

Novel Routes to Urethane Acrylates

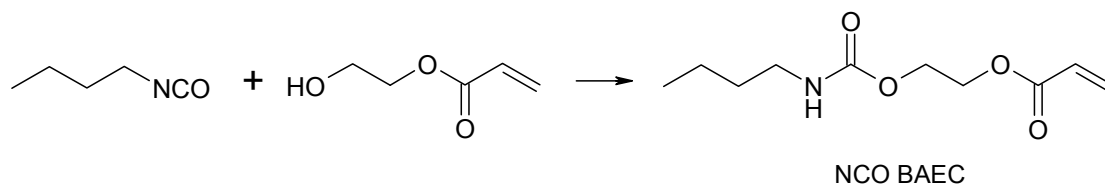
Vincent W. Stone, Peter Burie, Hugues Van den Bergen and Jurgen Van Hohen
Surface Specialties UCB, B-1620 Drogenbos, Belgium

Introduction

Mono and multifunctional urethane acrylates are widely used in radiation curable varnishes, inks and adhesives since they are known to be able to enhance numerous key performances like adhesion, toughness, flexibility, abrasion resistance, pigment wetting or cure speed¹. Monofunctional urethane acrylates are acknowledged as being able to bring unique properties to radiation curable pressure sensitive² or laminating³ adhesives.

The use of expensive and often highly toxic isocyanates in current industrial processes makes however the urethane acrylates the most expensive acrylated component of the formulations. In current processes, mono- and multifunctional isocyanates are reacted with hydroxyfunctional acrylate monomers like hydroxyethyl acrylate, hydroxypropyl acrylate or pentaerythritol triacrylate. To enlarge the range of accessible structures, multifunctional urethane acrylates can also be prepared by replacing a portion of the hydroxyfunctional acrylate monomers by other structures having OH groups.⁴

Besides being a driving factor for raw material costs, isocyanates may require being stored, handled and processed at large scale in secured industrial equipments with special safety procedures, which may have a strong impact on transformation costs. This is for example the case when n-butyl isocyanate is reacted with hydroxyethyl acrylate (HEA) to make n-butyl acryloyloxy ethyl carbamate (NCO BAEC, Scheme 1), a commercially-available urethane monoacrylate described for the first time 35 years ago.⁵



Scheme 1

Being a highly poisonous liquid (LC50 (inhalation, rat, 1h exposure)=105 ppm) with high risk of explosion (flash point=19°C), n-butyl isocyanate should indeed be stored and processed in a closed system.

The purpose of this paper is to describe new commercially-viable processes⁶ to make mono- and multifunctional “non-NCO” urethane acrylates using raw materials cheaper than isocyanates and only requiring standard industrial equipment and safety procedures to be processed at large scale. The process parameters have been optimized to make “non-NCO” versions of commercially-available products with at least as good quality and performances in formulations as their NCO counterparts, and new urethane acrylates impossible to make with isocyanates.⁵

Experimental

Preparation of the non-NCO urethane acrylates (transesterification)

Preparation of the hydroxycarbamate

Amine (1.05 eq) and cyclic carbonate (1 eq) were charged in a double-wall glass reactor sparged with nitrogen. A vacuum-jacketed distillation column was used with a liquid semi-automatic splitter using a solenoid-activated PTFE valve and timer to control the reflux and takeoff from the distillation column. The reaction mixture was left at 70°C max. to avoid side reactions such as decarboxylation of the cyclic carbonate or the hydroxyalkylcarbamate. Titration of the residual free amine indicated when the reaction was complete. The reaction being too exothermic when a primary amine was used, the cyclic carbonate had then to be slowly added to the amine. When the amine was volatile enough, the residual free amine was stripped.

