
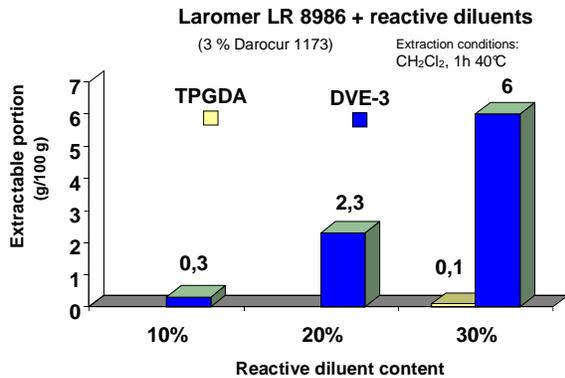
Figure 13:   Extraction of cured coating
Investigation of side reactions

The comparison of the extraction experiments of these coatings based on the epoxy acrylate (LR 8986) formulated with TPGDA and DVE-3, respectively, as reactive diluents showed indeed, that under the applied exposure conditions, TPGDA is nearly quantitatively incorporated into the network even up to a content of 30%, whereas the vinyl ether is nearly completely consumed only at a 10% addition level. About 10% of the initial vinyl ether content is extractable in the formulation containing 20% DVE-3 and up to 20% of the initial value in the 30% formulation. Thus, higher contents should be avoided in order to minimize residual vinyl ethers, which are furthermore susceptible to hydrolysis reactions.

Amine modified formulations

Taking all these considerations into account (no acidic formulation, 10 % diluent amount) we compared the performance data of formulations based on an amine modified polyether acrylate (Laromer PO 84F) diluted with 10 wt.% TPGDA and DVE-3, respectively (table 2 and figure 14: best value = 100%).

Performance comparison: PO 84F + 10% TPGDA vs. DVE-3

3% Darocure 1173, 1800 mJ/cm^2

Performance	TPGDA	DVE-3
Viscosity (mPas)	300	195
Pendulum hardness (s)	87	87
Pencil hardness	2H	2H
Scratch resistance (% gloss loss)	60	50
Erichsen cupping (mm)	3,3	3,2
Reactivity (m/min)	10	15

Performance comparison

UV curing of PO 84F with 10% TPGDA versus DVE 3 as diluent
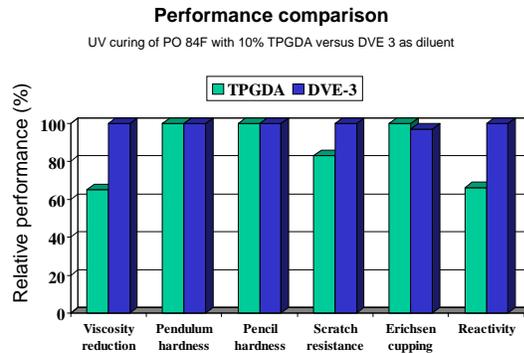
Table 2: Diluent comparison: 10% TPGDA vs. DVE-3   Figure 14: Relative performance comparison

As a reactive diluent DVE-3 gives at least similar good results compared to TPGDA with respect to the performance data. Furthermore, DVE-3 provides better diluting properties, shows improved scratch resistance due to a lower sensitivity towards oxygen inhibition and allows the formulation of labeling free products.

Vinyl amides monomers

Other classes of vinyl – monomers are vinyl amides. The five-member ring N-Vinyl pyrrolidone was used in many UV-curable applications but is banned now due to toxicity reasons. The six member ring N-vinyl valerolactam and seven member-ring N-vinyl caprolactam are used in coatings and ink application. NVC is used where high reactivity and good adhesion to plastic is required. Screen printing inks frequently include N-vinyl-caprolactam, especially when the inks are to be printed on to polymeric substrates. Indeed, N-vinyl-2-caprolactam is a key component of many ultraviolet light curable screen and digital inks due to its inherent properties, for example acting as a diluent monomer for viscous oligomers in such inks, and as a reactive monomer which cures with the ink. In practice, N-vinyl-caprolactam has been found to give a better reduction in ink viscosity than many acrylate monomers, for example phenoxyethyl acrylate, and tri-propylene glycol diacrylate. In addition to acting as a curable monomer and a viscosity reducing agent, the polarity of N-vinyl-caprolactam has been used to enhance

the wetting characteristics of inks when they are to be applied to plastics substrates, and its solvent power has contributed to the adhesion of these inks to such substrates. Screen printable, radiation curable inks frequently include components with acrylate functionality because the double bond of the acrylate group is highly reactive in free radically initiated polymerization reactions. Although the vinyl functionality of N-vinyl-caprolactam also reactive in free radically initiated polymerization reactions, it is generally slower to react than are acrylate groups. Typically, radiation curable inks contain from 5 to 35 percent by weight of N-vinyl-caprolactam [5], such amounts usually giving the inks commercially acceptable adhesion, viscosity, wetting and curing/drying times. Those screen inks may contain up to 50% of titanium-dioxide as pigment. N-Vinyl caprolactam is also used in high performance UV-coatings and UV-adhesives. Those formulations are often based on high viscous polyurethane acrylates. N-Vinyl-caprolactam reduces the viscosity of the formulation and improves the adhesion of the cured coating. Optical fiber coatings and scratch resistant optical films are often coated with formulations based on N-vinylcaprolactam[6].

