

# Novel UV Curable Polyurethanes from Glycidyl Carbamate (GC) Resins

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## **1. Introduction**

Glycidyl carbamate (GC) resins are produced by reaction of isocyanate functional compounds with glycidol. GC resins contain urethane (-NHCO-) and epoxy functional groups in their structure.<sup>1</sup> 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.<sup>2,3</sup> 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 self crosslinking to produce high performance coating systems.<sup>1,4</sup> The development of GC resin technology carried out in our group has produced promising results. Our group used GC resins to produce hybrid sol-gel coatings.<sup>5</sup> GC resins were also modified with several alcohols which could reduce their viscosity up to 90%. Their structure-property relationships with coatings were studied as a function of alcohol modification.<sup>6</sup>

Densely crosslinked polymeric materials are readily produced by UV curing technology. Photopolymerizable monomers, oligomers and polymers (based on acrylate, vinyl and epoxide groups) are widely used to produce UV curable coatings, inks, adhesives, composites, etc. UV curable coating technology is considered as an environmentally friendly (green) technology because use of reactive diluents in place of organic solvents significantly reduces the amount of volatile organic compound (VOC) emission. Structure and functionality of UV curable oligomers, polymers and reactive diluents and type of photoinitiators governs speed of cure, extent of crosslinking and final performance of coatings (flexibility, hardness, adhesion and scratch and chemical resistance).<sup>7,8</sup>

In the present study, we have reacted a GC resin with acrylic acid to generate a novel urethane-acrylate resin suitable for UV curable coatings. Several reactive diluents were used to make UV curable coating formulations and UV cured GC coatings were produced. Preliminary results of a study made to determine the performance of UV cured GC coatings are presented.

## 2. Experimental

### 2.1 Materials

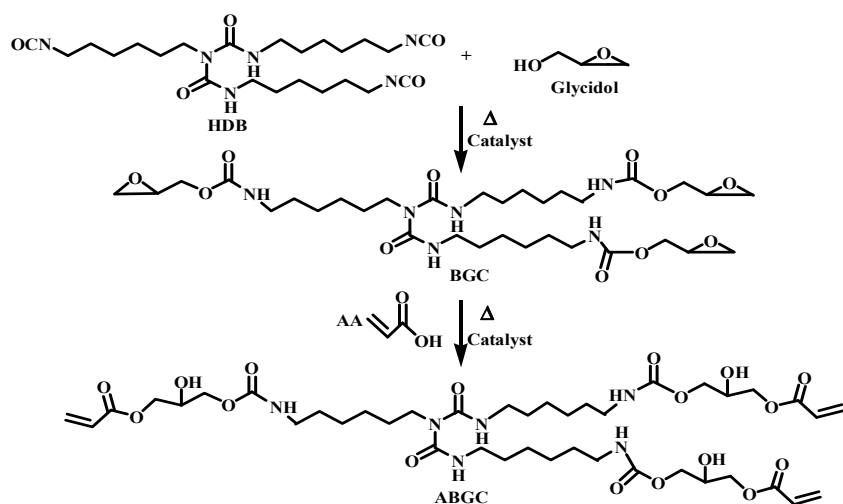
Hexamethylene diisocyanate biuret (HDB), a biuret resin condensate derived from hexamethylene diisocyanate (Tolonate HDB-LV), was provided by Rhodia Inc. HDB-LV has an NCO equivalent weight of 175.44 g/eq. Glycidol was supplied by Dixie Chemical. Glycidol was stored refrigerated to minimize the formation 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 inhibitor to avoid gelation by free radical polymerization during the esterification reaction. All reagents were used as received without any further purification. CN 929, a trifunctional urethane acrylate resin obtained from Sartomer was used as control. Reactive diluent used were 1,6 hexanediol diacrylate ester (SR 238), 2(2ethoxyethoxy)ethyl acrylate (SR 256), ethoxylated trimethylolpropane triacrylate (SR 454) provided by Sartomer. CN 373, 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 resin

A 500 ml four neck reaction vessel was used for the synthesis of biuret glycidyl carbamate (BGC) resin. 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. The stoichiometric equivalent amount of isocyanates and glycidol based on –NCO and –OH groups used for the synthesis of BGC resin was 1:1 (NCO:glycidol). During the synthesis of resins, the reaction vessel was charged with HDB-LV followed by addition of the required amounts of glycidol and modifier. The reaction mixture was stirred for about 45 – 60 min. at 40 – 45 °C to ensure a homogeneous mixture. The catalyst (DBTDL), in the form of solution in tertiary butyl acetate (1 – 2 % by wt.), was added after the completion of mixing. 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 FTIR spectra disappeared completely.

Acrylated BGC (ABGC) resin was obtained by reaction of BGC resin with AA. The reaction was carried out in a similar four neck reactor assembly used for the synthesis of BGC resin. The required amount of reactants, BGC resin and AA (1:0.8 molar ratio), were added to the reactor. The reaction

mixture was stirred for about 20 min. at 45 – 50 °C to obtain a homogeneous mixture. After completion of mixing, 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 the temperature between 65 – 75 °C. After 2-3 hrs of reaction, reactive diluents SR 238 and SR 256 were added (each 12 % by wt. of the total reactants) to the reaction to reduce the viscosity of resin. The reaction progress was monitored by acid value titration. The reaction was continued until acid value reached around 8 and became constant. Figure 1 is a schematic representation of the synthesis of ABGC resin. The resin was collected in a glass jar. Analysis of the resin was done by <sup>13</sup>C NMR to confirm the functionalization of BGC resin by AA.



