

UV-cured and elastomeric coatings - a contradiction?

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Summary: In common perception, UV-cured coatings are associated with properties like high hardness and abrasion resistance. They are often used in applications such as flooring that require only a limited amount of flexibility. Urethane acrylate chemistry offers the freedom to design coating raw materials with elastomeric properties. To date, most commercial urethane acrylates have tensile elongation values below 50 % and only very few products were reported with values of approx. 100 %. We investigated the syntheses of elastomeric urethane acrylates. Samples with elongation at break values of 500 % and more were produced. Their physical properties, aspects of formulation and applications will be discussed.

Introduction:

Coating systems based on unsaturated acrylates and cured by exposure to ultraviolet light have become widespread in industrial coatings technology. The cured coatings generally exhibit very high crosslinking density and thus yield very hard coatings with little flexibility. However, polyurethane chemistry does permit highly flexible and even elastomeric coating systems, such as those used in coatings for textiles and leather. Polyurethane chemistry has also been used in combination with radiation-curing acrylates, and there are numerous urethane acrylates commercially available for industrial coating applications. One primary application is sealers for parquet floors which, in addition to high chemical and mechanical resistance, also require toughness with flexibility to ensure high abrasion resistance. Special urethane acrylates also exhibit good weather stability and thus are thought to have the greatest potential as topcoats with improved scratch resistance for automotive applications.

Relatively little attention has been paid to the possibilities presented by elastomeric urethane acrylates. Elastomeric products with tensile elongation values between 50 and 100 % are rare among commercial products. Patent literature includes only a handful of scattered references to products with even greater elasticity. We are unaware of any systematic investigation of the relationships between structure and properties. We investigated the extent to which radiation curing of urethane acrylates can increase coating elasticity and what factors of the polymer structure are responsible for the elastomeric properties.

Experimental

The basic relationships for the "design" of urethane acrylates have been identified^[1]. The factors double-bond density, acrylate functionality and molecular weight, in particular, influence the viscosity and UV reactivity of the binder, as well as hardness, elastomeric and resistance properties of the crosslinked coating. Also of significance are the type and functionality of the low molecular weight acrylate reactive thinner. Figure 1 shows the parameters that should result in high elasticity during the formulation of urethane acrylates, as well as the theoretical

weaknesses that can be expected. When binder viscosity is high, low UV reactivity and low resistance levels should be assessed critically.

<u>Parameter:</u>	<u>Possible negative consequences:</u>
- Low resin functionality	- low reactivity, low resistance
- Low double-bond density	- low reactivity, low resistance
- High molecular weight	- high viscosity
- Monofunctional reactive thinner	- low reactivity, low resistance

Figure 1. Guidelines for the design of elastomeric urethane acrylates

A system comprising a linear polymeric diol, monomeric diisocyanates and monomeric hydroxyalkyl acrylates, which are reacted in low-functionality acrylate reactive thinners to form the binder, was chosen for this study. The influence of photoinitiators, conventional coating additives and extenders was not investigated.

Because of the large number of possible synthetic combinations, statistical design of experiments was coupled with the use of parallel reactors so that, in an initial screening phase, a large number of products could be formulated in small quantities, dissolved in inert solvents and subjected to simplified application-related pretests so that the relevant ranges of a multidimensional parameter space could be identified. These pretests emphasized UV reactivity, viscosity and elastomeric properties. In a second phase, selected laboratory formulations were prepared in quantities up to 1 kg and studied in greater detail, including the recording of tensile elongation curves and the performance of dynamic-mechanical analyses.

