Envirez™ Technology: Incorporating Renewable and Recycled Feedstocks into Unsaturated Polyester Resins

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The United Soybean Board; sponsored the Life Cycle Assessment (LCA) study of the first soy-based Envirez resin.

Project Title: Envirez™ Technology: Incorporating Renewable and Recycled Feedstocks into Unsaturated Polyester Resins

Most recent milestone: A lower emissions version of Envirez was introduced to the market in 2011. This technology uses a proprietary, bio-based reactive intermediate to lower the styrene content of the resin. The Premanufacture Notice under TSCA has cleared the U.S. EPA process and field trials with this new technology at numerous composite fabricators are underway.

The technology is not eligible for the small business award or the academic award.

This technology fits Focus Area 3: The design of greener chemicals.

The research and development for the technology in this nomination was conducted in the U.S.

Abstract: The annual production of unsaturated polyester resins in North America is approximately 1 billion pounds. Historically, this chemistry has relied almost exclusively on virgin petrochemical feedstocks. Ashland's Envirez™ resins are a novel, versatile family of unsaturated polyester resins that incorporate both renewable and recycled raw materials. Envirez technology leads to reduced dependence on petroleum, lower emissions and a smaller carbon footprint.

The renewable raw materials are obtained from soybeans, corn, and other sources of biomass. These bio-based building blocks include soybean oil, ethanol, 1,3-propanediol, and other proprietary monomers. Recycled monomers and polymers, including post-consumer polyethylene terephthalate (PET), are used to provide other building blocks that are "upcycled" into Envirez resins.

When the first Envirez resin was introduced, it was applicable to a specific application and a specific composite fabrication method and thus had limited market and environmental impact. With new technology development, Ashland has recently expanded the Envirez family of resins in several significant ways:

- Envirez resins now contain a wider assortment and higher percentage of renewable raw materials. Resins with as high as 40 percent renewable content have been commercialized.
- The first Envirez resins that employ recycled raw materials and that use combinations of both recycled and renewable raw materials were developed. Over 12 million pounds of recycled PET have been incorporated in the last 3 years.
- Envirez resins with reduced hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) have been developed. A novel, bio-based reactive intermediate has been essential to these advancements.
- Envirez resins now exist for a wide variety of composite fabrication methods, expanding the reach of Envirez into a much wider assortment of products and markets, including green buildings and wind energy.

Envirez resins have become an enabling technology for composite fabricators who are interested in creating products using sustainable components. With the growing, widespread acceptance of Envirez, this product line has experienced double-digit growth in the past several years.

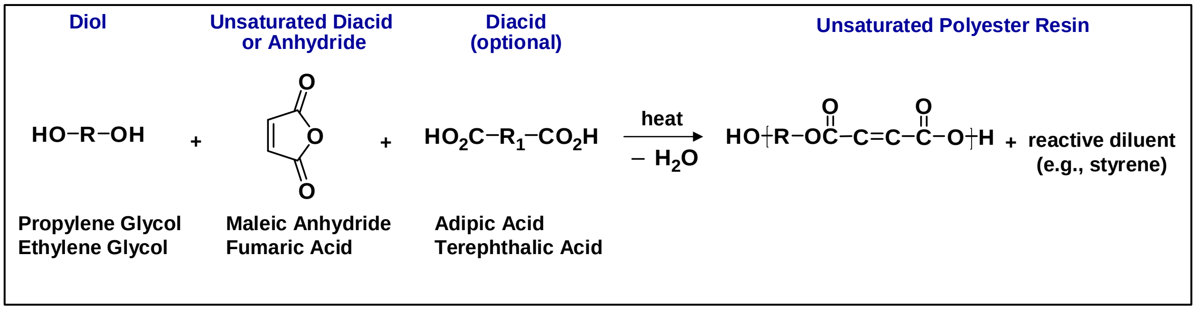
I. Background

Fiber-reinforced plastic (FRP) thermoset composites are used in a variety of applications across a broad range of industries, such as transportation, building and construction, and marine. These composites can provide an assortment of benefits ranging from durability and strength to reduced weight and exceptional corrosion resistance. Example products include boat hulls, auto and tractor body panels, tanks and pipes, tub and shower basins, sinks, countertops and furniture. Approximately 2.4 billion pounds of FRP composites were shipped in North America in 2010.[1]