**Figure 1.** Schematic representation of the synthesis of ABGC.

### 2.3 UV curable formulation and coating preparation

Several combinations of reactive diluents and photoinitiators were used to produce defect-free (wrinkles and tack) UV cured coating films. The formulation recipe is shown in Table 1. The required ingredients were added in a plastic cup, warmed and mixed to ensure homogeneous mixing. The drawdowns were made at 8 mils wet thickness on steel panels (Q panels, QD 36). The coated panels were exposed to UV radiation (lamp power 38mW/cm<sup>2</sup>, Dymax model 2000 flood) for 60, 90 and 120 seconds to obtain tack free cured films. Film formation was tested by dry-through time method (ASTMD 1640).

**Table 1.** UV curable coating formulation.

Ingredients	Parts per weight of total weight
ABGC or CN 929	43
SR 238	13
SR 256	17
SR 454	9
Irgacure 184	13
CN 373	5

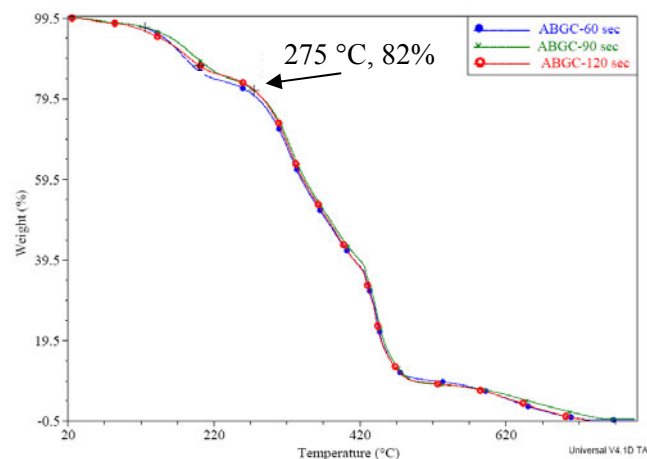
### 3. Results and discussion

Performance of UV cured coatings was evaluated by determining their hardness, MEK double rubs, adhesion, impact strength and flexibility. Table 2 shows the properties of the coatings cured at different exposure times. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was used to determine glass transition temperature ( $T_g$ ) and thermal stability of coatings, respectively. Table 2 shows that adhesion and reverse impact strength of the coatings made from ABGC is higher than that from CN 929. Coatings made from ABGC showed good solvent resistance.

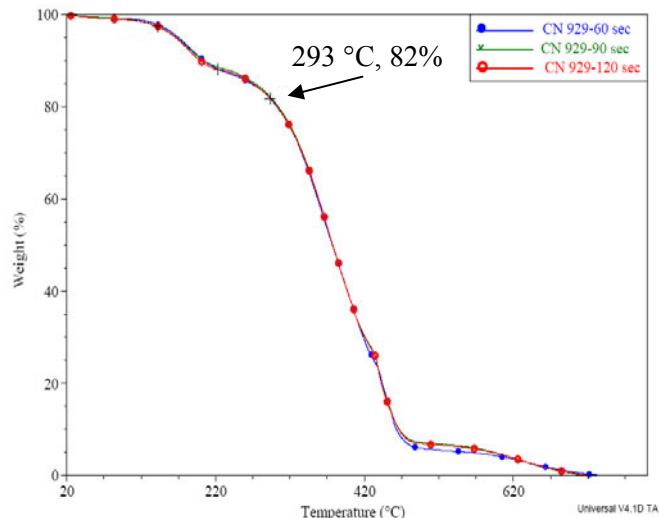
**Table 2.** Properties of UV cured coatings.

Properties Curing time →	ABGC			CN 929		
	60s	90s	120s	60s	90s	120s
$T_g$ (°C)	27	28	32	-7	-4	-8
König hardness (sec)	8	17	12	26	23	26
MEK double rubs	>400	>400	>400	350	>400	>400
Cross hatch adhesion (5B=Best)	2B	3B	1B	0B	0B	0B
Reverse impact (in-lb)	76	56	80	76	88	80
Conical mandrel (cm) (0 cm=Best)	0	0	0	2	0.5	0

Figure 2 and Figure 3 shows thermo gravimetric analysis of the coatings made from ABGC and CN 929 resins, respectively. Coatings made from ABGC were stable around 275 °C whereas coatings made from CN 929 were stable around 293°C.



**Figure 2.** TGA of the coatings made from ABGC resin.



**Figure 3.** TGA of the coatings made from CN 929 resin.

## 4. Conclusions

GC resins can be acrylated and can be formulated with common reactive diluents to produce UV curable coatings. Initial results of UV cured GC coatings are promising to obtain coatings with good adhesion, flexibility, solvent resistance and thermal stability. Further detailed study will be done to explore the kinetics of photopolymerization and structure-property relationships.

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