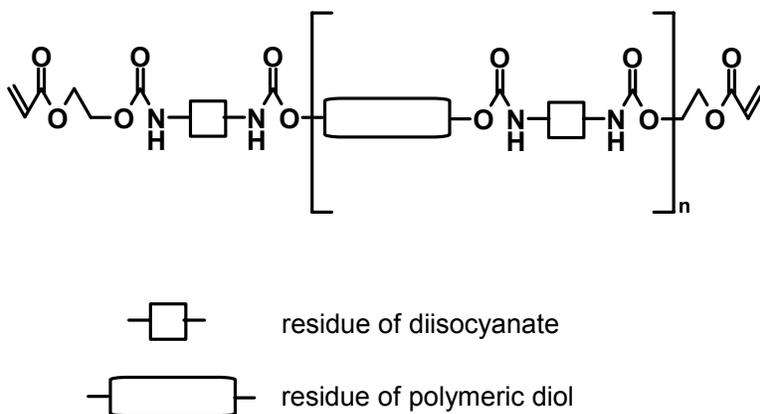


Figure 2. Scheme of linear urethane acrylates

Results and discussion

The first selected series of experiments investigated the influence of the diisocyanate components. Four of the diisocyanates most commonly used in coatings technology –

hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 4,4'-Bis-isocyanatocyclohexyl methane (H₁₂MDI) and toluene diisocyanate (TDI) - were each reacted in a monofunctional reactive thinner with an aliphatic linear polyester diol (M_w = 2,200) and a hydroxyalkyl acrylate. The molecular weights of the products, which were thinned to 80 % in reactive thinner, were all around 16,000 g/mol (M_w per GPC). After incorporation of a standard photoinitiator (5 % of an alpha-hydroxyacetophenone), films with a dry film thickness between 100 and 150 μm were produced via knife coating and exposure to UV light at a dose rate of approximately 4,000 mJ/cm² (medium-pressure mercury lamp / 80 W/cm). Figure 3 compares the dynamic viscosities of the binders at 60 °C, elongation at break in % and ultimate tensile stress of the cured films.