Vinyl ester monomers

The synthesis of mono vinyl esters is a well-known process. Vinyl esters can be obtained from carboxylic acids and acetylene or by transvinylation with vinyl acetate[1]. However, these processes are limited to monocarboxylic acids. A new process has been developed to produce divinylic esters on an industrial scale. This process is suitable to produce divinyl esters of dicarboxylic acids independently on the chemical structure of the dibasic acid. Thus, a large variety of divinyl esters are now accessible (fig. 15). Depending on the chemical structure of the dicarboxylic acid, a wide range of physical properties are available. For example, the divinyl esters are either solids (divinyl adipate, divinyl terephthalate) or liquids (divinyl cyclohexyl dicarboxylate) at room temperature. The use of esters as reactive diluents in radiation curable coatings enables a formulator to modify and adapt coatings properties to meet specific application requirements.

Vinyl ester		Boiling point	Melting point
Divinyl adipate AVES		> 230 ℃	26 ℃
Divinyl terephthalate TVES		> 230 ℃	85 ℃
Divinyl cyclohexyl dicarboxylate CHVES		> 230 ℃	8 ℃
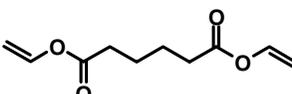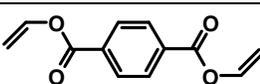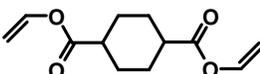
Figure 15: Vinyl ester monomers

Materials and Equipment
Divinyl adipate was selected to investigate the properties of divinyl esters in radiation curable coating formulations. The properties of AVES have been measured in comparison to hexanediol diacrylate HDDA and tripropyleneglycol diacrylate TPGDA, both are well-established acrylic reactive diluents for acrylate resins. Table 3 summarizes the physical properties obtained with these reactive diluents.

	Divinyl adipate AVES	Tripropylenegylcol diacrylate, TPGDA	Hexanediol diacrylate, HDDA
Boiling point	79-81 ℃ (1 mbar)	103 ℃ (0,3 mbar)	107 ℃ (0,3 mba r)
Melting point	26 ℃	< - 60 ℃	8 ℃
Viscosity	2,5 mPas (30 ℃)	15 mPas (25 ℃)	6 mPas (25 ℃)

Table 3: Comparison of reactive diluents

Epoxy acrylate EA (Bisphenol-A-digylcidyldiacrylate) and a trifunctional urethane acrylate were used as acrylic resins. Irgacure®500 from Ciba (1-Hydroxycyclohexylphenylketone/Benzophenone 1:1) was used as photoinitiator. The UV exposure equipment from IST contains two Hg quartz tubes with a total power of 120 W/cm². The energy applied was determined by the speed of a conveyor belt moving the samples through the irradiating beam of the lamps. The real time infrared (FT-IR) spectroscopy measurements were done with a Bruker IFS-66 with rapid scan.

Study of photoinduced radical copolymerization
The photopolymerization behavior of AVES in formulations with EA and urethane acrylate was determined by real-time FT-IR spectroscopy. Figure 16 shows a typical absorption spectrum which is used to calculate the conversion of vinyl functions from the intensity of the absorption band of vinyl esters (875 cm^{-1}) and acrylates (810 cm$^{-1)}$).
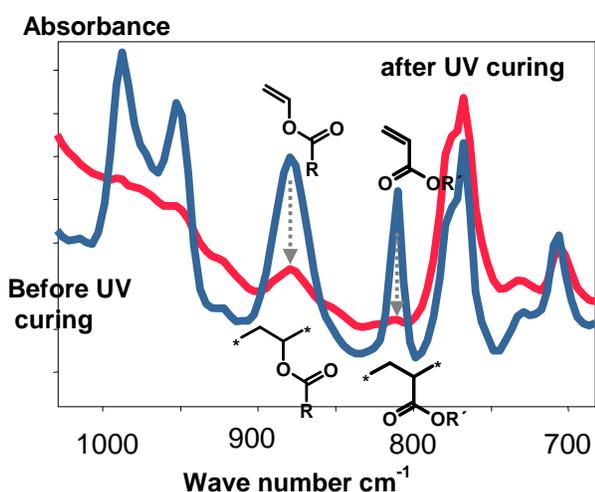
Figure 16: IR-FTIR spectroscopy of AVES/urethane acrylate formulation 30/70
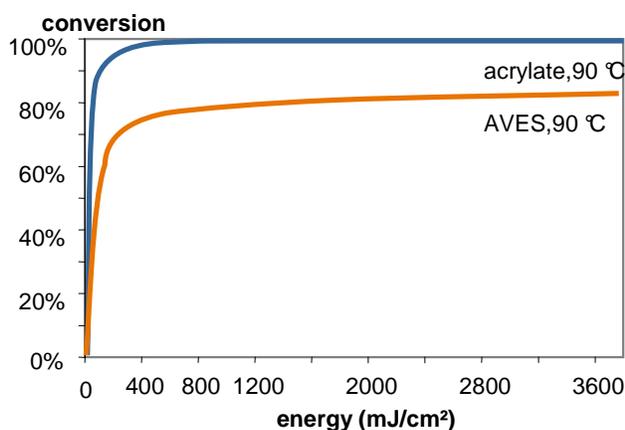
Figure 17: Conversion of vinyl functions of an AVES urethane acrylate formulation 30/70