Transesterification reactions

Transesterification of the hydroxyalkylcarbamate was carried out adding the alkyl acrylate in large excess (equivalent ratio alkyl acrylate to hydroxyalkylcarbamate between 4.5 and 7.6) and 2, 6-di-*tert*-butyl-4-methylphenol and phenothiazine as stabilizers. At this stage, air was injected throughout the reaction mixture. Before adding a catalyst prone to hydrolysis, about 10% of extra alkyl acrylate was added in the reactor and this extra amount was distilled over at the boiling point of the water/alkylacrylate azeotrope in order to dry the reaction mixture. After addition of the catalyst (1-5%w/w on end product), the reaction mixture was maintained at a given temperature by applying a slight vacuum, if needed. The alcohol generated was taken off overhead as an alcohol/alkyl acrylate azeotrope, such a removal being followed by a temperature sensor located at the column's head. The azeotrope was removed as soon as the temperature at the top of the column decreased down to the temperature corresponding to a near-to-theoretical azeotrope composition. When an organozirconate or an organotitanate was used as catalyst, the latter was removed from the reaction mixture by washings or precipitation. Typical residual Zr or Ti levels were 10 ppm, as measured by Atomic Absorption Spectroscopy. The alkyl acrylate excess was removed by concentration/stripping under vacuum (100 mmHg), injecting air to prevent polymerization.

Preparation of the non-NCO urethane acrylates (direct esterification)

When the acrylation of the hydroxyalkylcarbamate was performed through direct esterification, an azeotropic distillation column having a Dean-Stark separator at its overhead was used. Acrylic acid, toluene (37% by weight of the reacting mixture), methyl ether hydroquinone, H₃PO₂ and p-toluene sulfonic acid (PTSA) were added to the hydroxyalkylcarbamate. An air sparge was injected to prevent gelation. The mixture was slowly heated, reducing the pressure in the reaction vessel so as allowing a reflux of the toluene/water azeotrope at the lowest possible temperature. The reaction mixture was left at this temperature until no more water was collected in the Dean Stark. The mixture was then neutralized at 60°C by the addition of a 50% solution of NaOH in water. This mixture was washed three times with water containing 20 % NaCl, dried via azeotropic distillation with air sparge to remove all the water and finally filtered. The toluene was distilled and stripped under

vacuum while sparging air.

Preparation of polypropylene glycol bis cyclic carbonate

Polypropylene glycol diglycidyl ether, tetrabutylammonium bromide (2%w/w) and methylhydroquinone were added in a double-wall glass pressure vessel designed to withstand 12 bar. The reactor was fitted with a thermometer, an agitator, a gas inlet tube, a pressure gauge, a rupture disc, a baffle and a bottom valve. The air inside the reactor was replaced by carbon dioxide and the pressure was increased to an absolute pressure of 5 bar. The mixture was heated to 95°C until no more carbon dioxide was consumed. ¹H NMR indicated complete transformation of the oxirane into cyclic carbonate groups. Potentiometric titration of the cyclocarbonate groups of the final product lead to a cyclic carbonate equivalent weight of 382 g/eq (theory: 365 g/eq).

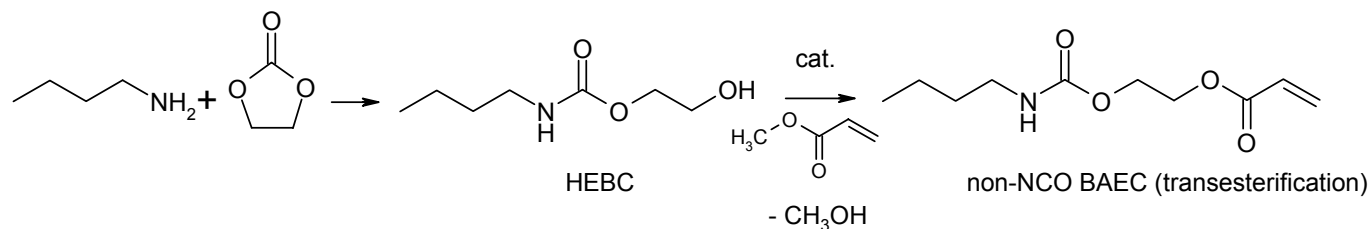
Product Characterization

Product compositions were determined by ¹H-COSY NMR (300 MHz, Brücker, CDCl₃ as solvent). Side products with low molecular weight were quantified by GC. HEA contents were measured by HPLC. Free isocyanate contents were determined by titration.

