Unsaturated Polyester Resins Incorporating Bio Succinic Acid

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INTRODUCTION

BioAmber is a renewable chemicals company. Its proprietary technology platform combines industrial biotechnology and chemical catalysis to convert renewable feedstock into chemicals for use in a wide variety of everyday products including plastics, resins, food additives and personal care products. BioAmber offers a portfolio of renewable chemicals; both a C4 Platform, based on bio succinic acid and it's derivatives, including 1,4 butanediol, and a C6 Platform which includes bio adipic acid, HMDA, caprolactam and caprolactone. BioAmber was first to market with commercial scale bio succinic acid, and has been operating a plant producing at a 350,000 liter scale in Pomacle, France since 2010. The company is now building a 30,000 ton/year commercial facility in Sarnia, Canada to meet the growing market demand for bio succinic acid.

Succinic Acid has emerged as one of the most competitive of the new bio based chemicals. As a platform chemical, bio based succinic acid has a wide range of applications, including as a dibasic acid monomer for unsaturated polyester resins (UPRs). UPRs are synthesized by the polycondensation of glycols with saturated or unsaturated dibasic acids. Often, a number of glycols and dibasic acids are used in combination in order to tailor the properties of the cured UPR thermoset. Typical glycols include propylene glycol, diethylene glycol and ethylene glycol. Typical saturated dibasic acids used in UPRs include isophthalic acid, phthalic anhydride, and adipic acid. These acids are used in combination with an unsaturated dibasic acid, most often maleic anhydride.

BioAmber’s bio succinic acid is easily incorporated into UPR formulations using standard reaction conditions. The bio succinic acid can be used in combination with other dibasic acids in order to achieve the desired properties of the cured thermoset resin. Additionally, incorporation of bio succinic acid improves the environmental profile of the UPR by introducing renewable content made from plant materials. When combined with a number of glycols, this new bio based building block offers unsaturated polyester resins with good reactivity, mechanical and thermal properties.

In many application areas, bio succinic acid has been found to replace petroleum based adipic acid with little or no impact on final properties. In UPR formulations, adipic acid is used for two major purposes. Adipic acid can provide flexibility or higher elongation to the resin. Many times, polyester resins with high levels of adipic aced are used as flexible blending resins. These resins are blended with other unsaturated polyester resins in order to achieve the desired level of flexibility. Secondly, adipic acid based polyesters are often used to make low profile additives in order to impart surface smoothness. Bio succinic acid offers a renewable alternative made from plant materials to petroleum adipic acid.

Here we describe the incorporation of BioAmber’s bio succinic acid into unsaturated polyester resins with maleic anhydride, propylene glycol, ethylene glycol and diethylene glycol. The addition of bio succinic acid to the resin compositions requires no change in resin reaction conditions. The unsaturated polyester resins are easily diluted with styrene monomer. During cure, the bio succinic acid containing UPRs show fast gel times indicating good reactivity of the resin compositions with styrene during cure. Viscosities of the resins in styrene generally range from 850-1700 cps measured at room temperature with 65% non-volatile loading. Cured thermoset compositions based on UPRs with mixed glycols, maleic anhydride and varying amounts of bio succinic acid show a wide range of thermal and mechanical properties. Particularly interesting resin compositions incorporate 25-55% bio succinic acid with propylene glycol and diethylene glycol. These compositions show high glass transition temperatures while maintaining ductility as indicated by tensile elongation measurements.

EXPERIMENTAL

Unsaturated polyester resins were synthesized using maleic anhydride and BioAmber bio succinic acid as diacid monomers (Figure 1), and propylene glycol, ethylene glycol and/or diethylene glycol as comonomers (Figure 2). A resin kettle equipped with both overhead and pot temperature controls was preheated to approximately 50 °C under nitrogen. The kettle was charged with maleic anhydride, dibutyl tin monohydrate catalyst, approximately 100 ppm inhibitor and glycols, and the temperature was raised to approximately 100-110 °C. Following the peak exotherm, succinic acid was charged, and the temperature was slowly raised in order to keep the overhead temperature at 100 °C. Water is removed overhead by distillation. Once the overhead water removal had minimized, the temperature was slowly raised to approximately 190-200 °C. Samples are pulled at once per hour and tested for acid value and viscosity. The resin is allowed to react until the acid value is below 30. Adjustments to the stoichiometry can be made by addition of glycol or succinic acid if the viscosity and acid value targets are not met. Upon completion of the reaction, the resin kettle is cooled. The resin is thinned with 35 wt-% styrene and additional inhibitor is added. Resins were formulated using the monomer ratios outlined in Table 1.