A key component of composite products is an unsaturated polyester resin. Unsaturated polyester resins serve as the polymer matrix for the composite part (the unsaturated double bonds are capable of cross-linking by free radical polymerization) and often comprise 30-40 percent of the final composite product. In addition to the resin, a composite part typically includes reinforcement (such as glass strand) and/or inert fillers. The annual production of unsaturated polyester resins in North America is about 1 billion pounds.[1]

In the simplest description, unsaturated polyesters are prepared by condensation of a diol and diacid, without the use of solvent and yielding water as the only by-product (Equation 1). The unsaturation in the polyester is usually derived from the diacid (often in the form of maleic anhydride); other saturated diacids may be incorporated to impart specific properties. Styrene is often added as a reactive diluent. Unsaturated polyester resin (UPR) chemistry has historically relied almost exclusively on petrochemical feedstocks.

Equation 1: General Synthesis Scheme and Typical Reactants for Unsaturated Polyester Resins



In the late 1990s, Ashland initiated a program to develop unsaturated polyester resins from renewable raw materials. Initial efforts to design greener chemicals focused on incorporating soybean oil derived from domestically produced, renewable soybeans. These efforts expanded on the pioneering work of Professor Richard Wool at the University of Delaware.[2] Professor Wool demonstrated the synthesis of composite resins using chemically-modified soybean oil and continues to lead the industry in the development of plant oil-based resins and natural fiber-based composites.[3]

The first commercial unsaturated polyester resin developed by Ashland (using a patented process) was Envirez™ 1807 resin.[4] This resin incorporated approximately 18 percent renewable raw materials by weight, including unmodified soybean oil and corn-derived ethanol. Envirez 1807 resin was suitable for use in a compression molding process, which is employed in the transportation and agricultural equipment industry. With the commercialization of Envirez 1807, international agricultural equipment producer John Deere began using this resin in its combine panels in 2001 (Figure 1). By 2004, John Deere expanded production to include the use of Envirez 1807 in tractor hoods, side panels and backhoe hood

Figure 1. John Deere equipment with composite parts from Envirez 1807

components. Ashland used the phrase "From Corn and Beans to Machines" to describe this first commercial success for Envirez, but for most of the early 2000s, this represented the only significant application of a bio-based UPR. It was an excellent "first step" for the industry, but the incorporation of soybean oil limited use in other processes and applications. The characteristic yellow color of soybean oil precluded use in any color-sensitive applications. In addition, the long-chain fatty acid triglyceride structure limited processing, performance and the amount of soybean oil that could be incorporated. Thus, in the following years, Ashland embarked upon the technology development described below.

II. Technology Development and Market Expansion of Envirez Resins

The past several years have seen a dramatic surge in the demand for products made with renewable and recycled raw materials, as well as materials with lower emissions. To meet this growing interest in sustainable materials and to increase the environmental benefits offered by Envirez, Ashland has invested heavily in Envirez R&D and strengthened and expanded this family of resins in several significant ways:

- Envirez resins now contain a wider assortment and a higher percentage of renewable raw materials.
- The first Envirez resins that employ recycled raw materials and that use combinations of both recycled and renewable raw materials were developed.
- Envirez resins with reduced hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) have been developed.
- Envirez resins now exist for a wide variety of composite fabrication methods. Formulations for infusion, pultrusion, casting and gelcoats have been developed, expanding the reach of Envirez into a much wider assortment of products and markets, including green buildings and wind energy.

Table 1 provides technical and marketing information for the family of Envirez resins that have been commercialized to date. With the exception of Envirez 1807, all of these resins have been commercialized within the last 4 years. The table includes data on renewable and recycled content and summarizes the ever-growing array of composite fabrication methods and applications where Envirez resins are now being used. Envirez resins meet the same performance and processing requirements of 100 percent petroleum-based unsaturated polyester resin products. The table also includes data from Life Cycle Analyses (LCA) that quantify the reductions in greenhouse gas emissions and energy consumption that can be achieved with Envirez. The sections that follow describe these attributes and benefits in more detail.

