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UV curable glycidyl carbamate based resins

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ABSTRACT

The synthesis and characterization of UV curable resins based on glycidyl carbamate chemistry have been explored. Glycidyl carbamate (GC) functional resins have been used to obtain crosslinked coatings with a wide range of properties using several crosslinking techniques such as epoxy-amine, self-crosslinking, and sol–gel. GC resin technology was further expanded to UV curable coatings by reacting polyfunctional GC resins with acrylic acid to yield acrylated glycidyl carbamate (AGC) resins. Alcohol-modified UV curable GC resins were also prepared to obtain lower viscosity. Commonly used reactive diluents were used to prepare a UV curable GC coating formulations. The coatings were cured in air using a Fusion LC6B Benchtop Conveyer with an F300 UV lamp. The degree of conversion of acrylic double bonds during UV curing was determined using real time FTIR and showed that the resins had fast cure rates and high extents of conversion of acrylate groups. Coating properties such as hardness, impact strength, methyl ethyl ketone double rubs, flexibility, and adhesion were studied. Dynamic mechanical analysis was used to determine crosslink density of the coatings. Differential scanning calorimetry and thermogravimetric analysis were used to study the thermal properties of the coatings. The type of polyisocyanates and the extent of modification in GC resins influenced the degree of conversion, crosslink density, and coating performance.

1. Introduction

UV-curing or radiation curing has gained interest due to its unique economic and ecological advantages. These unique advantages are ultrafast curing at ambient temperatures or below and 100% solids or low VOC coating formulations, as in most cases solventless liquid monomers, oligomers, or polymers are used [1–4].

Radiation curing or photocrosslinking produces densely crosslinked polymeric materials within a very short time (s) from multifunctional monomers, oligomers or telechelic polymers upon exposure to radiation such as ultraviolet light (UV) or electron beam (EB) [5–7]. For more than three decades radiation curing has been successfully used for many applications such as coatings, adhesives, inks, optical waveguides, and microelectronics. UV curable coatings are widely used for furniture, plastic substrates, optical fibers, compact discs, headlight lenses, and metal substrates [4,8]. Photopolymerizable monomers, oligomers and polymers (based on acrylate, vinyl and epoxide groups) are widely used to produce UV curable coatings, inks, adhesives, composites, etc. The structure and functionality of the UV curable oligomers, polymers and reactive diluents and type of photoinitiators governs the speed of cure, extent of crosslinking and final performance of coatings (flexibility, hardness, adhesion, and scratch and chemical resistance) [4,7,9–12].

Glycidyl carbamate (GC) functional resins are obtained from the reaction of isocyanate functional compounds with glycidol. GC resins contain urethane (–NHCO–) and epoxy functional groups in their structure. Thus, an unique property of GC resins is that the performance of urethane and the reactivity of epoxide are combined in a single resin structure [13,14]. Polyurethane and epoxy resins are widely used in numerous commercial applications such as coatings, composites, high performance polymers, etc. Urethane coatings offer excellent toughness, adhesion, flexibility and chemical resistance. Epoxy coatings offer excellent corrosion and solvent resistance, adhesion and versatility of crosslinking (curing) mechanisms [15,16]. The combination of urethane and epoxy functional groups in GC resins imparts an excellent set of properties to GC-based coatings. Reactive epoxy groups in GC resins can be crosslinked using amines and by thermally induced self crosslinking to produce high performance coating systems [13,14,17,18]. GC resins have also been used to produce organic–inorganic hybrid coatings by sol–gel crosslinking [19–21]. Highly functional GC resins can have a very high viscosity due to intermolecular hydrogen bonding, however, modification of GC resins with alcohols reduces their viscosity up to 90%, and produces coatings with a wide range of properties [22].

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Table 1
Recipes for the synthesis of acrylated GC resins.

Synthesis of GC resin						Synthesis of acrylated GC resin			
GC resin	Desmodur N 3200 (gm)	Desmodur N 3600 (gm)	EP (gm)	Glycidol (gm)	EEW (g/eq)	Acrylated GC resin	GC resin (gm)	AA (gm)	Final acid value (mg KOH/gm)
BGC	100	–	–	40.50	273	ABGC	83.12	21.92	7
IGC	–	100	–	40.45	276	AIGC	75.26	19.70	7
IGC-EP 15%	–	150.65	12.87	51.80	338	AIGC-EP 15%	75.10	16.16	6
IGC-EP 33%	–	150	28.14	40.04	425	AIGC-EP 33%	95.30	16.13	7

With the realization that GC resins produce coatings with an excellent combination of properties when crosslinked by amines, self-crosslinking, and by hybrid sol–gel crosslinking, it was of interest to extend the technology of GC resins for use in UV curing. While the endcapping of epoxy and polyurethanes with acrylate groups is well-known, it appears that reaction of glycidyl carbamate groups with acrylic acid to form acrylated GC resins has not been explored. Thus, the goal of the research presented in this article was to carry out a preliminary study on the synthesis of UV curable GC resins and study the properties of the cured coatings. Biuret glycidyl carbamate (BGC), isocyanurate glycidyl carbamate (IGC) and alcohol-modified IGC resins were synthesized and reacted with acrylic acid to obtain a series of acrylated GC resins. Several reactive diluents were used to prepare UV curable coating formulations. UV cured acrylated GC coatings were produced and their properties were studied.

