



# Investigation of non-isocyanate urethane dimethacrylate reactive diluents for UV-curable polyurethane coatings

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## ABSTRACT

Three non-isocyanate urethane dimethacrylate reactive diluents 2-(methacryloyloxy)ethyl 2-(methacryloyloxy)ethylcarbamate (EOAED), 2-(methacryloyloxy)ethyl 3-(methacryloyloxy)propylcarbamate (POAED), and 1-(methacryloyloxy)propan-2-yl 3-(methacryloyloxy)propylcarbamate (POAPD) were synthesized by the reaction of a cyclic carbonate with an amino alcohol followed by a second reaction with the methacrylic anhydride. These reactive diluents were formulated with an acrylated polyester (APE) oligomer and free radical photoinitiator to prepare UV-curable polyurethane coatings. For comparison with urethane dimethacrylate reactive diluents, ethylene glycol dimethacrylate (EGDMA) was also used. The effect of reactive diluent type and content on the viscosity of the APE oligomer was measured. After UV curing, the viscoelastic, tensile, and thermal properties of the cured films were evaluated as a function of the reactive diluent using dynamic mechanical thermal analysis (DMTA), tensile, differential scanning calorimeter (DSC), and thermal gravimetric analysis (TGA). In addition, coating properties such as pencil hardness, chemical resistance, impact resistance, and gloss were also investigated. It was found that crosslink density, storage and tensile modulus, pencil hardness, chemical resistance, gel content, total water absorption, and glass transition temperature ( $T_g$ ) were directly proportional to the amount of the reactive diluent. The urethane dimethacrylate reactive diluents show significant improvements in impact resistance and elongation-at-break properties compared to the EGDMA. It was found that the optimum level of the urethane dimethacrylate reactive diluents concentration is between 10 and 20 wt%.

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## 1. Introduction

UV-curable coatings have received considerable increasing attention on account of fast curing and low energy consumption [1]. Formulations for UV-curable coatings usually consist of three major components: photoinitiator, oligomer, and reactive diluent [2]. The oligomer is functionalized with reactive end groups that participate in the film formation process, and the structure of the oligomer governs the viscoelastic properties of the final cured film. The reactive diluent lowers the viscosity of the resin, and copolymerizes with oligomer to form the crosslinked film [3].

There are three major types of oligomers widely used in free radical UV-curable coatings: epoxy acrylate, polyester acrylate (acrylated polyester, APE), and urethane acrylate oligomer. Urethane acrylate oligomers are usually prepared by the reaction of a polyol with a diisocyanate to yield an isocyanate terminated oligomer. This oligomer is then reacted with a hydroxyethyl acrylate monomer [4]. Urethane acrylates are widely used as oligomers

for UV-curable coatings, as a consequence of excellent mechanical properties, combined with excellent chemical resistance [1,4–8]. A drawback of the urethane acrylate is the toxicity of the isocyanate starting material [9].

Reactive diluents for free radical based UV-curing systems are usually acrylic or methacrylic monomers which are added to reduce the viscosity of precured liquid oligomer and modify the property of final cured solid film [10]. Generally, mono-functional reactive diluents lead to decreased modulus and increased ductility, whereas di- and multi-functional reactive diluents lead to the opposite effect [11]. It was well established that a high degree of functionality leads to high reaction rate and high degree of crosslink density [12]. The high degree of functionality also can lead to low final degree of conversion, because the early gelation of the irradiated sample restricts the mobility of the reactive sites. In addition, the high degree of functionality also can lead to glassy polymer materials, which are harder and less flexible than monofunctional type systems [13,14].

