

Water-soluble UV curable urethane methyl acrylate coating: preparation and properties^{*}

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Received Sept. 29, 2003; revision accepted Dec. 26, 2003

Abstract: Two kinds of water-soluble and ultraviolet (UV) curable oligomers were synthesized and characterized. The oligomers were evaluated as resins for water-based UV curable coating. The rheology of the two oligomers' aqueous solutions was investigated in terms of solid fraction, pH dependence, and temperature dependence. The solutions were found to be Newtonian fluid showing rather low viscosity even at high solid fraction of 0.55. The drying process of the coatings and the properties of the cured coatings were studied by comparing them with water-dispersed UV-curable polyurethane methyl acrylate. It was evident that the water-soluble coating dried more slowly; and that the overall properties were inferior to those of the water-dispersed coating.

Key words: Urethane acrylate oligomer, Ultraviolet curable, Water-borne coating

Document code: A

CLC number: O631.3⁺⁴

INTRODUCTION

During the last 20 years, UV coatings have grown from their first applications in furniture coatings to embrace many industries including electronics, printing and automotive. Because of their fast production rates, low temperature cure and volatile organic compound (VOC) reduction, UV curable coatings have achieved fast growth in the coating market. However, in the conventional UV-cured coating system, the reactive diluents used to reduce the viscosity have strong odor, toxicity and cause skin irritation. In many cases, a certain amount of VOCs are still needed. In order to reduce the use of VOC and reactive diluents,

water-borne UV curable coatings have been developed recently. Water used as the diluent or the dispersing medium can decrease air pollution, risks of fire and improve occupational health and safety. Additionally, it is easier to control the viscosity of water-based formulation and it is more convenient to apply and clean (Noireaux, 1996; Stenson, 1990; Odeberg *et al.*, 1996).

There are mainly two kinds of water-borne system: water-soluble and water-dispersible. Conventional UV-curable prepolymers/oligomers can obtain hydrophilicity by incorporating ionic groups or nonionic polyoxyethylene chain. For the water-soluble UV curable system, viscosity can be controlled by concentration and molecular weight of oligomers. Usually, incorporation of intensive hydrophilic groups would weaken the properties of the coatings, especially the resistance to water. In the latter case, UV-curable prepolymers containing

^{*} Project (No. 20125617) supported by the National Science Fund for Distinguished Young Scholars, China

less hydrophilic groups in their backbone can be self-emulsified in the water. Even without strong shear force, self-emulsification can yield fine particles with improved dispersion stability. It can also reduce the sensitivity of the coating to water (Kim, 1996; Kim and Lee, 1994; Lee *et al.*, 1999; Wang *et al.*, 1999; Kim *et al.*, 1998; Odeberg *et al.*, 1996).

We report two new kinds of water-soluble urethane acrylate oligomers synthesized and evaluated as resin for UV-curable water-based coating. Our ultimate aim was to understand the interplay and relationship between resin structures and coating rheology, coating drying, and performance of the cured coating.

EXPERIMENTAL DETAILS

Materials

Isophorone diisocyanate (IPDI, >99.5%), 2, 4-Tolylene diisocyanate (TDI) were vacuum distilled before use. Dimethylol propionic acid (DMPA, >99%), polypropyleneoxide glycol (PPG 400, Mn=400) were maintained in vacuum at 80 °C for 2 hours to remove the moisture. 2-Hydroxyethyl methacrylate (HEMA, >98%), glycol (analytically pure), N,N-Dimethyl acetamide (DMAc, analytically pure), acetone (analytically pure) and triethylamine (TEA, analytically pure) were dried by molecular sieves. Dibutyltin dilaurate (DBTL, analytically pure) was used as catalyst. P-Hydroxyanisole (analytically pure) and Hy-

droquinone (analytically pure) were used as inhibitors. 1-Hydroxy-cyclohexyl-phenyl-ketone (IR-GACURE184, Ciba) and 1-Hydroxy-2-methyl-1-phenyl-propane-1-one (DAROCUR1173, Ciba) were used as photoinitiators.

Synthesis of UV-curable water borne urethane acrylate oligomers and polyurethane acrylate prepolymer

All of the prepolymer/oligomers were synthesized in a glass reactor with a stirrer, a reflux condenser, thermometer and nitrogen gas inlet system. The amount of the -NCO during reaction was monitored using dibutylamine back titration method and infra-red spectra.

(1) Water-soluble oligomers TDG and IDG

The water-soluble oligomers (as shown in Fig.1) were synthesized by a three-step route.

