

WATERBASED RADIATION-CURABLE POLYURETHANE ACRYLATE COATINGS

by Y. Heischkel*, K. Menzel+, E. Beck+, K. O. Sass&, C. A. Glotfelter§, F. Masson#, C. Decker#, and R. Schwalm*, BASF AG, *Polymer Research Laboratory, +Performance Chemicals for Coatings, 67056 Ludwigshafen, Germany; BASF Corp., Performance Chemicals for Coatings, §07828 Mt Olive, &28216 CHARLOTTE, USA, #Departement de Photochimie Générale, Université de Haute Alsace, ENSCMu, France

Introduction

Radiation-curing has established itself as an efficient and environmentally friendly technology over the past 20 years. In a typical procedure, a substrate is coated with a radiation-curable resin without the use of solvent. Curing starts upon irradiation with UV light if a photoinitiator is used or when the coated substrate is exposed to an electron beam. The coating is cross-linked by a polymerization reaction in bulk within a few milliseconds.

Increasing environmental concerns and the ensuing legislation to cut emissions of volatile organic compounds (VOCs) are major driving forces for the development of radiation-curable coatings.¹ Low molecular weight acrylates can not be used in all applications to adjust viscosity. Monomeric thinners often penetrate into porous substrates, e.g. wood, where they are unavailable for the curing process and can be emitted during lifetime of the coated substrate. However, volatile organic thinners are often essential to achieve matting effects or enhance the wood grain.

In combination with emulsifying or dispersing agents, water is an alternative thinner for radiation-curable binders. The development of this technology started with aqueous emulsions based on unsaturated polyesters, polyether or epoxy acrylates. An important milestone was achieved with new, physically drying, radiation-curable polyurethane dispersions. These water-based coatings open up a wide application field for radiation-curable coatings which was not accessible to 100 % systems. They can be used for two- or three-dimensional objects due to their low viscosity which is an essential requirement for spraying. There is no need to use additional monomers or organic solvents.

Experimental

Polyurethane acrylate prepolymers and dispersions were prepared by a procedure described in the literature.² The polyurethane acrylates were mixed with the photoinitiator (2.9 wt.-% Irgacure®2959) and cast onto a glass plate or a barium fluoride crystal with a thickness of approximately 70 µm. The coatings were cured by passing the sample under a medium pressure mercury lamp (80 W/cm, 600 mW/cm²) at a speed of 20 m/min. The temperature of the sample during irradiation with UV light was set between 25 and 100 °C. The conversion during photo-polymerization was measured by infrared spectroscopy.³ The polymerization of the acrylate double bonds was determined from the decrease of the IR band at 1410 cm⁻¹ (CH₂=CH twisting vibration).

Results and Discussion

Aqueous coatings based on dispersions typically show thermoplastic behavior. Therefore, the dry film exhibits poor blocking resistance, and poor scratch resistance. Introducing unsaturated functional groups, e.g. acrylic esters, which enable photoinduced cross-linking of the coating, can eliminate these disadvantages. Self-drying polyurethane dispersions are well

known for their excellent properties in numerous application fields. High performance coatings are obtained if a radiation-cured acrylate network is combined with the properties of polyurethane films.⁴ The coatings possess excellent mechanical and chemical resistance due to their film morphology.

The synthesis of polyurethane acrylates is depicted in Figure 1. In the first step, a urethane prepolymer is formed by reacting an excess of diisocyanate with a mixture of polyols and acrylic esters containing reactive hydroxyl groups in an organic solvent, e.g. tetrahydrofuran, or acetone. Aromatic isocyanates improve the toughness of the coatings. Aliphatic isocyanates are known for their low photo-yellowing and good chemical resistance. The acrylate groups are introduced via mono- or higher functional hydroxyacrylates, e.g. hydroxyethylacrylate HEA. Epoxyacrylates or polyether- and polyesteracrylates with hydroxyl groups can also be used to link polymerizable acrylic ester groups to the polyurethane backbone. Polyester- or polyether-type polyols act as soft segments. Polyesters combine good abrasion resistance with high toughness. Polyetherols provide flexibility and elasticity, whereas their chemical resistance and weathering stability is lower compared with polyesterols. The hard segment is formed by chain-extension of the prepolymer with low molecular weight diamines. Anionic groups are introduced into the polymer backbone either during the prepolymer reaction or by chain extension. They stabilize the organic polymer in water. The polyurethane acrylate prepolymer solution can be mixed with water to give dispersions after removal of the organic solvent.