Results and Discussion

Monofunctional non-NCO urethane acrylates

Monofunctional non-NCO urethane acrylates can be prepared by a two-step process. First, a monofunctional primary or secondary amine is reacted with a monofunctional cyclic carbonate. Second, the hydroxyalkylcarbamate is acrylated by a transesterification reaction with an alkyl acrylate. Scheme 2 illustrates this approach using N-butyl amine and ethylene carbonate to generate 2-hydroxyethyl butyl carbamate (HEBC) and subsequent use of methyl acrylate to achieve the final product (BAEC).

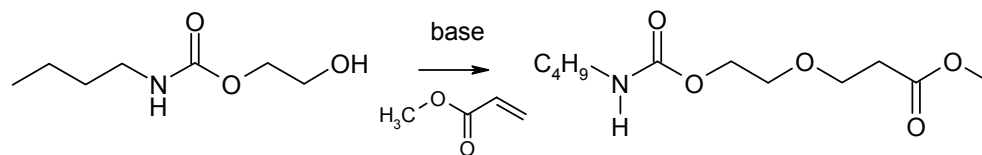


The NCO version being available commercially, BAEC was chosen to illustrate the critical process parameters to obtain a non-NCO product with at least equal quality.

Choice of the transesterification catalyst

The choice for commercially-available transesterification catalysts being very large⁷, a screening study has been carried out to determine the catalysts showing the best compromise between chemoselectivity and activity.

- **Chemioselectivity.** Base activators like Li_2O , LiOH , calcium acetylacetonate or sodium methanolate are often successfully used for transesterification reactions. In this case however, these catalysts were found to promote almost exclusively the Michael addition of the hydroxyalkylcarbamate on the alkyl acrylate (Scheme 3)



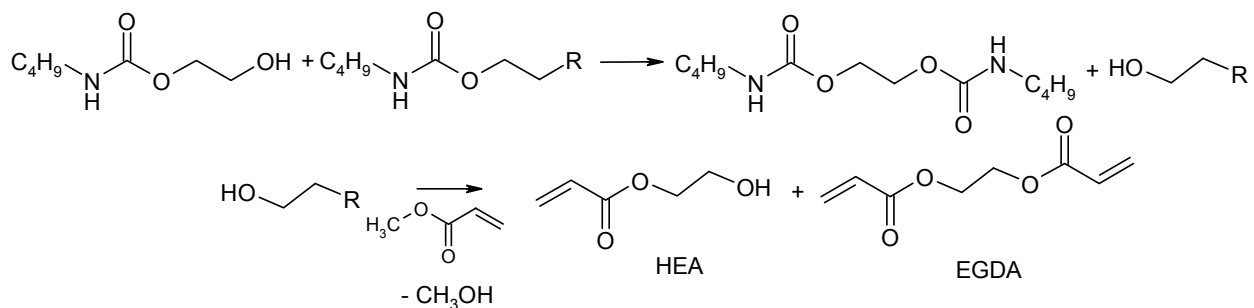
Scheme 3

Lewis acids like butyltin tris(2-ethylhexanoate), dibutyltin dilaurate, titanium tetraisopropoxide ($\text{Ti}(\text{OPr})_4$) or zirconium acetylacetonate (ZrAcAc) all showed good to very good chemioselectivity towards the acrylation reaction.

- **Activity.** Among the Lewis acids, titanium and zirconium tetraalkoxides have been found to be the most active. A further advantage of these catalysts being that they are easily removed from the reaction mixture at the end of the reaction, ensuring a good chemical stability of the end product.

