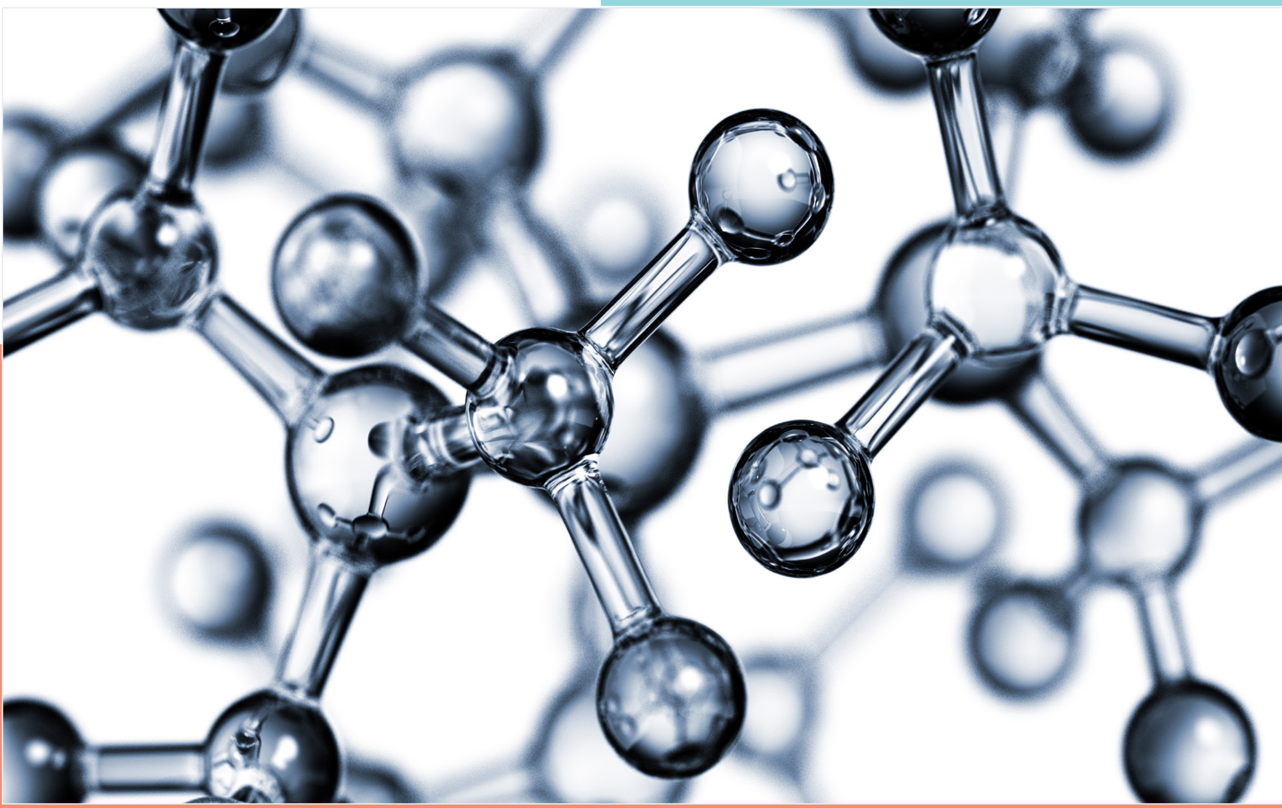
Water-Reducible Urethane Acrylates: An Alternative to UV-PUDs



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Abstract

UV–PUDs are widely used in coatings industry. Unfortunately, UV–PUDs contain about 60% water and shipment of large amount of water in UV–PUDs incurs substantial cost. We have developed novel water–reducible urethane acrylates (WR–UAs) which contain 10–30% of water. Customers dealing with the suggested WR–UAs can easily dilute them on site. Properties and advantages of using the original WR–UAs are discussed.

Introduction

Waterborne UV–curing coatings are being increasingly used as primers and topcoats for wood in furniture, kitchen cabinets, and doors.[1] Conventional 100% solids UV–coatings suffers from poor adhesion to wood due to insufficient wetting, and uncured reactive diluents may damage wood.[2] These same reactive diluents also incur additional processing risks associated with operator handling of formulations containing low molecular weight (meth)acrylates (skin irritancy, sensitization, etc.). Waterborne UV coatings are much easier to matt due to significant volume shrinkage during the evaporation of water.[3]