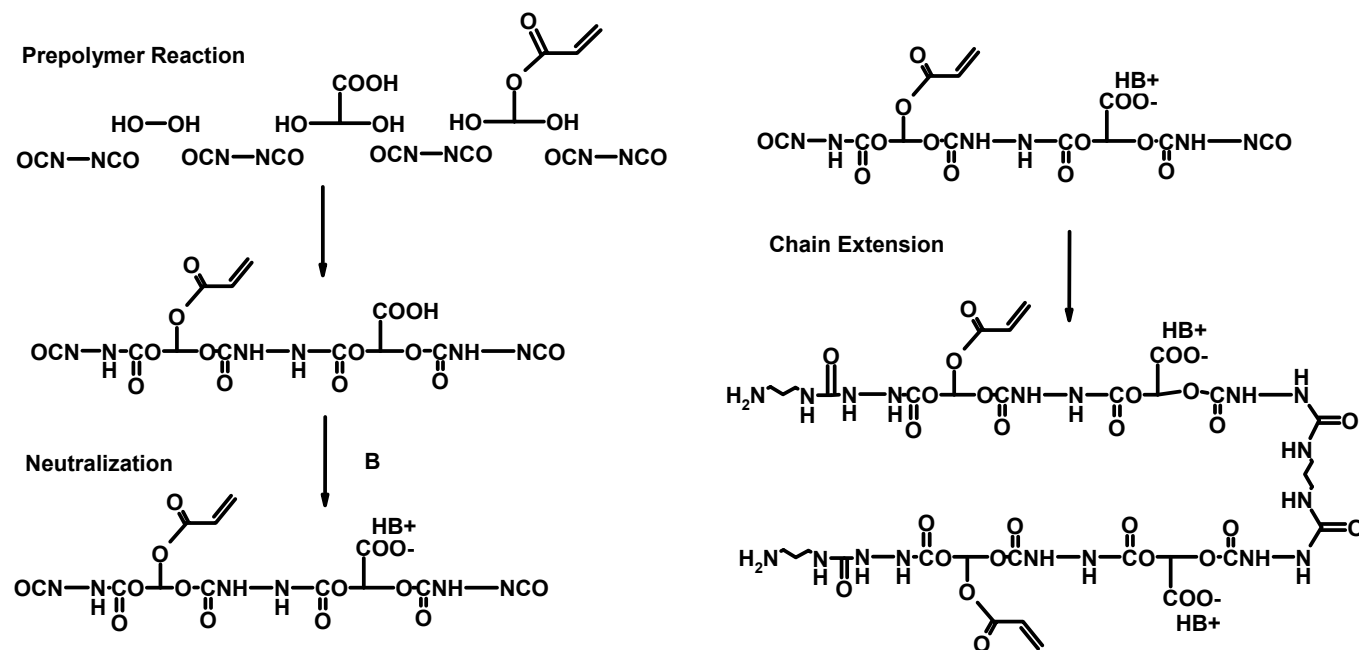


Figure 1. Reaction sequence to build up the polyurethane acrylate.

Properties of Polyurethane Acrylate Dispersions. The physical data of the different polyurethane acrylates are given in Table 1. The content of carboxylic groups was varied from 12 mg KOH/g to 29 mg KOH/g (PUA 1 – PUA 4). The acid groups were neutralized with sodium hydroxide. The solvent-based reference PUA 5 contains no acid groups. The physical properties strongly depend on the concentration of acid groups. Particle size and viscosity of

the polyurethane acrylate dispersions decrease with increasing number of carboxylate groups. In comparison, the viscosity of the solvent-based PUA 5 in butyl acetate is much higher.

Table 1. Polyurethane Acrylates synthesized from polycaprolactone diol, HEA, isophoron-diisocyanate IPDI, hexamethylene isocyanurate and dimethylolpropanoic acid, 35 wt.-% in water.