Influence of reaction temperature and catalyst concentration on side products generation

Main side reactions observed during the transesterification of HEBC catalyzed with Lewis-acids were transurethanization reactions (Scheme 4) between the hydroxyalkylcarbamate and itself ($\text{R} = \text{OH}$) or with the monofunctional urethane acrylate ($\text{R} = \text{OC}(\text{O})\text{CH}=\text{CH}_2$). Along with a biscarbamate product, HEA and ethylene glycol diacrylate (EGDA) are also generated by these side reactions. The latter should ideally be controlled and minimized since critical either from a regulatory (free HEA amount determines European labeling), or from an application (EGDA will act as an unwanted cross-linker in UV-adhesives) standpoint.



Scheme 4

These side reactions can be minimized by optimizing the catalyst concentration and reaction temperature. Figure 1 shows the weight percentages (excluding methyl acrylate and the catalyst) of BAEC, HEA and EGDA in the reaction mixture for different reaction times when TPT was used as catalyst. The higher the reaction temperature and catalyst concentration, the

higher the conversion rate in BAEC but the faster the by-product generation. Maintaining a temperature of 70°C and using a concentration of 3.8%w/w on end product allowed a highly pure (96.5%w/w) product in a reasonable reaction time (11h) with no detectable HEA and very low EGDA level.

