Aqueous Dispersions for Ultraviolet Light Curable Coatings

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Aqueous dispersions of ultraviolet light (UV) curable resins have been prepared and evaluated. The physical and rheological properties of these dispersions have been determined, and the performance of these dispersions in coating systems has been studied. Coatings based on these dispersions have faster UV cure speed, better surface hardness, and better flexibility compared with coatings based on undispersed resins.

INTRODUCTION

Radiation-curable, waterborne products are experiencing rapid growth in the marketplace as a result of both technological advances and increasing environmental pressures to reduce volatile organic compounds (VOCs). These products not only maintain the performance and VOC advantages over the use of conventional solvent-based resins, but also present novel design opportunities because aqueous systems decouple the polymer or oligomer molecular weights from the formulating viscosity. These advantages for many industrial applications have been discussed previously in the literature.[1-3]

Recently, we have dispersed several types of radiation-curable oligomers in water in our R&D laboratory. These oligomers include acrylated epoxides, acrylated urethanes, and acrylated polyesters. In this paper, the physical and rheological properties of these dispersions will be presented. In comparison, the properties of the coatings made from the undispersed resins will also be described. (Selected dispersions are available from UCB as experimental products).

EXPERIMENTAL SECTION

The oligomers (urethane acrylates, epoxy acrylates, and polyester acrylates) were dispersed in deionized water using appropriate surfactants. In general, the resulting dispersions were about 65% solids. Dispersion viscosity was measured at 25°C using a Brookfield™ (model DV-II) viscometer. The particle size and particle size distribution of the dispersions were also observed using light scattering or microscopic techniques.

Darocur™ 1173 (4 pph on solids; available from Ciba-Geigy) as a photoinitiator was added to the dispersion or resin system and mixed until homogeneous. Approximately 4-6 mil films were then drawn down on Parker Bonderite 40 steel panels. For the dispersion-based coatings, the water was evaporated by heating the sample with a heat gun or infrared lamps unti the film cleared. The panels were then cured in air using one or two 300 watt/inch mercury vapor electrodeless lamps, at the maximum belt speed that gave a tack-free film. The properties of these films were then tested according to the following ASTM[4] methods: adhesion (ASTM D 3359), hardness (ASTM D 3363), flexibility (ASTM D 522 and ASTM D 2794), and gloss (ASTM D 523). In addition, methyl ethyl ketone (MEK) and water resistance were determined using the double rub method (ASTM D 4752).

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RESULTS AND DISCUSSION

Several widely used types of radiation-curable oligomers have been successfully dispersed in water. Chemically, these oligomers include acrylated epoxides, aromatic and aliphatic urethane acrylates, and acrylated polyesters, all of various functionality. Rheologically, these oligomers vary in viscosity from 80 cps to greater than 1,000,000 cps at room temperature.

Particle Size

These dispersions were characterized by their particle size and particle size distribution. In most cases, the particle size of the dispersions prepared in our laboratory fell between 0.1 μm and 2.0 μm. The particle size distribution can vary within this range depending on the chemical and physical properties of the oligomers. As an example, the dispersion of an acrylated epoxy oligomer has an average particle size of 0.45 μm (see *Figure* 1).

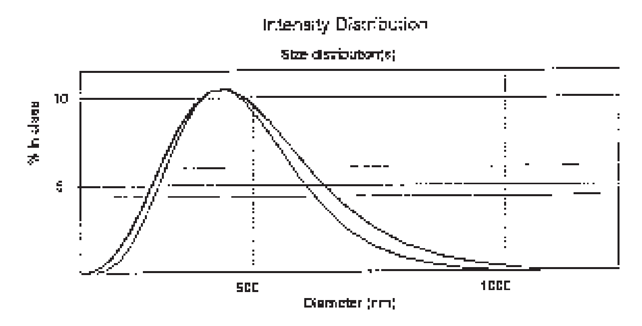

Figure 1—Particle size and particle size distribution measurements by light scattering technique.