The conversion of the acrylate and vinyl ester functional groups can be followed separately as a function of the irradiation energy. Figure 17 shows an example of the conversion of AVES and urethane acrylates which can achieve very high rates at a temperature of 90 ℃.

The results of the real-time-FTIR spectroscopy show that the AVES copolymerizes well with acrylates to very high conversion. The conversion of the acrylate functions is not influenced by the presence of vinyl esters.

Performance data
AVES was investigated as reactive diluent in formulations with EA and an urethane acrylate. Both resins are highly viscous without any reactive diluent and hence not optimized for use in coatings applications. Therefore, it is necessary to reduce the viscosity of the resins to provide formulations with a target viscosity of lower than 5 mPas. The diluting ability of AVES is compared with HDDA and TPGDA and are shown in figure 18.
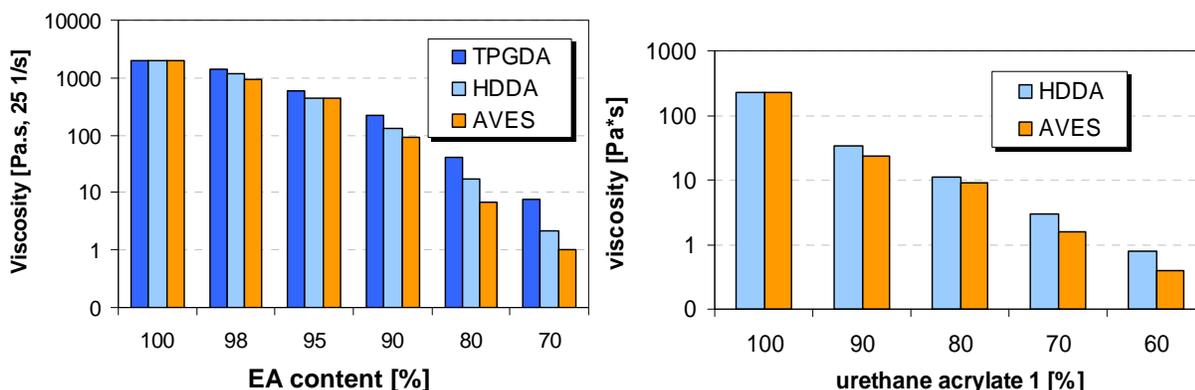
Figure 18: Viscosity reduction

The viscosity data demonstrate that AVES is an excellent diluent and in this instance 30 weight-% of AVES reduces the viscosity of acrylate resins below 1 mPas. This diluting effect is independently of the chemical type of the resin.

Beside the reduction of viscosity, a reactive diluent can also influence the physical properties of the cured coating. As an example, we determined the coatings properties of the urethane acrylate diluted with 30 weight-% AVES in comparison to a HDDA-based formulation according to a typical evaluation procedure. The data are summarized in table 4.

Reactive diluent	AVES	HDDA (ref.)
Pendulum hardness (s)	202	174
Erichsen cupping (mm)	5,7	4,7
Elongation at break (%)	3	3
Tensile strength (N/mm²)	57	47
E-modulus (N/mm²)	1400	1650
Glass transition temperature (°C)	64	64

Table 4: Coatings properties (UV curing: 4 % Irgacure 500, 1350 mJ/cm^2, 100 °C)

The use of AVES results in an increased surface hardness and improves the elasticity of the cured coating. All other physical coatings properties of the AVES-based urethane formulation are comparable to the HDDA formulation.

Summary and conclusions

It has been shown that vinyl ethers are very effective reactive diluents in radiation curable coatings. Due to their low toxicity they can be used in labeling free formulations like radical curing acrylate or unsaturated polyester systems. However, due to their reluctance to homopolymerize radically vinyl ether contents should be chosen such that they copolymerize completely. In unsaturated polyester systems equimolar ratios of vinyl ether can be incorporated into the fumaric groups. In our investigated acrylate formulations 10% DVE-3 has been completely converted. With optimized vinyl ether contents improved performance can be achieved. Vinyl esters are a new and very effective class of reactive diluents for radiation curable coatings. They can be used up to 30 % in acrylate formulations and provide better diluting properties than existing functional acrylates while maintaining the physical properties of the cured coating.

Acknowledgement

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