In previous study, the effect of the functionality and chemical structure of the reactive diluents (ethylhexylacrylate, hexanediol diacrylate, and isobornyl acrylate as reactive diluents) on the thermal and mechanical properties of the UV-curable urethane acrylate oligomer were investigated [15]. The functionality of the reactive

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diluent did not affect the onset value of the glass transition temperature. However, the amount of the diacrylate reactive diluent did have a proportional effect on the equilibrium and storage modulus in the rubbery state [15]. The structure of the reactive diluent has a effect on oxygen inhibition of (meth)acrylates photopolymerization. Compared to acrylates, methacrylates are much less sensitive to oxygen [16].

More recently, urethane dimethacrylate monomers prepared via the non-isocyanate route from the reaction of a urethane diol with methacrylic anhydride have been reported [17–19]. Photopolymerization of the urethane dimethacrylate monomer was investigated with respect to polymerization rates and conversions using photoinitiated differential scanning calorimetry (photo-DSC) [17]. Although the photopolymerization of monomers were reported, the monomers were not used as reactive dilute that is with a reactive oligomer.

In this paper, UV-curable polyurethane (PU) coatings were prepared using an acrylated polyester (APE) reactive oligomer with three urethane dimethacrylate reactive diluents, respectively. Three reactive diluents 2-(methacryloyloxy)ethyl 2-(methacryloyloxy)ethylcarbamate (EOAED), 2-(methacryloyloxy)ethyl 3-(methacryloyloxy)propylcarbamate (POAED), and 1-(methacryloyloxy)propan-2-yl 3-(methacryloyloxy)propylcarbamate (POAPD) were synthesized by the reaction of the cyclic carbonate with the amino alcohol followed by the reaction with the methacrylic anhydride. For comparison, ethylene glycol dimethacrylate (EGDMA) was also used as reactive diluent. The viscoelastic, tensile and thermal properties of the cured films were evaluated as a function of the reactive diluent. In addition, coating properties such as pencil hardness, chemical resistance, impact resistance, and gloss were also investigated.

## 2. Experimental

### 2.1. Materials

Adipic acid (AA, 99%), isophthalic acid (IPA, 99%), 1,6 hexane diol (HD, 97%), trimethylolpropane (TMP, 98%), *p*-xylene (99%), dibutyl tin oxide (DBTO, 98%), ethylene carbonate (EC, 99%), propylene carbonate (PC, 99%), 2-aminoethanol (EOA, 99%), 3-aminopropanol (POA, 99%), methacrylic anhydride (MAA, 94%), dichloromethane (99%), hydroquinone (99%), triethyleneamine (TEA, 99%), potassium hydroxide (KOH, 85%), chloroform-*d* (CDCl<sub>3</sub>, 100%), dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>, 100%), anhydrous magnesium sulphate (99%) all Aldrich products were used as received. 4-(dimethylamino)pyridine (DMAP, 99%) was obtained from Acros Organics. Photoinitiator Darocur 4265 was obtained from Ciba Specialty Chemical, NY. Aluminum panels (type A with number A-36, bare surface, smooth mill finish, 3 × 6 in.) were obtained from Q-panel Lab Products.

### 2.2. Instrumentation

The nuclear magnetic resonance (NMR) spectra were taken in a Varian Mercury 300 MHz spectrometer. Molecular weight and its distribution were determined by gel permeation chromatography (GPC) (Waters Corporation). The coating was cured by a Fusion UV-curing chamber (F300SQ Series) having a mercury arc bulb (150 mW cm<sup>-2</sup>, UVB, 257 nm). Tensile tests were performed on an Instron 5567 (Instron Corp., Grove City, PA). The viscoelastic properties were measured on a dynamic mechanical thermal analyzer (DMTA, Q800, TA Instruments). The thermal properties were characterized by differential scanning calorimeter (DSC, Q200, TA Instruments) and thermogravimetric analysis (TGA, Q50, TA Instruments).