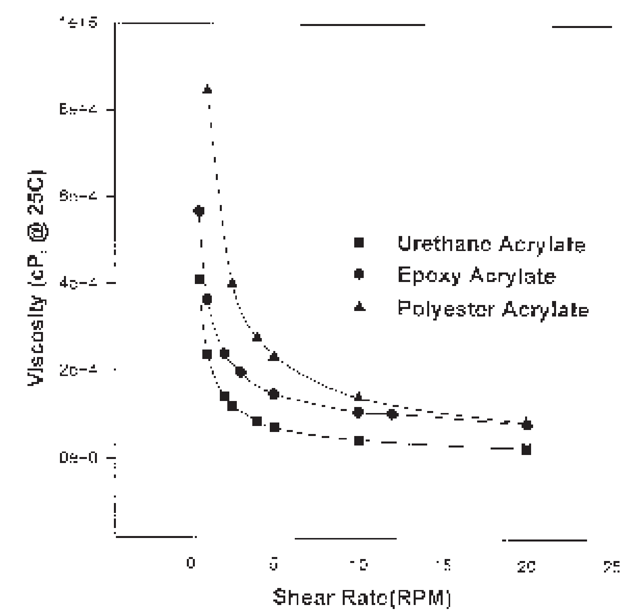

Figure 2—Rheological behavior of UV-curable aqueous dispersions.

Rheological Behavior

Flow properties of the aqueous dispersions were determined. The viscosities of the dispersions (at about 65% solids) vary over a wide range of 1,200 to 10,000 cps at 25°C. The experimental investigations indicate that viscosity is closely related to the particle size and particle size distribution of the dispersions. For those dispersions containing the same percentage of water, the smaller the average particle size, the greater is the viscosity. It is also clear that, under otherwise identical conditions, the viscosity of a dispersion increases with the increasing volume content of the dispersed phase, i.e., the oligomer phase. It is important to point out here that all dispersions evaluated to date in our laboratory have pseudoplastic rheological behavior. The dispersion viscosity decreases with increasing shear rate, but returns to its original value immediately after removal of the shear stress. *Figure* 2 illustrates this pseudoplastic rheological behavior for three types of dispersions: dispersion of acrylated urethane oligomer, dispersion of acrylated epoxy oligomer, and dispersion of polyester acrylate oligomer.

Stability

Long-term and accelerated stability testing have been assessed for many of these dispersions. In general, most of these dispersions are stable at room temprature for at least six months, with no phase separations and no significant particle size changes. The majority of these dispersions also pass thermal testing at 60°C for three days without phase separation or particle size changes. Several of these dispersions pass 1-3 freeze/thaw cycles, also without phase separation or particle size changes. Work continues in this area to provide even better stability.

Film Performance

The properties of the films based on the aqueous dispersions have been investigated. These properties are summarized in *Tables* 1-4 for four different types of films. As a typical example, we will discuss the results in *Table* 1, which contains the properties of the film made from the dispersion of an acrylated epoxy oligomer. For comparison purposes, the properties of films

Table 1—Properties of Films Based on Acrylated Epoxy Oligomer[a]

Property	Dispersion (in 35% Water)	Oligomer (in 45% TRPGDA)	Oligomer (neat)
Viscosity (cps, 25°C)	4120	4270	>1,000,000
Cure speed (fpm)	200	100	100
Lamps (H lamp, 300 wpi)	1	2	2
Adhesion (%)	100	66	61
Pencil hardness	9H+	9H+	4H
Conical bend (inches of crack)	0	0	0
Reverse impact (in lbs)	6	2	0
MEK double rubs	200+	200+	200+
Water double rubs	200+	200+	200+
Gloss[b] (60°)	100	104	107

(a) Formulation: 100 parts acrylate: 4 parts Darocur™ 1173 (based on solids), ~5 mils film on Bonderite.
(b) Average of three readings.

Table 2—Properties of Films Based on Amine Modified Acrylated Epoxy Oligomer[a]

Property	Dispersion (35% Water)	Oligomer (neat)
Viscosity (cps)	3,160 at 25°C	1100-1600 at 65°C
Cure speed (fpm, 1 H lamp, 300 wpi)	200	200
Adhesion (%)	100	100
Pencil hardness	9H+	9H+
Conical bend (inches of crack)	0	0
Reverse impact (in lbs)	14	4
MEK double rubs	200+	200+
Water double rubs	200+	200+
Gloss[b] (60°)	98	110

(a) Formulation: 100 parts acrylate: 4 parts Darocur™ 1173 (based on solids), ~5 mils film on Bonderite.
(b) Average of three readings.