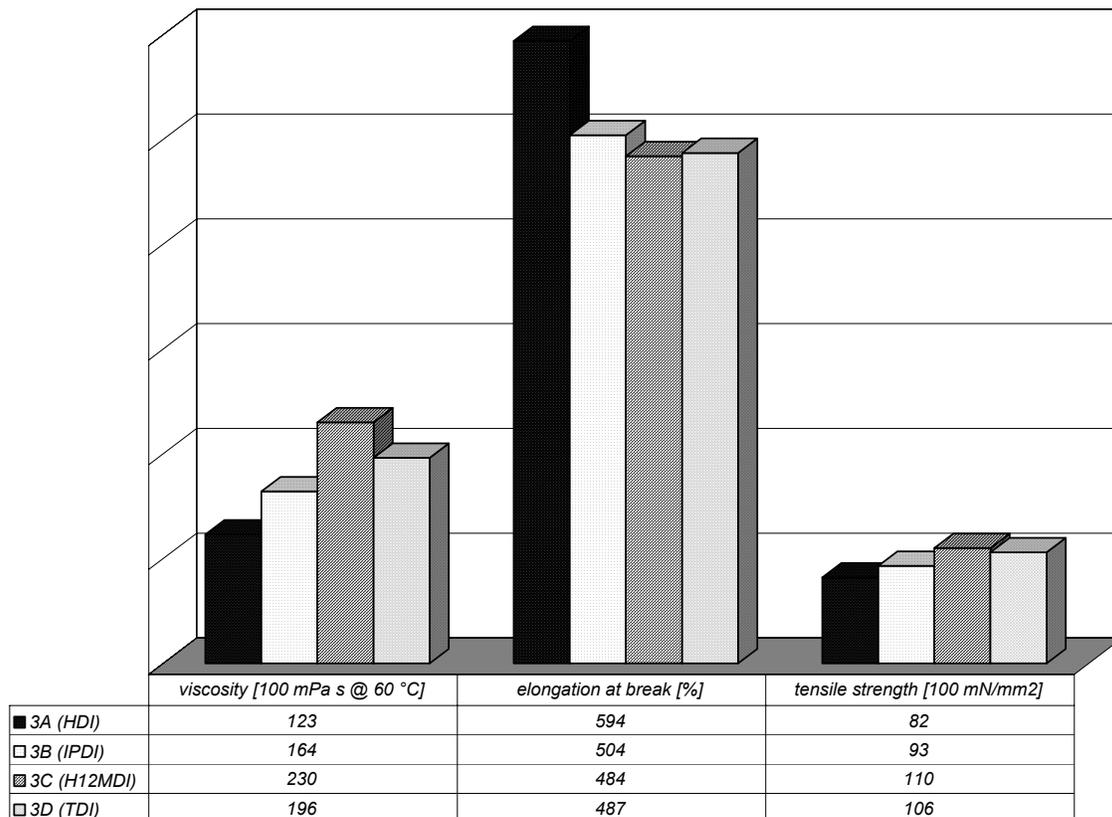


Figure 3. Viscosity, elongation at break and tensile strength of urethane acrylates based on different diisocyanates.

The influence of the diisocyanate on the viscosity of the product is significant: the lowest and highest viscosities are separated by a factor of two. Comparing the elongation at break, one sees that Product 3A based on hexamethylene diisocyanate (HDI) has the lowest viscosity but also the greatest elongation at break of nearly 600 %. The products based on the other diisocyanates all had values below 500 % but had slightly higher values for ultimate tensile stress. On the basis of these results, the HDI used in Product 3A was selected as the diisocyanate with the greatest potential for use in elastomeric urethane acrylates.

In another series of experiments, the same urethane acrylate was thinned to 80 % in various reactive thinners. It was discovered during the combinatorial screening of various commercial monofunctional acrylates and methacrylates that not all reactive thinners are compatible with urethane acrylates, e.g. those of type 3A, and that when certain reactive thinners are used, UV reactivity is too low to obtain completely cured films. A product without reactive thinner in butyl acetate and a product in the difunctional reactive thinner tripropylene glycol diacrylate (TPGDA) were formulated for comparison with products selected on the basis of positive performance. Figure 4 illustrates the dramatic influence the reactive thinners have on film properties.