Table 1. Summary of Envirez Resins

Entry	Product	Process	Application	Renewable Content[a]	Recycled Content[a]	CO_2 Savings[b,d]	Energy Savings[c,d]
1	Envirez 1807	Compression Molding	Tractor panels, Car parts	18	0	1.10	4.0
2	Envirez 1807 R1			40	0	n.d.	n.d.
3	Envirez 1807 R2			18	22	n.d.	n.d.
4	Envirez Q 11500	Infusion	Boats, Furniture	9	0	0.49	1.8
5	Envirez 86400 INF			12	0	0.19	4.8
6	Envirez SS 70419	Casting	Countertops, Sinks	18	0	0.31	7.8
7	Envirez MR 80220			20	0	0.29	7.3
8	Envirez L 86300	Open Molding	Tubs, Showers	12	0	0.20	5.0
9	Envirez LF 60380			20	0	0.62	12.2
10	Envirez 50483	Pultrusion	Utility poles, Window frames	0	42	0.35	16.0
11	Envirez 50380			0	47	0.37	17.0

[a] weight percent. [b] kg of CO_2 equivalents per kilogram of resin; savings vs. comparable petroleum-based resin.
[c] MJ per kg of resin; savings vs. comparable petroleum-based resin. [d] Values calculated from LCA of Envirez 1807 resin[5] and information provided by raw material suppliers. n.d. = not determined

Broader Use of Renewable and Recycled Feedstocks

One of the most significant technical advances has been the incorporation of renewable diols into Envirez resins. In 2003, DuPont and Genencor International received a Presidential Green Chemistry Challenge Award for the microbial production of 1,3-propanediol (PDO) from renewable resources. Prior to this development, PDO was limited in availability and prohibitively expensive for composite applications. As a result, petroleum-based 1,3-propanediol has not been used traditionally in unsaturated polyester resin synthesis and therefore could not be simply substituted with bio-based PDO. In addition, while the molecular formula of PDO is identical to the widely-used 1,2-propanediol (i.e., propylene glycol in Equation 1), the linear structure of PDO introduced a variety of challenges. Early synthesis attempts resulted in resins with unacceptably high viscosities and hazy appearance. However, through its new technology development efforts, Ashland successfully incorporated bio-based PDO into unsaturated polyester resins and significantly expanded the Envirez product line. As indicated in Table 1, the incorporation of 1,3-PDO, soybean oil, and/or other proprietary renewable feedstocks has enabled an increase in bio-content up to 40 percent for commercial Envirez products introduced in 2008 and beyond. Up to 55 percent bio-content has been achieved in laboratory formulations.

In the past several years, Ashland has also dedicated a significant development effort to incorporate recycled materials into Envirez resins. Recycled feedstocks for Envirez resins include post-consumer PET bottle scrap (which is a source of both ethylene glycol and terephthalic acid in Equation 1) and recycled airplane de-icer fluid (which is a source of diol in Equation 1). The use of recycled PET reduces the depletion of and reliance on petrochemical resources by substituting a recycled material for virgin ethylene glycol and terephthalic acid and also offers cost benefits compared to virgin material. However, the incorporation of recycled PET into Envirez resins presented a significant technical challenge. In contrast to the short chain diol and diacid monomers described in Equation 1, the higher molecular weight PET polymer was insoluble and unreactive in a standard unsaturated polyester synthesis mixture. To overcome this challenge, Ashland developed a depolymerization process that enabled the successful incorporation of recycled PET. Envirez resins containing 22-47 percent recycled material are now available (Table 1, Entries 3, 10-11). Over 12 million pounds of recycled PET have been incorporated in the last 3 years.

Ashland has also increased the renewable content of the original Envirez 1807 resin. Since 2009, newer versions of Envirez 1807 have been developed that contain 40 percent renewable raw materials (Table 1, Entry 2). An Envirez 1807 resin containing both renewable and recycled materials (18 and 22 percent by weight, respectively) is also now available (Table 1, Entry 3).

Lower Emissions

There is an increasing demand for products with lower emissions, with significant focus on hazardous air pollutants (HAPs). The largest HAP contributor in most unsaturated polyester resins is styrene, which is added as a reactive diluent to improve processing and performance properties. The goal of lower styrene resins is not new to the industry; styrene emissions are regulated in reinforced plastic composites production at both federal (e.g. US EPA National Emissions Standards for HAPs) and local levels (air permits). However, lowering styrene levels has remained a formidable challenge for the industry. The primary technical solution has been to lower the molecular weight of the polyester. The use of lower molecular weight polymers reduces the level of diluent required to meet processing and application properties. However, while effective at reducing HAPs, this solution often results in lower performance of the finished composite part.

To address the need for lower emissions without compromising performance, Ashland developed new technology that uses a proprietary, bio-based reactive intermediate to lower the styrene content of the resins by more than one third (vs. a comparable resin). The environmental benefits of this new resin system are summarized for a typical resin in Table 2. Envirez Low Styrene resins have the physical properties required for processing and the mechanical properties required for composite performance. The renewable content of these new resins can be as high as 46 percent, making them some of the highest bio-content Envirez resins developed to date.