First, 0.4 mole IPDI/TDI was poured into the reactor under nitrogen atmosphere. Then 0.2 mole DMPA containing 0.5 wt% DBTL dissolved in DMAc was dripped into the reactor for 4 hours until the amount of -NCO reached 0.4 mole. Second, glycol dissolved in 0.5 wt% DBTL was slowly added at proper temperature into the reactor until the -NCO value reached to 0.2 mole. Finally, excessive HEMA (>0.2 mole) with 0.5 wt% inhibitor was added to react with the residual -NCO until the -NCO value became almost zero.

(2) Water-dispersed polyurethane acrylate TDP400

TDP400 was synthesized in acetone solution. PPG400 and TDI were reacted at 40 °C for 2 hours.

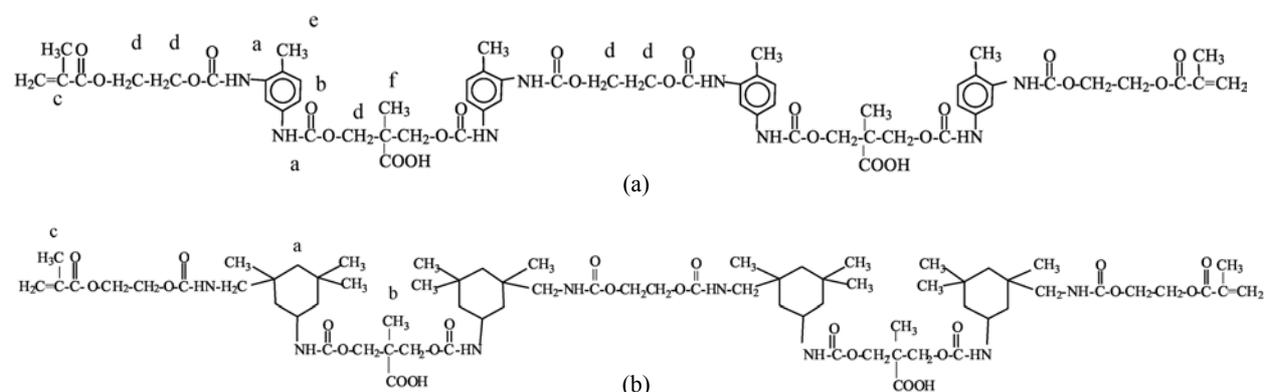


Fig.1 The molecular structures of (a) TDG and (b) IDG

DMPA neutralized by a stoichiometric amount of TEA was dissolved in acetone. Then the solution of DMPA was added to extend the polymer chain and incorporate the carboxyl as a hydrophilic group. In the end, HEMA was poured into the reactor to react with the residual -NCO and incorporate unsaturated C=C group into the prepolymer. The molecular weight and carboxyl amount were controlled by the ratio of the reacted monomers. In the current experiment, the molecular weight of the synthesized prepolymer was 4000 g/mol and the carboxyl amount of it was 0.3 mmol/g.

Preparation of UV-curable coatings

(1) TDG and IDG water solution

The DMAc solutions of TDG and IDG were precipitated from the water and filtered to remove the DMAc solvent and unreacted monomers. After purification, the oligomers neutralized with TEA were diluted with water at room temperature and formulated with 5 wt% DAROCUR1173 as photoinitiator. In order to get an appropriate viscosity for applying coating, the weight fraction of TDG and IDG solution was adjusted to 35 wt%.

(2) TDP400 water dispersion

After having dissolved 3 wt% IRGACURE184, water was added under agitation into the TDP400 acetone solution at a rate of 50 ml/hour to form an aqueous dispersion. During this process, emulsion phase inversion occurred and TDP400 dispersion with water as the continuous phase was achieved. The dispersion solution was distilled to remove the acetone solvent and its solid content was adjusted to 40 wt%.

The coatings of these formulated solutions/dispersion was prepared according to GB 1727-92. Drying and curing were carried out on the tailor-made UV curing apparatus with a medium pressure mercury lamp (4 kW) and 4 infrared lamps (2 kW/lamp).

Analysis

The H-NMR spectra of solutions in CD_3COCD_3 were obtained using an AVANCE DMX500 spectrometer. Molecular weight distributions were measured by a Waters 150-C ALC/

GPC using THF as the carrier solvent. The acidic content was measured by KOH titration method. The rheologic behavior of the oligomers' solutions was measured (with Rheolab MC1 Rheometer) below temperature of 45 °C for preventing the polymerization of the vinyl groups. The test of Pencil hardness, Crosshatch adhesion (/25), impact strength, Gloss (60°) and absorbability of water for the coatings followed GB/T 6739-1996, GB 9286-88, GB/T 1732-93, GB 1743-79, and GB/T 1738-1979 (Chinese National Standard), respectively. The gel content of coating was measured by Soxhlet extraction method using tetrahydrofuran as solvent.