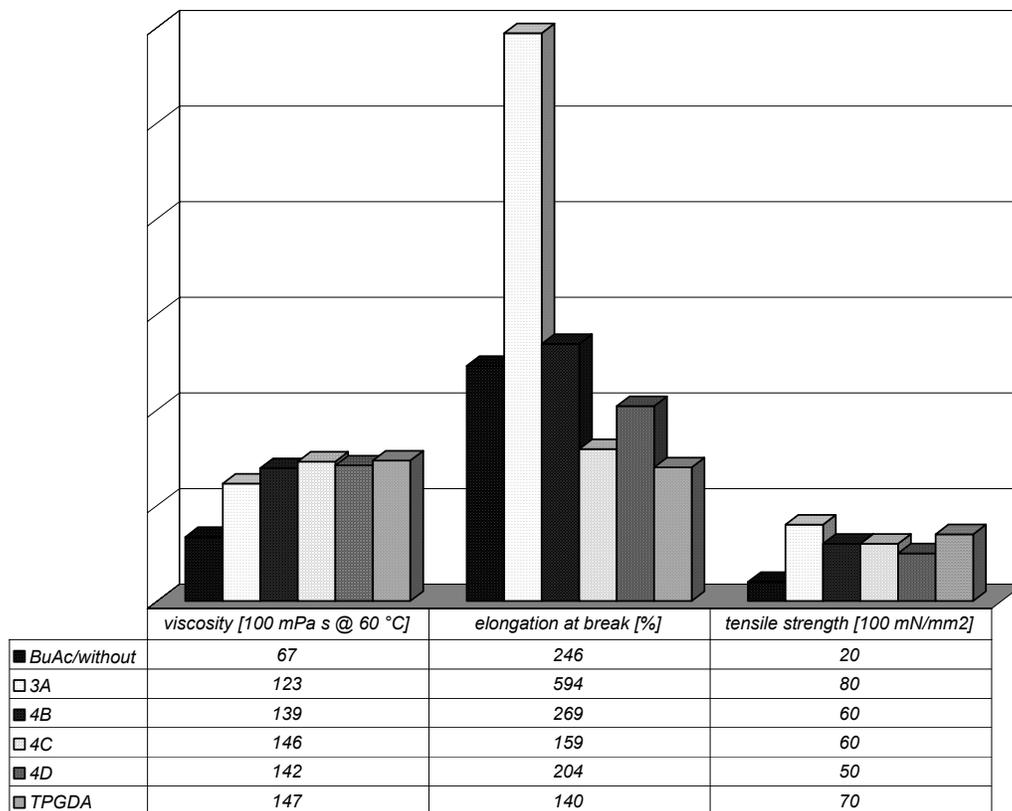


Figure 4. Viscosity, elongation at break and tensile strength of urethane acrylates dissolved in different reactive diluents.

Compared to the product without reactive thinner, TPGDA and three other reactive thinners shown here either have only a minor positive or even negative effect on the elongation at break. Only the reactive thinner used with Product 3A resulted in an approx. 250 % increase in elongation at break to nearly 600 %. Product 3A also has the lowest viscosity of all the products shown that contain reactive thinner. A possible explanation for this phenomenon is suggested by an additional observation. If additional reactive thinner of the type used is added to Product 3A, an incompatibility leading to separation is soon observed. The other reactive thinners exhibit significantly better compatibility. The extremely high elongation at break of Product 3A can thus be attributed to an at least partial separation of the urethane from the acrylate phase. Dynamic-mechanical analyses also suggest such separation.

The chemical nature of the polymeric diol used also has a profound influence on the elastomeric properties of the urethane acrylate. Tested were pure polyether, polyester with short ether segments, polyester, polyester polycarbonate and polycarbonate, all with molecular weights around 2,000 g/mol. Molar ratios, diisocyanate, reactive thinner and hydroxyalkyl acrylate were the same as with Product 3 discussed previously.