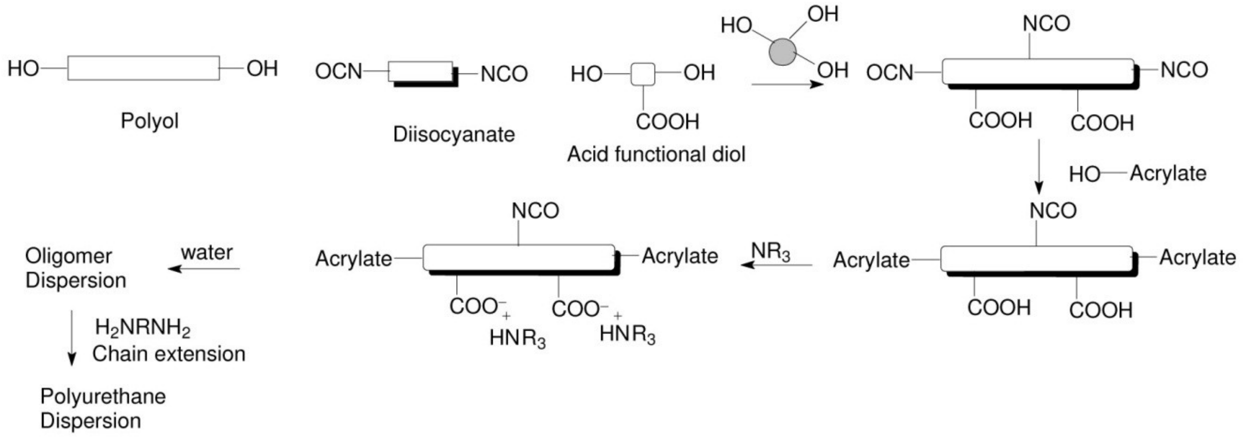
UV–curing water based systems are generally divided into three categories: water–soluble resins, emulsions, and dispersions. Polyethylene glycol diacrylates, and highly ethoxylated polyurethane acrylates are some of the examples of water soluble resins. Dispersion is the term for two phases one of which is distributed in the other whereas emulsion is a mixture of two liquids that are not soluble in each other. However, in coatings industry, the difference between emulsions and dispersions are often distinguished by the physical state of the coating obtained after the evaporation of water. Dispersions result in tack–free films prior to UV–curing whereas emulsions result in tacky films.[4]

Emulsions are usually prepared from polyether acrylates or polyester acrylates by the addition of an emulsifier or amine to neutralize free carboxylic acid groups (in polyester acrylates).[5] Because of their high viscosities, polyurethanes generally need co–solvents in order to be emulsified.

UV–curable polyurethane dispersions (UV–PUDs) are synthesized through a multistep reaction in a solvent as shown in Figure 1. An acid functional oligomer is synthesized first and then neutralized with an amine. To obtain dispersion in water, neutralized oligomer is added to water. High molecular weights are obtained in water with using a diaminoalkyl chain extender. Molecular weights of typical UV–PUDs are greater than 50,000 g/mol. Chemical resistance and mechanical properties of UV–PUDs depend on the crosslink density and molecular weight between crosslinks.[3]

Typical UV–PUDs contain 60 to 70 percent water. In cost–driven industries, reduction of shipment costs is very important. To eliminate the cost of shipment of water, we developed water reducible urethane acrylates (WR–UAs). Unlike conventional UV–PUD preparation, WR–UAs do not need to be added to water. Similar to UV–PUDs, WR–UAs also give tack–free films after the evaporation of water and neutralizing amine.

Figure 1. Preparation of UV–PUDs



Experimental

All the products discussed in this study were analyzed with gel permeation chromatography (GPC) and infrared spectrometer (IR). GPC device of Polymer Labs PL–GPC 50 was equipped with an RI detector and mixed D–columns. The IR spectrometer was Perkin–Elmer Spectrum One model with a diamond crystal UATR. Formulations were cured in the air with a Fusion 300 processor, D–bulb, belt speed 20 ft/min, one pass.

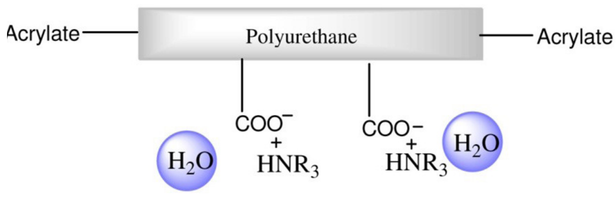
The viscosity was measured with a Brookfield RVT viscometer with a small adapter (spindle SC4–15). Methyl ethyl ketone (MEK) resistance was measured by MEK double rub test according to ASTM D4752–03. Scratch resistance was tested by using a 0000 steel wool on the peen end of an 16 oz ball–peen hammer.