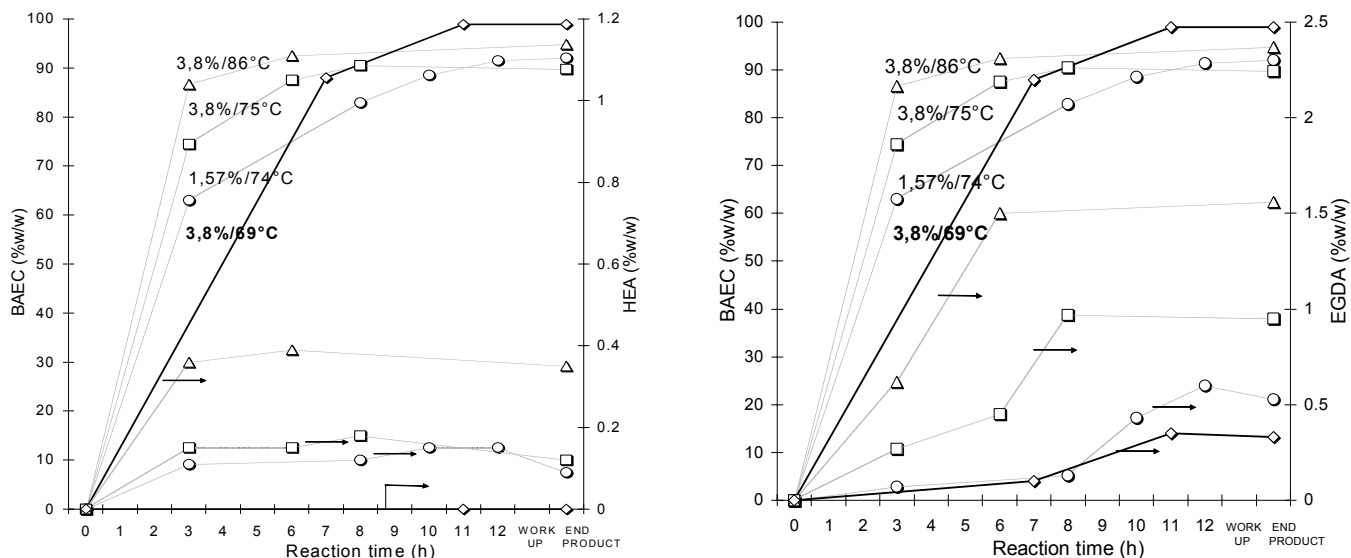


Figure 1. Side products generation during the transesterification reaction

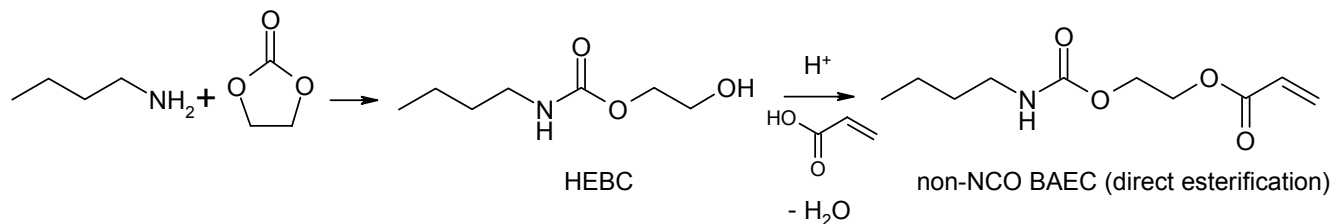
Table 1 indicates that under these conditions, main product characteristics are very similar to the ones obtained through the traditional NCO process.

Table 1. BAEC: end product properties obtained through different processes

Product	Höppler Viscosity (25°C, mPa.s)	Color (Apha)	Purity (%w/w)	Yield (%w/w)	HEBC (%w/w)	EGDA (%w/w)	HEA (%w/w)	NCO (%)
NCO BAEC	25	15	94.4	93	-	0.3	0.2	0.1
non-NCO BAEC (transesterification)	27	36	96.5	92	2.1	0.3	<0.01	<0.02
non-NCO BAEC (direct esterification)	45	25	75	77	20.2	2.3	0.8	<0.02

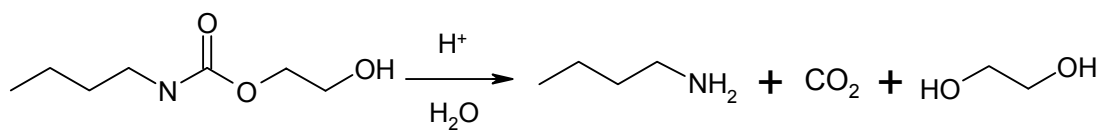
Transesterification vs. direct esterification

Attempts have already been made in the past to make monofunctional urethane acrylates without isocyanates. Cowherd, III *et al.*⁸ claimed that the hydroxyalkylcarbmates could be acrylated with a commercially-acceptable yield through a direct esterification with acrylic acid in presence of a strong Brönstedt acid as catalyst, as shown for BAEC in Scheme 5.



Scheme 5

Provided the reaction temperature was maintained below 75°C, the acidic-catalyzed hydrolysis of the urethane linkages from the hydroxyalkylcarbamates (shown for HEBC in Scheme 6) was claimed to be minimized. This side reaction leads to a deactivation of the acidic catalyst (neutralization by the back-generated amine) and generation of HEA and EGDA (acrylation of the generated ethylene glycol).