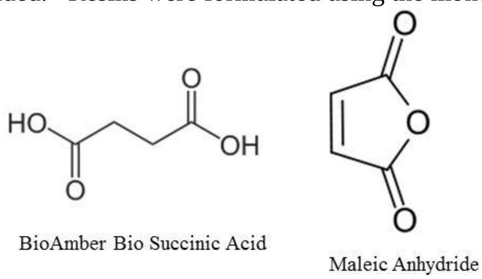

Figure 1. *Diacid Monomers for Unsaturated Polyester Resins*

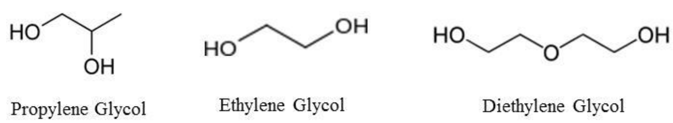

Figure 2. *Glycol monomers for Unsaturated Polyester Resins*

Table 1. Composition of Unsaturated Polyester Resins (Mole %)

Sample	Maleic Anhydride	Succinic Acid	Propylene glycol	Ethylene Glycol	Diethylene Glycol
1	75	25	100	0	0
2	75	25	60	20	20
3	58	42	36	31	33
4	85	15	85	15	0
5	54	46	60	0	40
6	45	55	70	0	30
7	50	50	0	100	0
8	50	50	25	75	0
9	50	50	0	73	27

RESULTS AND DISCUSSION

Succinic acid was easily incorporated into unsaturated polyester resins using typical reaction conditions. All reactions were complete in 9 hours or less showing that the addition of succinic acid does not reduce the rate of reaction. Table 2 shows the gel time and peak exotherm at room temperature for the unsaturated polyester resin formulations containing bio succinic acid. The compositions all have fast gel times indicating good reactivity, with peak exotherms ranging from 143 °C to 197°C. If longer gel times are required, inhibitor levels can be adjusted in order to lengthen the time to gel.

Table2. Gel Time and Room Temperature Peak Exotherm for Succinic Acid Containing UPR			
Sample	Gel Time (min)	Peak Exotherm (°F)	Peak Exotherm (°C)
1	32.3	381.4	194
2	191.4	313.7	157
3	29.2	354.8	179
4	13.3	387.2	197
5	27.4	309.1	154
6	23.3	311.8	155
7	27.9	322.7	162
8	58.8	322.7	162
9	117.2	290.2	143

The resulting unsaturated polyester resins were thinned with styrene monomer to give formulations with 65% non-volatile resin loading. Viscosity was measured on the resin styrene mixtures at room temperature using a #3 spindle at 30rpm. Resins were also tested for isomerization of the maleic anhydride during the resin synthesis. Table 3 shows the resulting viscosities, percent fumarate, and molecular weights of the unsaturated polyester resin compositions dissolved in styrene. Composition 7 was not tested due to resin insolubility in styrene monomer. The UPR Composition 7 with 100% ethylene glycol was crystalline, leading to a biphasic mixture when combined with styrene.

Table3. Viscosity, Isomer Content and Molecular Weight of Succinic Acid Containing UPR				
Sample	Viscosity* (cps)	Fumarate Content (%)	M_n (g/mol)	M_w (g/mol)
1	880	81	2758	9352
2	1666	59.5	2839	52119
3	1150	62.5	3581	14345
4	1660	87	2248	8938
5	1264	78	3745	19258
6	1188	89	3839	14200
7	2-Phase	64	3391	10477
8	1188	68	3238	9584
9	-	56	3802	12959

*Measured at 65% non-volatile resin; 35% styrene

The unsaturated polyester resin compositions dissolved in styrene were cast and cured for thermal and physical property testing. Tensile and Flexural properties were measured, along with the glass transition temperature of the cured resin systems. Table 4 summarizes the properties of the cured resins.