Results and Discussion

Water Reducible Oligomers

Water reducible acrylics, polyesters, alkyds and epoxy esters are well known in coatings industry.6 These resins usually contain about 25 to 40 % solvent and require addition of neutralizing amine and water to reduce the viscosity to application viscosities. For UV–curing coatings, solvents are highly undesirable. In this study, we have found out that neutralizing amine and a small amount of water can provide a stable emulsion. The rest of the water required can be added later on to obtain a sprayable application viscosity. A generic scheme for WR–UAs is given in Figure 2.

Figure 2. Acid–amine stabilized WR–UAs.



Stability of the WR–UAs strongly depends on the amount of water added to the neutralized UA oligomer. We observed two modes of stability failure:

- gelation: hydrogen abstraction from tertiary amine neutralizer causes free radical crosslinking
- colloidal stability: irreversible coagulation of the oligomer phase

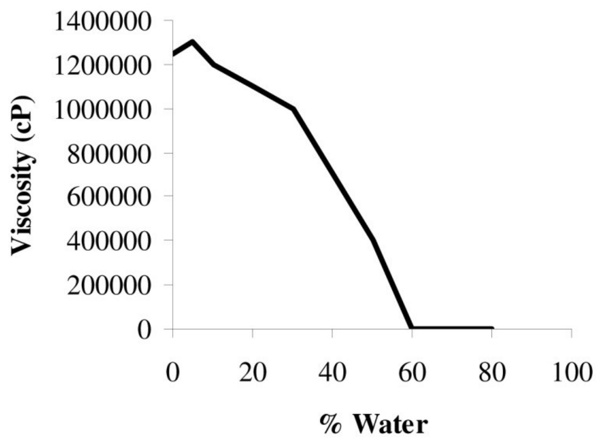
Six different WR–UAs are prepared with the same neutralizing amine and with different number of acrylate functionalities, molecular weights, and isocyanates. Stability test results at 60°C with changing water concentration are given in Table 1. Stabilizing effect of water against gelation is evident. Water addition promotes quaternary ammonium salt formation and therefore decreases the hydrogen abstraction from the amine and hence inhibits free radical formation and gelation or chain extension. We have found out that 30% and 70% water concentrations have the highest colloidal stability. In the 30% water addition case, oligomer is the continuous phase, whereas in 70% water addition, continuous phase changes to water. Viscosity change data for WR3 is given in Figure 3. At 30% water level, viscosity did not drop extensively since the added water only swells the oligomer, whereas after 60% water, continuous phase changes to water and viscosity drops dramatically.

Table 1. Stability Test Results of WR–UAs

	Acrylate fn	Polyol	Mw (g/mol)	Isocyanate	No Water	10% Water	20% Water	30% Water	50% Water	70% Water
WR1	2	Polyol #1	5000	Isocyanate #1	2 days:E[a]	7 days: C[c]	>15 days	>15 days	12 days: C	>15 days
WR2	2	Polyol #2	9000	Isocyanate #1	3 days: E	6 days: C	>15 days	>15 days	13 days: C	>15 days
WR3	6	Polyol #1	5000	Isocyanate #1	1 day: G[b]	3 days: G	9 days: G	>15 days	6 days: C	>15 days
WR4	6	Polyol #2	8000	Isocyanate #1	1 day: G	4 days: G	12 days: G	>15 days	7 days: C	>15 days
WR5	6	Polyol #3	5000	Isocyanate #1	1 day: G	3 days: G	12 days: G	>15 days	6 days: C	>15 days
WR6	6	Polyol #1	5000	Isocyanate #2	1 day: G	3 days: G	10 days: C	>15 days	6 days: C	>15 days

[a] E: chain extension | [b] G: gelled | [c] C: coagulation

Figure 3. Viscosity change with the addition of water for WR3



WR-UAs containing 70% water and 2% Irgacure 819DW as the photoinitiator are cast on glass plates to give 25µ dry film thickness after the evaporation of water and amine. MEK double rub and steel wool test results on the UV-cured coatings are given Table 2. Best MEK steel wool scratch resistance results are obtained with WR3: a low Mw high acrylate functionality WR-UA. Di-acrylate functional WR-UAs (WR1 and WR2) give the worst MEK and scratch resistance results due to insufficient crosslinking. Furthermore, change of polyol and isocyanate affected the MEK and scratch resistance of the films.

Water Dilutable Oligomers

The term, water dilutable, is used to differentiate the situation wherein an oligomer, when diluted with water, forms a homogeneous phase with water and therefore there is no phase inversion and sudden viscosity drop. Water dilutable oligomers can be diluted with water at any quantity. In common water dilutable oligomers, water dilution property comes from the hydrophilic groups in the oligomer backbone. Therefore, these oligomers reveal poor water sensitivity and solvent resistance. We have developed a new class of water dilutable oligomers which consist from a highly branched, hydrophobic core and covalently attached to this core hydrophilic dangling groups. A representative scheme of the new water dilutable oligomers is given in Figure 4.