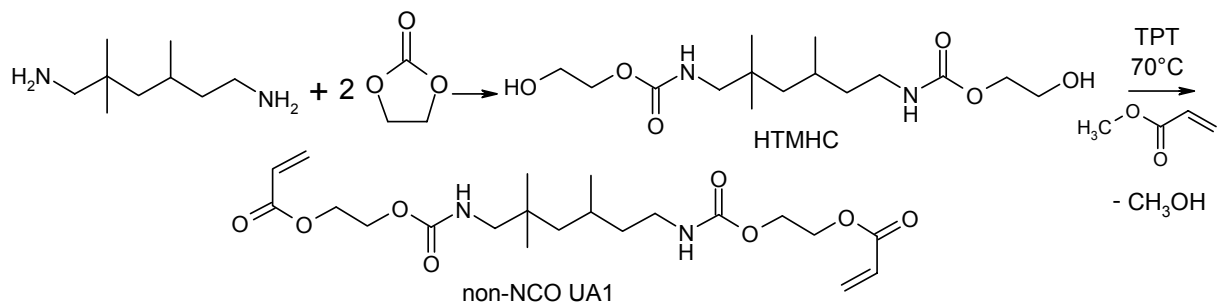
Scheme 6

Despite large acrylic acid excesses (equivalent ratios acrylic acid to hydroxyalkylcarbamate over 1.15) and very high catalyst concentrations (over 0.1 mol per mol of hydroxyalkylcarbamate), reported purities however remain in the 80% range, i.e. significantly below suppliers' specification of NCO monofunctional urethane acrylates (94% for BAEC). Reported yields were around 70%, i.e. much lower than typical yields achievable for acrylation reactions by direct esterification. No information was disclosed on side products.

Table 1 gathers the best results obtained from several attempts to make BAEC through direct esterification (Scheme 5). Acceptable purity (75%w/w) could only be achieved at 70°C using a large acrylic acid excess (equivalent ratios acrylic acid to hydroxyalkylcarbamate of 1.4) and very high catalyst concentration (0.18 mol per mol of hydroxyalkylcarbamate). Yield was much lower than what can be achieved through transesterification (77% vs. 92%). Much higher EGDA and HEA contents also were found. Together with the high catalyst amounts needed, this indicates that, even below 75°C, significant hydrolysis (Scheme 5) occurs. This shows that the milder conditions allowed by a transesterification reaction are necessary to lead to a commercially viable process and a product quality comparable to the NCO route.

Multifunctional non-NCO urethane acrylates

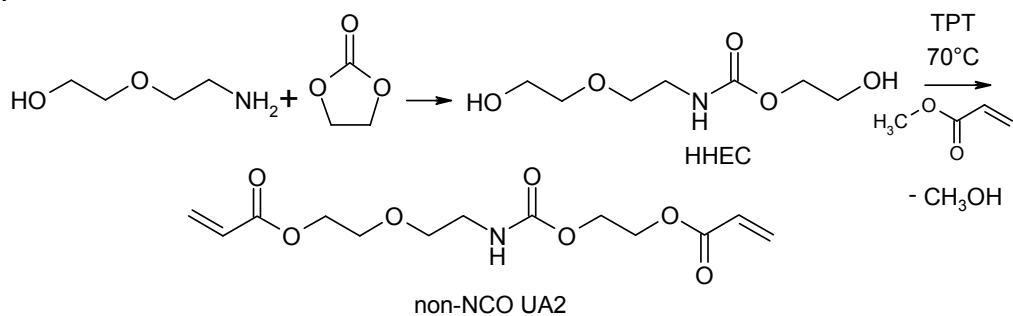
Multifunctional urethane acrylates can be prepared by two- or three-step processes. Scheme 7 illustrates a two-step non-NCO process that can lead to commercially-available NCO products. A multifunctional amine (e.g. 2,2,4 trimethylhexamethylene diamine) and a monofunctional cyclic carbonate (e.g. ethylene carbonate) are reacted to give a multifunctional hydroxyalkylcarbamate (e.g. 2-hydroxyethyl 6-[[2-(2-hydroxyethoxy)carbonyl]amino]-2,2,4-trimethylhexyl carbamate (HTMHC)) that is acrylated in a second step by transesterification with an alkyl acrylate (e.g. methyl acrylate).