RESULTS AND DISCUSSION

Characterization of molecular structure of TDG and IDG

Figs.2 and 3 show the H-NMR spectra of TDI-DMPA-Glycol and IPDI-DMPA-Glycol.

In Fig.2 and Fig.3, H-NMR signals for TDG were assigned as follows: $\delta=7.9 \times 10^{-6}$ (Ha) for the -NH- group of TDI; $\delta=7.2 \times 10^{-6}$ (Hb) for the phenyl group of TDI; $\delta=5.6 \times 10^{-6}$ and 6.1×10^{-6} (Hc) for the

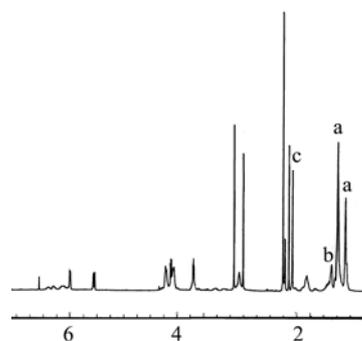


Fig.2 H-NMR spectra of TDG

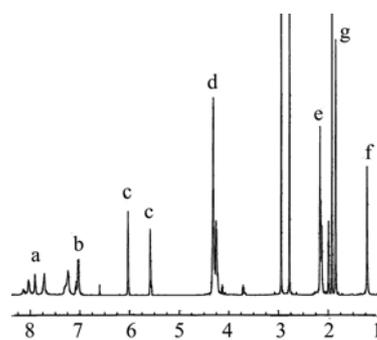


Fig.3 H-NMR spectra of IDG

H₂C=C- of HEMA; $\delta=4.3 \times 10^{-6}$ (Hd) for the methylene group of DMPA; $\delta=2.2 \times 10^{-6}$ (He) for the methyl group of TDI; $\delta=1.3 \times 10^{-6}$ (Hf) for the methyl group of DMPA. The ratio of the unsaturated C=C to the phenyl group was calculated by the areas of Hc and He: $c/2:e/3=1.623/2:5.403/3 \approx 1:2$. The ratio of phenyl group to carboxylic group was calculated by: $e:f=5.403:3 \approx 2:1$. H-NMR signals for IDG were as follows: $\delta=1.0 \times 10^{-6}$ and 0.9×10^{-6} (Ha) for the cyclohexyl group of IPDI; $\delta=1.2 \times 10^{-6}$ (Hb) for the methyl group of DMPA; $\delta=1.9 \times 10^{-6}$ (Hc) for the methyl group of HEMA. The ratio of phenyl group to carboxylic group was calculated by: $e:f=5.403:3 \approx 2:1$. The ratio of IPDI, DMPA and HEMA was calculated by the same way: $a/3:b/c=7.0447/3:1.3904:1.1357 \approx 2:1:1$.

The acid contents of TDG and IDG were 87.1 mg KOH/g and 75.8 mg KOH/g, which accorded well with the calculated values from the structures shown in Fig.1.

The average molecular weights of TDG were $M_n=2.21 \times 10^3$ g/mol and $M_w=2.80 \times 10^3$ g/mol and that of IDG were $M_n=1.90 \times 10^3$ g/mol and $M_w=3.10 \times 10^3$ g/mol. The indexes of polydispersity (IP) of TDG and IDG were 1.26 and 1.63 respectively. During the process of synthesis, it was inevitable that some of the oligomers with two -NCO on the ends reacted with di-hydroxyl compounds and the molecular chains were extended. So, the products synthesized were a mixture of molecules with different chain lengths.

It is reasonable to conclude that the oligomers designed were synthesized.

Rheologic behavior of TDG and IDG solutions

The rheologic behaviors of urethane acrylate oligomers' solutions were measured with varying weight fraction of the oligomers, temperature, and pH and are shown in Fig.4.

In Fig.4, all the curves are linear, indicating that the viscosity of the urethane acrylate solution was independent of the shear rate. All of the solutions of different fractions had flow index n equal to 1.0. It was apparent that they were Newtonian fluids in the experiments; the weight fraction reached 0.5.