Table 3—Properties of Films Based on Acrylated Aromatic Urethane Oligomer[a]

Property	Dispersion (35% Water)	Oligomer (neat)
Viscosity (cps, 25°C)	2,200	24,500-32,500
Cure speed (fpm, 1 H lamp, 300 wpi)	150	150
Adhesion (%)	100	100
Pencil hardness	9H+	4H
Conical bend (inches of crack)	0[c]	0[c]
Reverse impact (in lbs)	0	0
MEK double rubs	200+	200+
Water double rubs	200+	200+
Gloss[b] (60°)	99	103

(a) Formulation: 100 parts acrylate: 4 parts Darocur™ 1173 (based on solids), ~5 mils film on Bonderite.
(b) Average of three readings.
(c) No cracking, but lack of adhesion.

made from neat acrylated epoxy oligomer and from acrylated epoxy oligomer diluted with tripropylene glycol diacrylate (TRPGDA) monomer are also listed in *Table* 1.

The viscosities of the dispersions are much lower than those of the undispersed oligomers. Also, the viscosity of a dispersion can be easily adjusted to meet the requirements of an application technique through the addition of more deionized water. This type of dilution does not typically affect the stability or the final properties of the dispersion. *Table* 1 compares a water and monomer dilution of an epoxy acrylate oligomer with the same viscosity, as well as neat epoxy acrylate oligomer with much higher viscosity.

It was surprising to find that films made from the aqueous dispersions can have faster cure speeds than films made from undispersed oligomers. As we can see from *Table* 1, the film based on the dispersion has a cure speed of 200 feet/minute with one F-300 H bulb lamp (available from Fusion Systems Corporation). In contrast, the non-aqueous based films have a cure speed of only 100 feet/minute with two F-300 H bulb lamps. It is believed that a water vapor layer is formed on the surface of the film during the drying process. This water vapor layer then acts as an oxygen barrier, and mitigates oxygen inhibition of cure. Consequently, the films based on dispersions can have faster UV cure speed than the films made from undispersed oligomers. (No cure speed differences are seen for those resin systems that were originally designed to give good surface cure, i.e., amine modified epoxy acrylates).

A simple experimental investigation has proved our assumption. No differences in cure speed are seen if the aqueous dispersion based films are dried, and then allowed to sit at room temperature for 30 min to allow the water vapor layer to dissipate. Moreover, the degree of cure of films made from water dispersions and the corresponding undispersed oligomers were measured by FTIR-ATR (attenuated total reflectance) spectroscopy. A peak whose absorbance did not change upon cure was used as an internal reference. The relative change upon cure in acrylate absorbance at 810 cm^{-1} was noted. The relative change in the 810 cm^{-1} absorbance was then used to calculate the percent Reacted Acrylate Unsaturation (% RAU). Percent RAU was 60.0 for "wet films," and 52.0 for "dried films." These results confirm that the level of unreacted double bonds is lower when the films are cured under wet conditions.

It is also interesting to note that films made from dispersions have relatively higher pencil hardness than films made from undispersed oligomers. This improved hardness may be related to better surface cure from the mitigation of oxygen inhibition.

The results of the conical bend and reverse impact tests indicate that the films made from the dispersions have better flexibility than the films made from undispersed oligomers. The cause of this increased flexibility is not clear. One possible reason is that the surfactant and residual water in the films act as plasticizers that flexibilize the films. The increase in adhesion could also be due to this plasticization.

Significantly, unlike many conventional water-soluble polymers, all films made from these dispersions have very good chemical and water resistance. There are only slight differences in the film gloss of dispersions and the film gloss of the corresponding undispersed resins.

Table 4—Properties of Films Based on Acrylated Aliphatic Urethane Oligomer[a]

Property	Dispersion (35% Water)	Oligomer (neat)
Viscosity (cps)	2,488 at 25°C	150-550 at 65.5°C
Cure speed (fpm, 2 H lamps, 300 wpi)	150	100
Adhesion (%)	100	100
Pencil hardness	9H+	9H+
Conical bend (inches of crack)	0[c]	0[c]
Reverse impact (in lbs)	0	0
MEK double rubs	200+	200+
Water double rubs	200+	200+
Gloss[b] (60°)	100	87

(a) Formulation: 100 parts acrylate: 4 parts Darocur™ 1173 (based on solids), ~5 mils film on Bonderite.
(b) Average of three readings.
(c) No cracking, but lack of adhesion.

CONCLUSIONS

Widely used radiation curable oligomers have been successfully dispersed in water by employing and developing dispersion technology. As expected, the dispersions prepared in our laboratory are much lower in viscosity than the corresponding undispersed resins, and are quite stable. Films based on the dispersions can have faster UV cure speed, better surface hardness, and better flexibility compared with films based on undispersed resin systems. These films also have excellent chemical and water resistance. Further research on the cure mechanisms and properties of radiation curable dispersions and their end use applications are currently underway in our laboratory.

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