Scheme 7

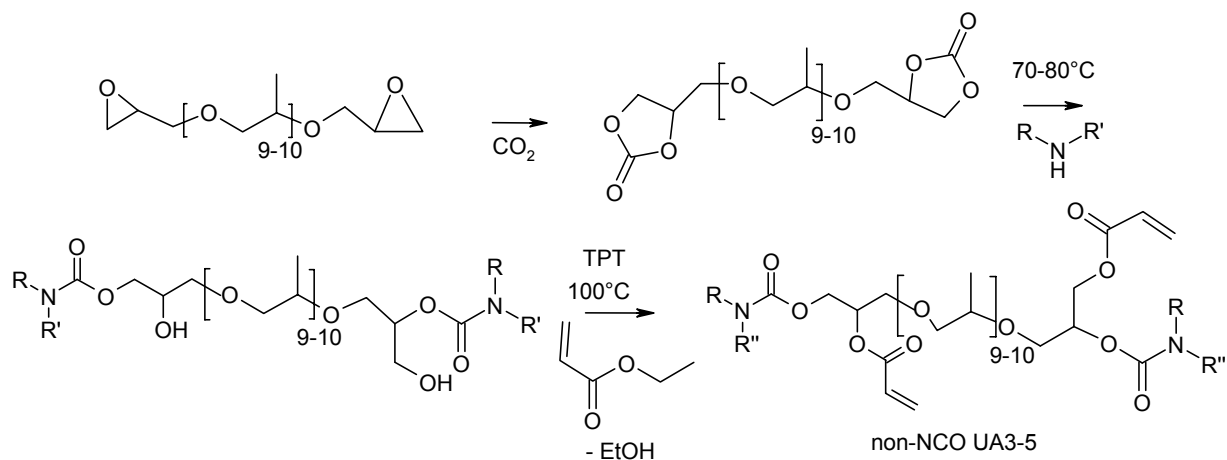
As shown in Table 2, non-NCO UA1 could be made through Scheme 6 with very similar purity and viscosity comparable to the commercially available NCO version (NCO UA1) made from 2,2,4 trimethylhexamethylene diisocyanate and HEA.

Schemes 8 and 9 illustrate processes leading to structures unachievable with isocyanates. In the first two-step process (Scheme 8), a monofunctional alkanolamine (e.g. 2-(2-aminoethoxyethanol)) and a monofunctional cyclic carbonate (e.g. ethylene carbonate) are reacted to lead to a (e.g. 2-hydroxyethyl 2-(2-hydroxyethoxy)ethyl carbamate (HHEC)) that is subsequently acrylated by a transesterification reaction with an alkyl acrylate (e.g. methyl acrylate).



Scheme 8

In the second three-step process (Scheme 9), the glycidylether groups of a multifunctional epoxide (e.g. polypropylene oxide diglycidylether) are firstly carbonated with CO_2 . The so generated multifunctional carbonate (e.g. polypropylene glycol bis cyclic carbonate) is then reacted with a monofunctional primary (e.g. n-butylamine, R/R'= butyl/H) or secondary (e.g. n-methylbutylamine, R/R'= butyl/methyl) amine or a monofunctional alkanolamine (e.g. 2-(2-aminoethoxyethanol), R/R'=2-(2-hydroxyethoxy)ethyl/H). The generated hydroxyalkylcarbamate is eventually acrylated by a transesterification reaction with an alkyl acrylate (e.g. ethyl acrylate).



Scheme 9

Being intrinsically too high viscous to be easily manipulated, most of the commercially-available urethane acrylates contain significant amounts of diluting monomers without urethane groups. The latter are either added at the end of the reaction and/or generated in-situ during their production. Most of the time, these urethane acrylates should be further diluted to be applied on a substrate, reducing again the possibility to maximize the beneficial effects of these structures. Table 2 show that schemes 8 and 9 can lead to urethane acrylates with *intrinsically* low viscosity, which should allow increasing freedom for formulation. Non-NCO UA2 is a difunctional urethane acrylate of high purity with a viscosity low enough to be used as a diluting monomer. When starting from multifunctional cyclic carbonates (Scheme 9), di- (non-NCO UA3) and tetra- (non-NCO UA5) functional urethane acrylates with surprisingly low viscosity can be made. Using a secondary amine instead of a primary one for making the hydroxyalkylcarbamate can further lower the viscosity of the acrylate (non-NCO UA4).

Table 2. Multifunctional non-NCO urethane acrylates: end product properties.