Dispersion	Viscosity (mPas)	Particle Size (nm)	pH	Acid Number (mg KOH/g)
PUA 1	30	32	7.6	29
PUA 2	73	70	7.6	24
PUA 3	169	132	8.0	18
PUA 4	dilatant	469	8.3	12
PUA 5 (60 wt.-% in BuAc)	2120	-	-	0

UV Curing of Polyurethane Acrylate Coatings. The conversion during UV curing of the polyurethane coatings with respect to the UV dose recorded by real-time IR spectroscopy is shown in Figure 2. The highest conversion of 99 % converted acrylic double bonds was observed for the solvent-type PUA 5 without any acid groups. The final conversion decreases to 78 % with increasing acid number of the polyurethane acrylate. The observed trend can be explained by the mobility of the reactive acrylic groups. The cross-linking reaction proceeds very fast in a liquid film like PUA 5. Molecular mobility is significantly reduced at higher acid content resulting in a lower conversion. In contrast to the solvent-type PUA 5, the dispersions PUA 1-PUA 4 give tack-free films before curing due to their higher polarity. As a consequence, polyurethane acrylate dispersions are particularly suitable for UV coating of three-dimensional objects. Tack-free films coat surfaces inaccessible to UV radiation even if no polymerization occurs.

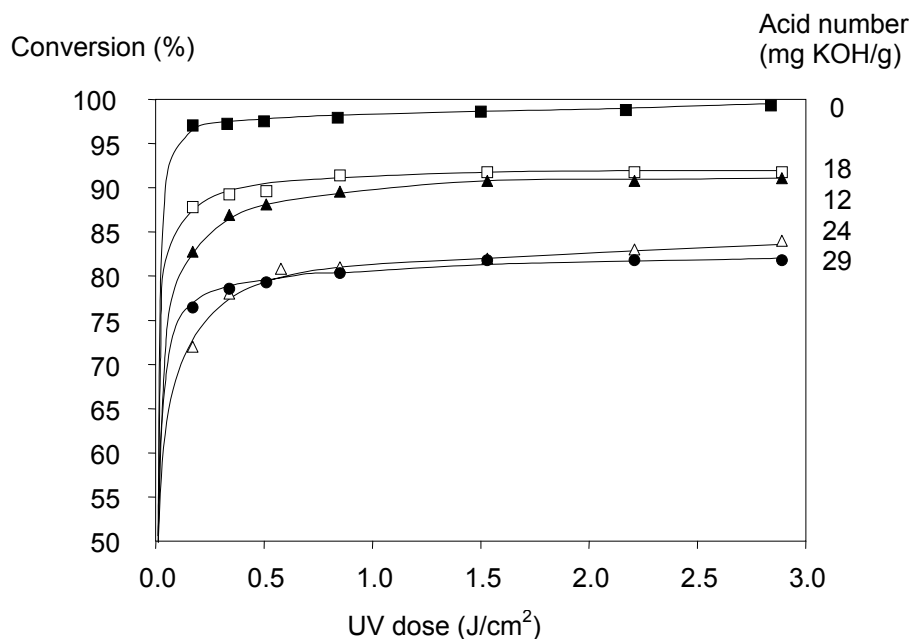


Figure 2. Influence of the acid content on the UV curing kinetics of PUA coatings. Drying/irradiation temperature: 80 °C, intensity = 600 mW/cm².

We have investigated the curing conditions for PUA 2 in more detail in order to achieve highly cross-linked acrylate networks. Figure 3 shows the influence of elevated temperatures on conversion of the acrylate groups of PUA 2. The conversion of photo-polymerization can be improved dramatically by performing the UV curing step at higher temperatures. Photo-polymerization at temperatures between 60 °C and 100 °C provided a sufficient degree of polymerization to achieve good coating properties. The mobility of the polymerizable groups is increased at temperatures above 60°C which facilitates the formation of an acrylate network. In an inline process, one would recommend performing the drying step at 80 to 100 °C, and irradiating the sample immediately afterwards.