Table 4. Properties of Unsaturated Polyester Resins Containing Succinic Acid							
Sample	Tensile Strength (psi)	Tensile Modulus (ksi)	Elongation at Max Load (%)	Elongation at Break (%)	Flexural Strength (psi)	Youngs Modulus (ksi)	T_g (°C)
1	8135	490	2.11	2.11	14,567	488	114
2	9366	453	4.17	4.16	15,732	459	93
3	6603	318	4.67	10.36	11,420	327	58
4	8140	514	1.92	1.92	18,633	530	89
5	7137	334	4.52	7.33	11,500	336	61
6	6408	315	4.18	13.7	10,636	315	53.5
7	Not tested due to insolubility in styrene						
8	7427	360	4.48	11.4	12,130	356	59
9	5103	224	5.0	5.54	8,076	235	44

Thermal and physical properties of the cured unsaturated polyester resins cover a wide range. Glass transition temperatures range from 44-114 °C. The highest Tg was obtained by using 25% bio succinic acid with 100% propylene glycol. Incorporating ethylene glycol and diethylene glycol slightly reduced the glass transition temperature, but increased the tensile strength, elongation at max load and elongation at break. The highest elongation at break was seen in Composition 3 and Composition 6. The elongation was achieved by incorporation of higher levels of succinic acid (greater than 40%) with a mixture of glycols (either approximately even amounts of all three glycols, or a high level of ethylene glycol). These resin formulations had lower glass transition temperatures than Composition 1, but still remain relatively high at 58 and 53.5 °C respectively. Compositions 1 and 6 are interesting due to their combination of elongation, physical properties and relatively high glass transition properties.

A number of unsaturated polyester resins containing bio succinic acid have similar tensile and flexural properties to commercially available resin systems. Table 5 gives properties of commercial unsaturated polyester resins available from Ashland. AROPOL 8722 is an example of a flexible blending resin. Flexible blending resins are used to improve toughness and flexibility of a brittle UPR formulation. Compositions 3 and 6 containing bio succinic acid could be off-sets for this type of application based on comparisons of their physical properties. Composition 6 is especially interesting due to its good physical properties given the low maleic anhydride content.

For the Ashland unsaturated polyester resins AROPOL 8422 and AROPOL 50256, Compositions 1 and 2 could be potential replacement compositions with varying levels of bio succinic acid. Composition 6 incorporates higher levels of bio succinic acid, thus increasing the renewable content derived from plant based materials. AROPOL 3058 is a PTE modified unsaturated polyester resin. Compositions 1, 2 and 3 have similar physical properties and could be considered potential offsets.

Table 5. Properties of Commercial Unsaturated Polyester Resins Available from Ashland

Sample	Description	Tensile Strength (psi)	Tensile Modulus (ksi)	Elongation at Break (%)	Flexural Strength (psi)	Young's Modulus (ksi)	HDT (°C)
AROPOL 8722	Flexible Blending Resin	4900	230	22	6800	210	41
AROPOL 8422	UPR	10000	670	1.8	16000	730	60
AROPOL 50256	UPR	8700	440	2.3	16600	440	-
AROPOL 3058	PET modified UPR	8850	500	2.1	14600	500	135

CONCLUSION

BioAmber bio succinic acid is easily incorporated into unsaturated polyester resins with maleic anhydride, propylene glycol, ethylene glycol and diethylene glycol. The addition of bio succinic acid to the resin compositions required no change in resin reaction conditions. Acid numbers below 30 were easily achieved in less than 9 hours reaction time. Isomerization of the maleic anhydride during resin reaction varied, ranging from approximately 55%-90%. All resin samples were easily diluted with styrene monomer giving single phase mixtures at 65% resin by weight, with the exception of Composition 7 containing 100% ethylene glycol. The bio succinic acid containing UPR show fast gel times indicating good reactivity of the resin compositions with styrene monomer during cure. Peak exotherms measured at room temperature ranged from 143 °C to 194 °C depending on the resin composition. Gel times and peak exotherms could be adjusted by increasing the inhibitor concentration. Viscosities of the resins in styrene are dependent on comonomer composition and overall molecular weight, but generally range from 850-1700 cps measured at room temperature with 65% non-volatile loading. A wide range of thermal and physical properties are achieved by altering the amount of bio succinic acid, and the glycol structures and loadings. Particularly interesting are resin compositions 1 and 6 which gave high glass transition temperatures while maintaining ductility as indicated by the tensile elongation measurements. These resin compositions incorporate increasing amounts of bio succinic acid respectively, showing that significant amounts of bio content can be incorporated into the UPR.

BioAmber

BioAmber is a next generation chemicals company. Its proprietary technology platform combines industrial biotechnology, an innovative purification process and chemical catalysis to convert renewable feedstocks into chemicals for use in a wide variety of everyday products including plastics, food additives and personal care products. For more information visit the company's web site at www.bio-amber.com.