Product	Theoretical MW (D)	Acrylate Functionality	Höppler viscosity (25°C, mPa.s)	Purity (% mol)
Non-NCO UA1	442	2	7100	93
NCO UA1	442	2	7010	92
Non-NCO UA2	301	2	89	95
Non-NCO UA3	984	2	1160	95
Non-NCO UA4	1016	2	495	91
Non-NCO UA5	1156	4	3370	92

Performances in radiation-cured varnishes and inks

Non-NCO vs. NCO products

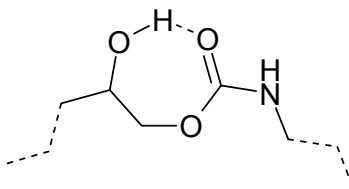
No difference in cure speed, yellowing, flexibility, transparency, gloss, hardness, adhesion could be observed when NCO BAEC was replaced by non-NCO BAEC (transesterification) as diluting monomer in an inkjet OPV formulation for PET/PVC and ABS cards. Doing the same in a blue screen ink for plastics did not lead to any significant difference

on cure speed, adhesion and flexibility on PVC.

Non-NCO UA1 and NCO UA1 (70 parts) were compared in formulations with Irgacure® 500 (4 parts) and HDDA or Ebecryl® 160 or NCO BAEC (30 parts). No significant difference on cure speed, adhesion, chemical and scratch resistances could be observed on 10 µm-coatings cured with a 80 W/cm/non focalized H bulb on Chamtenero 60 paper.

New non-NCO structures' performances

Non-NCO UA5 (70 parts) has been tested in a formulation with HDDA (30 parts) and Irgacure® 500 (4 parts). 10 µm-coatings of this very low viscous (Brookfield viscosity=260 mPa.s) formulation could be cured dry to touch, talc dry and ADR>50 at 35, 15 and 15 m/min, respectively. No visible change could be detected after exposing the surface of a 2x50 ADR cured coating to distilled water, 48% ethanol and paraffin oil. Strong marks and surface damages could be seen with 10% ammonia. Leaving (secondary) hydroxyl groups β to the urethane bonds (Scheme 10) intact by acrylating only partially the starting hydroxyalkylcarbamate could significantly improve the resistance to 10% ammonia. This higher hydrolysis resistance has been explained in non-NCO polyurethanes by the formation of 7-membered rings stabilized by intramolecular hydrogen bonds.⁹



Scheme 10

Conclusions

Commercially-viable processes have been developed to make urethane acrylates without isocyanates. Commercially-available structures made with these alternative processes have been shown to be able to be used as drop-ins in existing formulations optimized for various applications. These new processes can generate new urethane acrylates impossible to make with isocyanates showing interesting intrinsic properties like a low viscosity. Further tests are ongoing to identify further applications where these new structures could bring a decisive advantage over existing products.

Acknowledgements

The authors wish to thank Lieven Depuydt for his help in the synthesis work, Marc Heylen and Thierry Randoux for the application-oriented tests, Johan Van den Hauwe and Perrine Cahen for the analytical work.

References

- ¹ C. Lowe, G. Webster, S. Kessel, I. McDonald, G. Rayner (Eds.), "Chemistry and Technology of UV & EB Formulations for Coatings, Inks & Paints", Vol. 4, Formulation (1997), SITA Technology, London.
- ² e.g. WO9,425,537 (3M).
- ³ e.g. US4,600,640 (GE).
- ⁴ G. Webster (Ed.), "Chemistry and Technology of UV & EB Formulations for Coatings, Inks & Paints", Vol. 2, Prepolymers and Reactive Diluents (1997), SITA Technology, London, p. 79-131.
- ⁵ US3,674,838 (Ashland).
- ⁶ Patent pending.
- ⁷ J. Otera, "Esterification: Methods, Reactions and Applications", (2003), Wiley-VCH, Weinheim, p. 45-91.
- ⁸ US 4,126,747 (Ashland).
- ⁹ O. Figovski, J. of Mendeleev Chemical Society, 1988, **33**(3), 31.