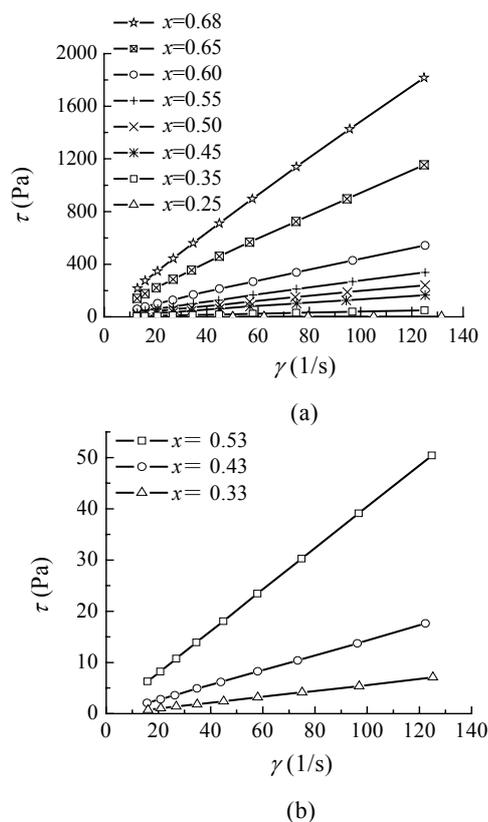


Fig.4 Shear stress versus shear rate for IDG (a) and TDG (b) in solutions of different fractions at the temperature of 23 °C, pH=7

IDG solution can keep the Newtonian fluid behavior when its weight fraction is 0.68. Fig.5 is the change of viscosity for IDG solution and TDG solution with the weight fraction of oligomers. The IDG solution and TDG solution having rather low viscosity, especially below the weight fraction of 0.5, could be attributed to their low molecular weight and molecular structure. The viscosity of TDG solution was lower than that of the IDG solution and less than 0.4 Pa·s below the weight fraction of 0.5. The viscosity of IDG solution rose sharply above that of the 0.35 weight fraction. The viscosity behaviors were like those in a colloid system. The molecular structures suggested that IDG resin is more hydrophobic than TDG resin. It seemed possible that the IDG solution might actually be a colloid system with very small particle size when the solid content were high.

Temperature is an important factor influencing the viscosity of oligomer solution. The viscosity of

IDG solution decreases continuously with increase of temperature (Fig.6). The same phenomenon was observed with TDG solution. The calculated flow activation energy of IDG solution was 56 J/mol when the weight fraction was 0.60 and 28 J/mol when the weight fraction was 0.23. It was found that the activation energy increased with the solution's fraction. In high fraction solution, the interaction between molecules was greater than that of the low fraction. So more energy was needed for a molecule to move in order to control the interaction.

As a kind of ionomer, the urethane acrylate had carboxyl group to obtain its hydrophilicity. After 100% neutralized by TEA, the solutions' viscosity did not change much with pH in the studied ranges (Fig.7).

Properties of the UV-curable coatings

Fig.8 shows the change of water content with heating time during the drying process. The water

borne UV solutions and emulsions were dried by infrared heaters. With increase of heating time, the drying curves leveled off in the end. It was found that it was difficult to remove water in the water-soluble coating with the current infrared heaters. In the dried coating, the water content was as high as around 0.15, which was much higher than that of the dried water-dispersed coating. At first thought, this could be ascribed to the higher hydrophilic group. However, when the drying curves of the coatings of mixing water-soluble and water-dispersed coating were checked, it was found that the water content in the water dispersed coating was very close to that of the water-soluble coating. It is suggested that the difference of two kinds of water-based coating in drying mode should play a key role in causing high water content of the dried coating. The different drying modes were also reflected in the drying rate; it was found that there was little difference between water-soluble and water-disper-

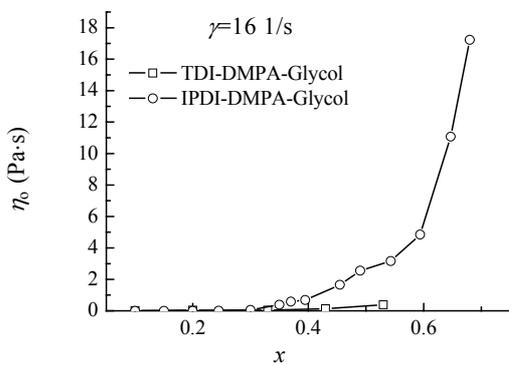


Fig.5 Viscosity change for IDG solution and TDG solution with the weight fraction in water at 23 °C, pH=7, Shear rate = 16 s⁻¹