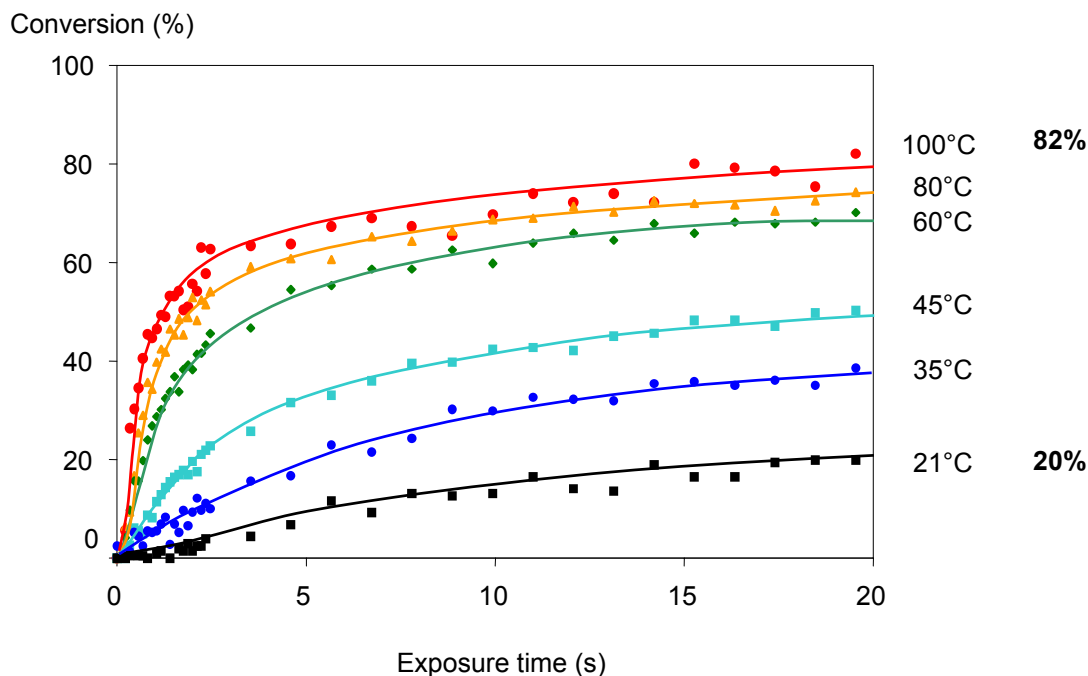


Figure 3. Temperature assisted UV curing of PUA 2. Intensity = 100 mW/cm².

In order to investigate the influence of the atmosphere on the curing kinetics, the PUA films were placed in a humid atmosphere. Figure 4 shows the influence of the relative humidity on the acrylate curing. The conversion of acrylate double bonds in PUA 2 increased from 20 % in dry air to 55 % in 100 % relative humidity. Water is able to penetrate into the dried coating upon storage due to the hydrophilic nature of PUA 2. Small molecules like water can act as plasticizer which enhances the molecular mobility of the reactive acrylic units.