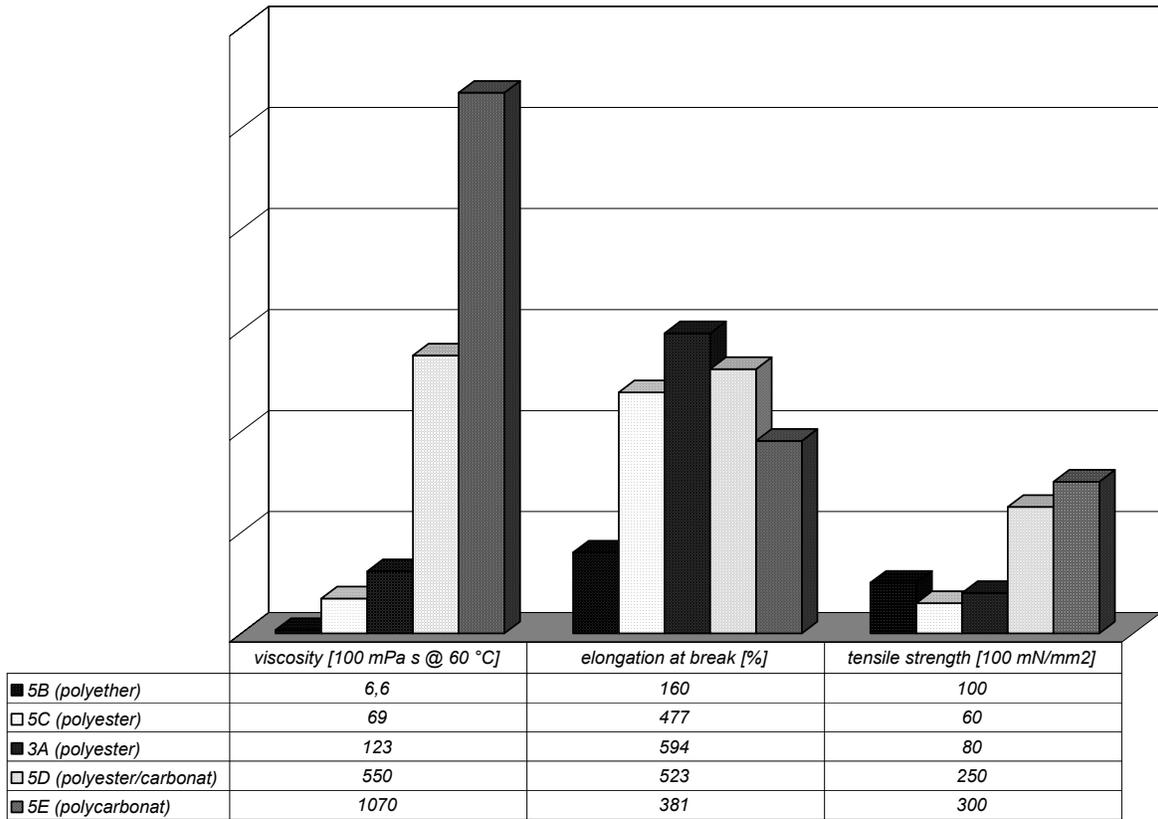


Figure 5. Viscosity, elongation at break and tensile strength of urethane acrylates based on different polymeric diols.

The trend from left to right in Figure 5 toward higher viscosities corresponds to an increase in ultimate tensile stress. Higher viscosities at comparable molecular weights can be explained by increasingly strong intermolecular interactions, such as hydrogen bridge bonds. The tensile elongation behavior of the urethane acrylates can be set within a wide range through the use of a suitable diol or diol mixture. Figure 6 shows the tensile elongation curves of products 5C, 3A, 5D and 5E.