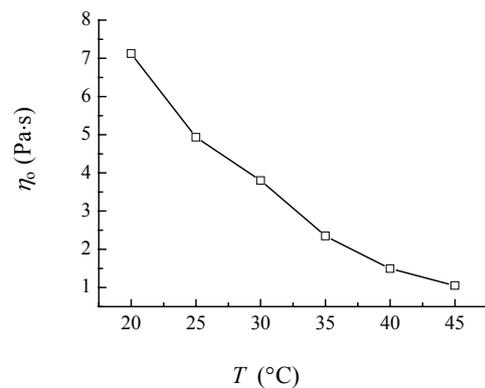


Fig.6 Viscosity of IDG solution of different temperature. Weight fraction=0.60, pH=7

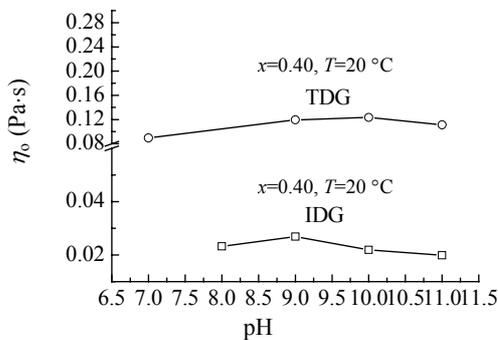


Fig.7 Viscosity of IDG and TDG solutions of different pH at 20 °C

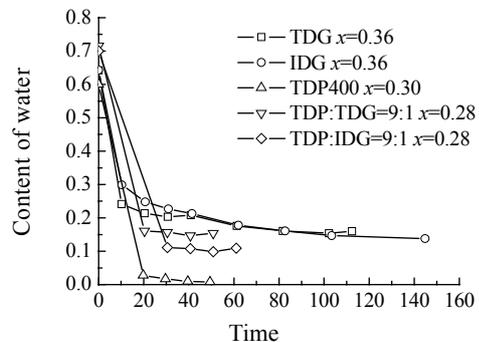


Fig.8 The drying curves of different waterborne system

Table 1 Coating properties of different waterborne system

Resin	AC ¹⁾	Water content	Gel content	PeH ²⁾	CA ³⁾	IS ⁴⁾	WA ⁵⁾	Gloss (60°)	
								Glass board	Steel board
TDG	1.56	15.4%	66%	4H	1~2	7	101%	155	111
IDG	1.35	13.8%	55%	3H	3~4	1	102%	134	94
TDP400	0.30	1.0%	92%	3H	0~1	>50	38%	143	100
TDP-TDG	0.43	14.7%	84%	4H	0~1	>50	57%	131	81
TDP-IDG	0.41	11.0%	85%	4H	0~1	>50	70%	132	94

¹⁾ AC: Acid content (mmol/g); ²⁾ PeH: Pencil hardness; ³⁾ CA: Crosshatch adhesion (/25); ⁴⁾ IS: Impact strength (50 cm);

⁵⁾ WA: Water absorbability

sed coating in the early stage. However, after the water content was decreased to lower than around 0.25, the drying rate of the water-soluble coating decreased dramatically.

Table 1 summarizes the properties of the cured coating. It was clear that the overall properties of TDP400 were better than those of IDG and TDG. Compared with TDP400 emulsion, the water-soluble urethane acrylate oligomers had lower gel content and poor impact strength. It is believed that the low molecular weight and absence of soft segments in the polymer precursor deteriorate the physical properties of the coatings. The high ionic content helped the urethane acrylate oligomers dissolve in water, but they made the coatings more sensitive to water. The water absorbability of the water-soluble oligomers' coatings was much higher than that of TDP400.

TDP-TDG was mixture of TDP400 emulsion and TDG solution. TDP-IDG was mixture of TDP400 emulsion and IDG solution. The mass ratio of TDP400 to the urethane acrylate was 9:1. It is found that the adding of water-soluble oligomers to the water dispersion did not influence much the coating's physical properties but only the coating's absorbability of water.

CONCLUSION

Water-soluble and UV-curable oligomers, TDG and IDG, were synthesized by incorporating dimethylol propionic acid (DMPA) and 2-hydroxyethyl methacrylate (HEMA) on the molecular backbone to obtain the hydrophilicity and unsaturated C=C groups for UV curing. Structures of the oligomers were confirmed by H-NMR spectra, acid

content and the -NCO value during reaction. The urethane acrylate aqueous solutions showed rather low viscosity below the 0.5 fraction and they were Newtonian fluids. The drying process of the coating was different from that of UV curable, especially in the late stage. The physical properties of the UV cured coatings turned out to be poor compared with that of TDP400 UV-curable emulsion. The UV cured coatings seemed to be more sensitive to water than that of UV curable emulsion.

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