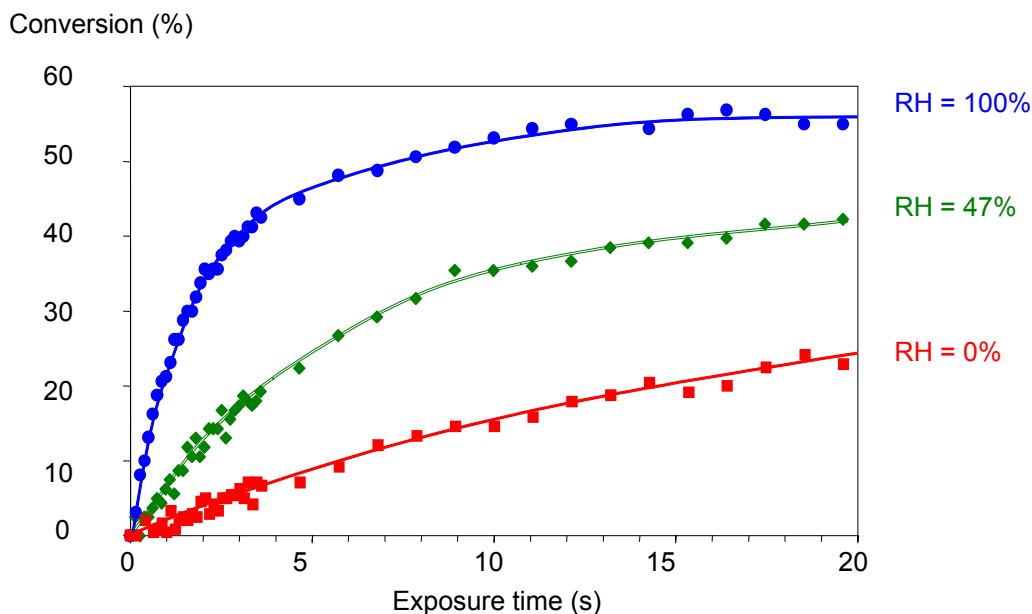


Figure 5. Influence of the atmospheric humidity on the acrylate double bond conversion during UV curing.

The weathering resistance of the cured PUA coatings was evaluated by monitoring the IR absorption of the chemical bonds upon accelerated wet-cycle QUV-A-aging. A comparison between the remaining infrared C-N absorption band of the water-based PUA 2 and the solvent-based PUA 5 is given in Figure 6. Despite of the polar character of the carboxylic groups in PUA 2, no enhanced photooxidation was observed under QUV-A aging. There was found no significant difference in photo-aging between a solvent-based and a water-based polyurethane acrylate coating.

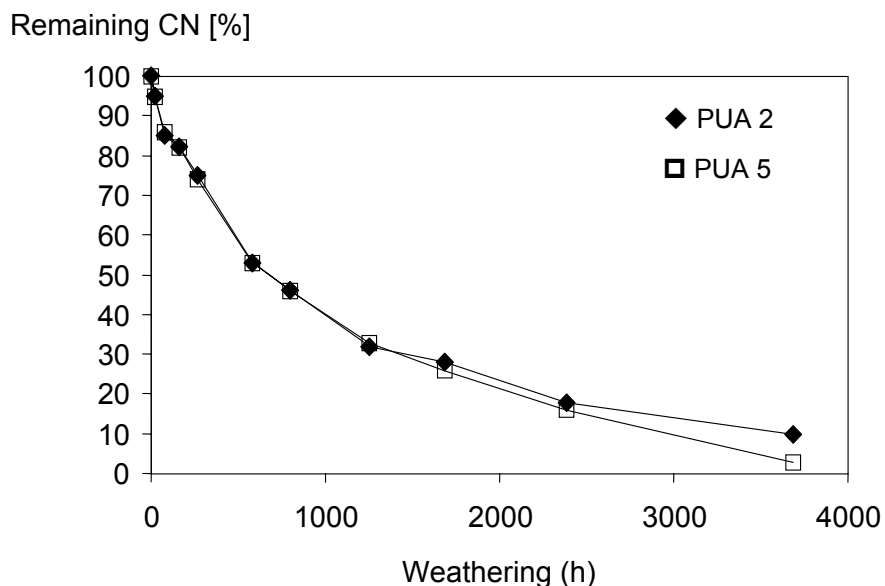


Figure 6. Weathering behavior of waterbased PUA 2 and solvent-based PUA 5 coatings monitored by IR spectroscopy.

Conclusion

Waterbased polyurethane acrylates can be cross-linked by irradiation with UV light without emission of any volatile organic compound. The conversion of acrylate groups strongly depends on the acid number of the polyurethane and the curing conditions. High cross-linking densities are obtained at 80 °C, or in a humid atmosphere. Water-based polyurethane acrylate coatings show a photooxidative stability which is comparable with solvent-based polyurethane acrylates. In addition, polyurethane acrylate dispersions form tack-free films before curing which makes them particularly suitable for application on three-dimensional substrates.

Acknowledgement. The authors like to thank Dr Jaworek, and Dr Königer for fruitful discussions.

References

- (1) Decker, C. *Progr. Polym. Sci.* **1996**, *21*, 593.
- (2) Masson, F.; Decker, C.; Jaworek, T.; Schwalm, R. *Progr. Org. Coat.* **2000**, *39*, 115.
- (3) Decker, C.; Moussa, K.; *Makromol. Chem.* **1988**, *189*, 2381.
- (4) Reich, W.; Enenkel, P.; Keil, E.; Lokai, M.; Menzel, K.; Schrof, W. *RadTEch '98 North America UV/EB Conf. Proc.* **1998**, 267.