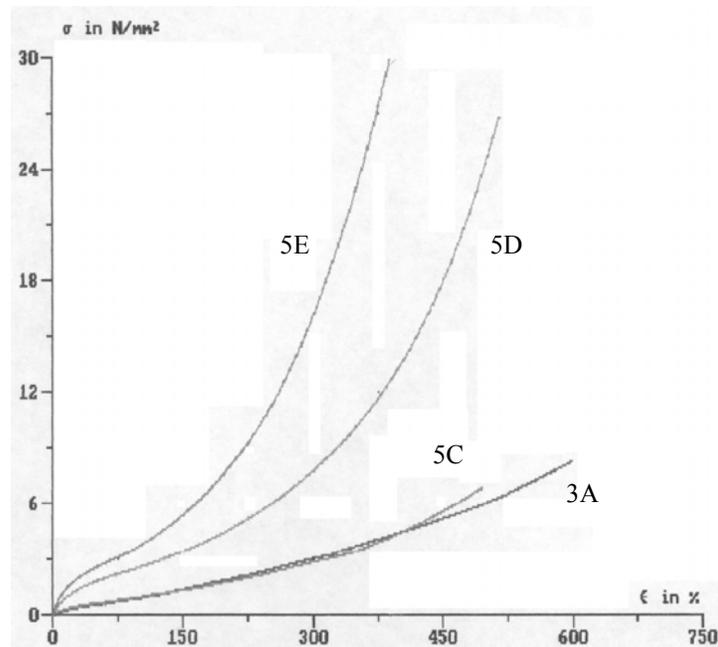


Figure 6. Tensile elongation curves of urethane acrylates 5C, 3A, 5D and 5E

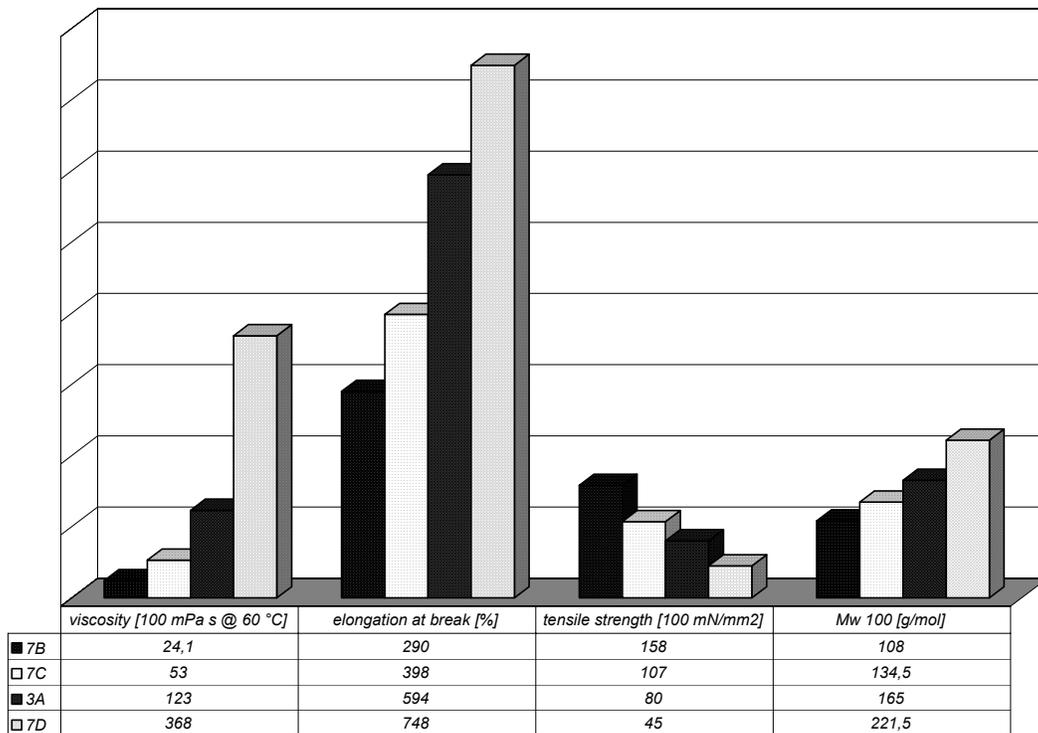


Figure 7. Viscosity, elongation at break, tensile strength and molecular weight of urethane acrylates with different molar ratios of hydroxyalkyl acrylate to polymeric diol.

In the last series of tests, the molar ratios of hydroxyalkyl acrylate to polymeric diol were varied. The viscosity of the product increases with increasing molecular weight M_w with a simultaneous decrease in double-bond density. Figure 7 uses the known Product 3A to illustrate how a change in the molar ratios influences the other properties. Greater elongation at break at a lower tensile

strength is achieved with increasing viscosity and molecular weight. An elongation at break of up to 750 % was achieved!

Summary of results:

Through the combination of statistical design of experiments and parallel reactors, we were able to formulate a large number of possible urethane acrylates. Based on the results of simple pretests, selected series of compounds were formulated on a larger scale and their elastomeric properties, among others, were tested. Values from 150 to 750 % were measured for the elongation at break. The elastic properties of urethane acrylates, such as elongation at break and tensile strength, can be set freely within a certain range through the selection of diisocyanate, polymeric diol and reactive thinner.

In addition to the expected relationships of elasticity, reactivity and viscosity as a function of molecular weight, functionality and double-bond density, an unexpectedly high elongation at break was found in those products for which a reactive thinner was chosen that was still easily miscible with the urethane acrylate phase but at the limits of compatibility.

Applications:

What are the potential applications for the elastomeric urethane acrylates presented? Elastomeric properties of this sort are required for coatings on leather or textiles. Beside good elongation at break and tensile strength, for example, such coatings must also exhibit good resistance and adhesion properties.