### 2.3. Preparation of the acrylated polyester (APE) oligomer

In a typical procedure, APE oligomer was prepared via a two-step reaction. The hydroxyl terminated polyester was synthesized in the first step. The molar ratio of alcohol to acid was 11:8. Adipic acid (AA) (100 g, 0.68 mol), isophthalic acid (IPA) (113.67 g, 0.68 mol), 1,6 hexane diol (HD) (161.71 g, 1.37 mol) and trimethylolpropane (TMP) (45.90 g, 0.34 mol) were charged in a 500 mL four-neck round bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap, and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt% (1.69 g) of DBTO, a transesterification catalyst, was used. Then, 3 wt% (12.64 g) of *p*-xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20 to 150 °C at a rate of 4.3 °C/min, and then from 150 to 210 °C at a rate of 0.25 °C/min. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin (ASTM D 1639-90). The hydroxyl number of polyesters (160.4 mg KOH/g resin) was determined by ASTM method (ASTM D 1957-86).

Acrylate terminated polyester was synthesized in the second step, the temperature was held to 120 °C. Acrylic acid (AA, the mole ratio of the acid group in the AA to the hydroxyl group in the polyester polyol kept at 1.05), 1 wt% (3.72 g, 21.6 mmol) of *p*-toluene sulphonic acid (*p*-TSA) catalyst and 0.05 wt% (186 mg, 1.7 mmol) of hydroquinone inhibitor were added, the temperature was maintained at 120 °C for 14 h. Then, 1.5 wt% (5.58 g, 54.6 mmol) of 3-methyl-3-hydroxymethyl-oxetane was added, and maintained at 120 °C for another 20 min. Then, solvent and volatile residuals were removed in vacuo resulting in a light yellow acrylated polyester oligomer: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 0.84–0.98 (m, 2 H) 1.33–1.47 (m, 8 H) 1.50–1.53 (m, 1 H) 1.56–1.69 (m, 11 H) 1.73–1.83 (m, 4 H) 2.22–2.39 (m, 6 H) 3.57–3.69 (m, 1 H) 3.99–4.16 (m, 6 H) 4.27–4.44 (m, 5 H) 5.75–5.89 (m, 1 H) 6.03–6.16 (m, 1 H) 6.32–6.44 (m, 1 H) 7.45–7.56 (m, 1 H) 8.11–8.28 (m, 2 H). The average molecular weight was found to be Mn = 3500, with a PDI = 1.8 via GPC.

### 2.4. Preparation of non-isocyanate urethane dimethacrylate reactive diluents

The synthesis process consists of two steps. In a typical procedure to prepare EOAED non-isocyanate urethane dimethacrylate reactive diluent, ethylene carbonate (88.06 g, 1.00 mol) was dissolved in 100 mL dichloromethane, and such solution was drop added into the 2-aminoethanol (61.08 g, 1.00 mol) and dichloromethane (200 mL) mixture at 0 °C. After finish adding, the mixture was stirred at room temperature for 24 h. The slightly yellow liquid (yield: 98%) was obtained after rotary evaporation of the dichloromethane. In the second step, urethane diol EOA-EC (14.9 g, 0.1 mol) was dissolved in 300 mL dichloromethane at 0 °C, 4-(dimethyl-amino) pyridine (DMAP) catalyst (122 mg, 1 mmol), and hydroquinone inhibitor (28 mg, 0.25 mmol) were added, followed by drop addition of triethylene diamine (TEA) (28.3 g, 0.28 mol), and then drop addition of methacrylic anhydride (39.4 g, 0.24 mol) under the N<sub>2</sub> atmosphere. The reaction mixture was stirred at 0 °C for 24 h. Then saturated sodium bicarbonate solution (294.7 g) was drop added to get two phase separated mixture. The product (top layer) was collected, washed with brine (300 mL 3×) and distilled water (300 mL 2×), and dried in anhydrous magnesium sulphate. After the dichloromethane was evaporated, a pale yellow liquid product was obtained (yield: 42%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ (ppm) = 1.86 (m, 6 H, -CH<sub>3</sub>), 3.27 (qd, *J* = 5.67, 1.39 Hz, 2 H,

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