2. Experimental

2.1. Materials

Polyisocyanate resins used to obtain GC resins were hexamethylene diisocyanate isocyanurate (Desmodur N 3600) and hexamethylene diisocyanate biuret (Desmodur N 3200) provided by Bayer MaterialScience. Dixie Chemical supplied Glycidol. Glycidol was stored refrigerated to minimize the formation of impurities. Dibutyltindilaurate (DBTDL), purchased from Aldrich, was used to catalyze the isocyanate and hydroxyl reactions to form the glycidyl carbamate (GC) resins. Acrylic acid (AA) was purchased from Sigma Aldrich. *p*-Toluenesulfonic acid (*p*TSA) purchased from Aldrich was used as a catalyst for transesterification reaction between AA and the epoxy group. Hydroquinone, purchased from Sigma Aldrich, was used as an inhibitor to avoid gelation during the esterification reaction. Ethylene glycol propyl ether (EP) was obtained from Fluka–Aldrich. All the reagents were used as received without any further purification. CN929, a trifunctional urethane acrylate resin obtained from Sartomer was used as a control. Reactive diluents used were 1,6 hexanediol diacrylate ester (SR 238), 2(2ethoxyethoxy)ethyl acrylate (SR 256), ethoxylated trimethylolpropane triacrylate (SR 454) provided by Sartomer. CN373, a reactive amine coinitiator obtained from Sartomer was used to improve surface cure. Photoinitiator Irgacure 184 (1-hydroxycyclohexyl phenyl ketone) was obtained from Ciba Chemicals.

2.2. Synthesis of acrylated glycidyl carbamate resins

The synthesis of the acrylated GC resins was carried out in two steps. In the first step, glycidyl carbamate resins, biuret glycidyl carbamate (BGC), isocyanurate glycidyl carbamate (IGC), and modified GC resins based on isocyanurate and EP were synthesized. In the second step, the epoxy groups of the GC resins were reacted with AA to obtain the corresponding acrylated GC resins. Table 1 shows the recipes for the synthesis of the acrylated GC resins.

A 500 ml four neck reaction vessel was used for the synthesis of acrylated GC resins. The vessel was fitted with a condenser, nitrogen inlet and Model 210 J-KEM temperature controller and mechanical stirrer. A water bath was used for heating and cooling the vessel. For the synthesis of BGC and IGC resins, the reaction vessel was charged with the polyisocyanate resin followed by addition of the required amounts of glycidol. For the synthesis of the alcohol-modified IGC resins, the vessel was charged with the required amount of isocyanurate polyisocyanate, glycidol, and the modifier EP. After the vessel was charged with the required amount of polyisocyanate, glycidol, and optional modifier, the reaction mixture was stirred for about 45–60 min at 40–45 °C to ensure a homogeneous mixture. The catalyst (DBTDL), in solution in tertiary butyl acetate (1–2% by wt.), was then added. The amount of catalyst added was 0.03% by wt. (of the total reaction charge). After the addition of catalyst around at about 40–45 °C, all of the reactions showed an exotherm, bubble formation and an increase in viscosity. The reactions were continued until the –NCO peak in the FTIR spectrum disappeared completely. The epoxy equivalent weight (EEW) of the GC resins was determined by titration.

In the second step, the acrylated GC resins were obtained by the reaction of the GC resins with AA. The reaction was carried out in a similar four neck reactor assembly used for the synthesis of GC resins. The required amount of reactants, GC resin, and AA (1:1 epoxy:acid stoichiometric ratio), were added to the reactor. The reaction mixture was stirred for about 20 min at 45–50 °C to obtain a homogeneous mixture. Then, the catalyst (*p*TSA) of about 0.03% by wt. (of the reactants) was added at 40 °C along with hydroquinone (0.02–0.09% by wt. of the total reactants). The reaction was carried out at 65–75 °C. The reaction progress was monitored by acid value titration and continued until the acid value reached 8.

2.3. FTIR measurements

A Nicolet 8700 FTIR spectrometer from Thermo Scientific was used for the FTIR measurements. Sample aliquots were taken and coated on a potassium bromide salt plate. Spectra acquisitions were based on 32 scans with a data spacing of 1.98 cm^{-1}. The change in band absorption of isocyanate (2272 cm^{-1}), –OH and –NH (3750–3000 cm^{-1}), amide (1244 cm^{-1}), epoxide (910 cm^{-1} and 859 cm^{-1}), and acrylate (810 cm^{-1}) bands were used to follow the reaction progress.

2.4. Epoxy titration

Epoxy equivalent weight of the resins was determined by titration with hydrogen bromide (HBr) according to ASTM D1652. The required amount of resin (0.06–0.8 gm) was dissolved in 5–10 ml of chloroform and titrated against a standardized HBr solution prepared in glacial acetic acid. The indicator used was a solution of crystal violet in glacial acetic acid. The end point of the titration was the appearance of permanent yellow-green color.