Elastomeric coatings applied in thick coats, such as domed labels or keyboard pads, are becoming increasingly important. The urethane acrylates presented here can also be UV-cured to yield peel-off films or temporary coatings, e.g. for the transportation of high-value goods.

If the products presented here are to be used as admixtures in flexibilizing a UV-curing coating formulation, please note that the special properties of the products presented here may be diminished or lost in some cases, e.g. where the partial incompatibility exploited by some of the products is lost when mixed with others. Despite this risk, the polishing properties of UV-curing coatings can usually be easily improved by the addition of the elastomeric urethane acrylates presented here. Last but not least, these very soft urethane acrylates in a formulation alter the handle of a coating, making soft-feel or soft-touch surfaces possible.

Outlook: Radiation-curing polyurethane dispersions

The high viscosities of the urethane acrylates presented here could be disadvantageous for many other applications. If the use of organic solvents is to be avoided, water can be used, thus making UV-curing polyurethane dispersions a viable alternative.

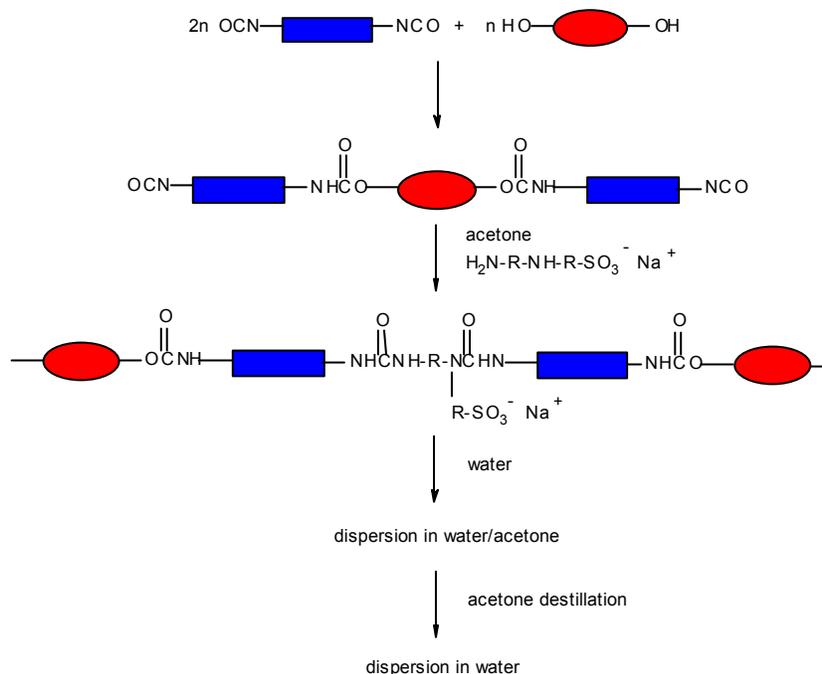


Figure 8. Schematic of the acetone process

Prepolymers with very high viscosities can be produced and placed into dispersion using a special manufacturing process called the acetone process. In this process, the prepolymers are manufactured in an acetone solution to prevent intolerably high viscosities. Once the prepolymer has been placed into aqueous dispersion, the acetone is removed by distillation.

This method has been used successfully to produce laboratory-scale quantities of some of the urethane acrylates discussed above as polyurethane dispersions. If the use of reactive thinners is to be avoided, the positive effect of limited compatibility on elongation at break observed in the non-aqueous products is lost. As compensation, the molecular weights of the urethane acrylates were increased by varying the molar ratios of the base monomers. Ionic or non-ionic emulsifiers were incorporated to provide the required compatibility with water. Using this method, it was possible to synthesize products with an elongation at break of more than 800 %.

^[1] Fischer, W., "New low viscous urethane acrylates for radiation-curing coatings", Conference Proceedings, Eurocoat Barcelona, 1999