Figure 4. Scheme of water dilutable oligomers

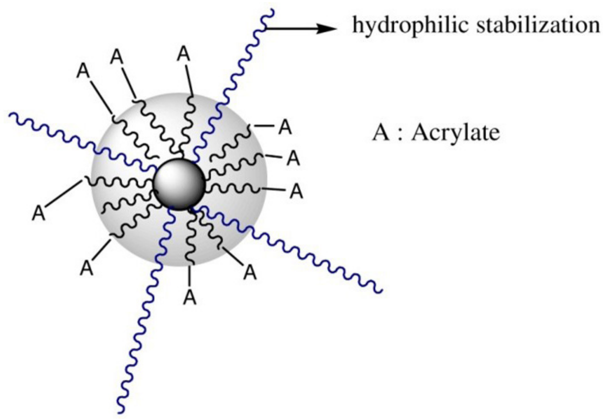
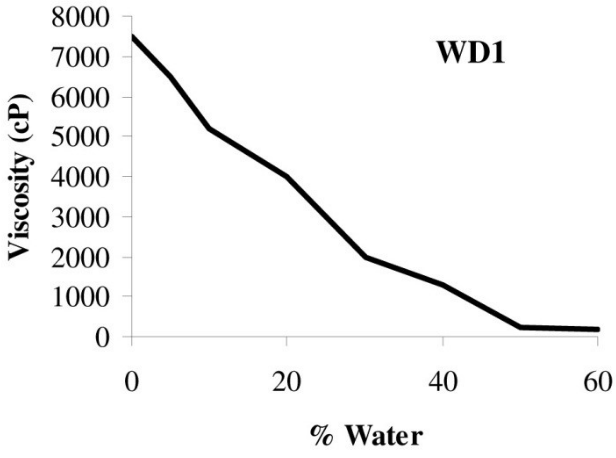


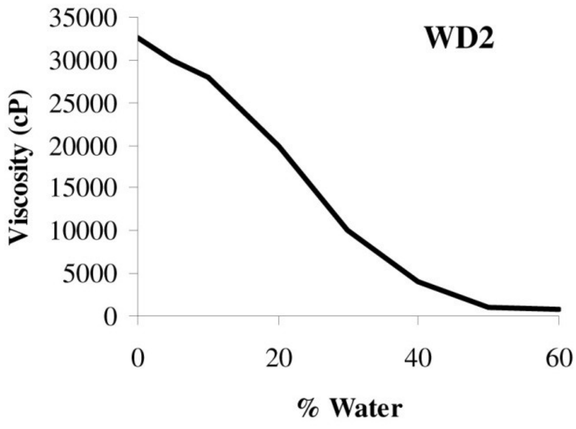
Table 1. Stability Test Results of WR-UAs

	Acrylate fn	Polyol	Mw (g/mol)	Isocyanate	MEK Double Rubs	Steel Wool Strokes	Haze After Steel Wool Strokes
WR1	2	Polyol #1	5000	Isocyanate #1	30	5	4*
WR2	2	Polyol #2	9000	Isocyanate #1	6	5	5
WR3	6	Polyol #1	5000	Isocyanate #1	>200	50	1
WR4	6	Polyol #2	8000	Isocyanate #1	130	5	3
WR5	6	Polyol #3	5000	Isocyanate #1	100	50	1
WR6	6	Polyol #1	5000	Isocyanate #2	>200	5	2

*5: the most haze formation, 1: the least haze formation

Figure 5. Viscosity change with the addition of water for WD1 and WD2





Two water dilutable oligomers are prepared: WD1 and WD2. Viscosity changes with the water dilution of these oligomers are given in Figure 5. Initial viscosities of the oligomers are much lower than WR–UAs and there is no sudden drop in viscosity with the water dilution.

Emulsions formed with water dilutable oligomers coalesce after the evaporation of water. Due to high crosslink density and hydrophobic nature of the core of the oligomers UV–cured films had good MEK and water resistance. MEK and water double rubs and steel wool scratch test results are given in Table 3. As can be expected, ten acrylate functional WD2 gave the best water, MEK, and scratch resistance due high crosslink density.

Table 3. Water dilutable oligomers' properties

	Acry-late fn	MEK Double Rubs	Water Dou-ble Rubs	Steel Wool Strokes	Haze After Steel Wool Strokes
WD1	6	>200	110	50	2*
WD2	10	>200	>200	50	1

Conclusions

We have developed novel water–reducible and water dilutable urethane acrylates. Customers dealing with these oligomers can dilute them on–site. The new waterborne oligomers may be utilized as an alternative to UV–PUDs or complimentary to UV–PUDs to increase the crosslink density.

References

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