Table 2. Environmental Benefits from Envirez Low Styrene Technology

Property	Reduction (%)[a]
Styrene Content	36
HAP Content	36
VOC Contet (via EPA Method 24)	19

[a] vs. comparable resin.

The Premanufacture Notice (PMN) under TSCA for the reactive intermediate has cleared the U.S. EPA process and their assessors have identified this technology for preliminary recognition of pollution prevention potential. Samples of Envirez Low Styrene resins have been provided to several large-volume customers in 2011 and their composite fabrication results have been positive. Full commercialization of these lower styrene resins is expected in 2012.

Lower Carbon Footprint

In 2009, Ashland supported a third-party cradle-to-gate LCA of the original Envirez 1807 resin in collaboration with the United Soybean Board.[5] This data is included in Table 1 (Entry 1) and shows that Envirez 1807 resin consumes 4.0 MJ/kg (1720 BTUs/lb) less energy during manufacture than a comparable 100 percent petrochemical resin prepared by Ashland. The calculation takes into account the energy consumed in manufacturing as well as by farming and processing soy and corn into oil and ethanol, respectively. Thus, compared to the petrochemical resin, Envirez 1807 requires 11.9 less barrels of crude oil to be extracted from the ground per standard (40,000 lb) batch.

In addition, the LCA demonstrated that the global warming potential (GWP) impact for Envirez 1807 resin is significantly lower than the petrochemical resin. Envirez 1807 produces 4.1 kg of CO_2 equivalents per kilogram of resin produced vs. 5.2 kg of CO_2 equivalents per kilogram of resin produced for the petrochemical-based resin. Thus, for a standard (40,000 lb) batch, the GWP impact is 44,000 lbs of CO_2 equivalent in favor of Envirez 1807. Although not calculated at this time, Envirez resins containing increased renewable and/or recycled content (e.g. Table 1, Entries 2-3) should have an even more favorable environmental performance.

The potential environmental impact of this technology is significant. If the unsaturated polyester resins produced annually in North America (approximately 1 billion pounds[1]) were converted to an Envirez 1807 resin technology, the environmental performance benefit could result in a savings of 298,000 barrels of crude oil and reduce the industry's GWP impact by 1.1 billion lbs of CO_2 equivalents per year.

Expanded Fabrication Methods & Applications

Because of the technology advancements described above, Envirez resins now exist for a wide variety of composite fabrication methods. Table 1 shows that formulations for infusion, casting, open molding and pultrusion have been developed, extending the reach of Envirez into a much broader assortment of products and markets.

Collaboration with composite fabricator partners has dramatically increased the number of products, as illustrated by the examples in Figure 2. Composite fabricators have also begun to combine Envirez resins with natural fibers as well as natural and recycled fillers to make composites with even higher renewable and/or recycled content.

Figure 2: Examples of products containing Envirez resins commercialized since 2008

2.1: Vendura's solid surface products are listed in the USDA's BioPreferred* Procurement database.
2.2: Monroe Industries' surfaces incorporate Envirez resin and recycled glass.
2.3: Campion Marine used Envirez resins in all boats in their 2010 & 2011 product line.
2.4: Envirez resins are being tested in wide variety of wind energy applications.

The building products shown in Figures 2.1-2.2 are representative of a particularly exciting and growing opportunity for composites made with Envirez resins – the green building market. Green building and construction is an area of extremely high interest, driven by sustainable building initiatives such as the U.S. Green Building Council's Leadership in Energy and Environmental Design (LEED) program, a nationally accepted benchmark for the design, construction, and operation of high-performance green buildings. The rapidly renewable content and the recycle content of these products can help architects, building designers and contractors qualify for LEED credits for their buildings.[6,7] Some of these products (e.g., Figure 2.1) have also qualified for listing in the USDA's BioPreferred* database.

To stimulate widespread usage of these types of products in the green building community, Ashland spearheaded the launch of CompositeBuild.com at the 2010 GreenBuild Expo, the largest trade show of its kind in North America with more than 25,000 attendees. The CompositeBuild.com booth featured a showcase of Envirez-containing interior and exterior building products for residential and commercial buildings that have been commercialized since 2008. This exhibit illustrated the versatility of these resins for making LEED-enabling building products for the green building market.

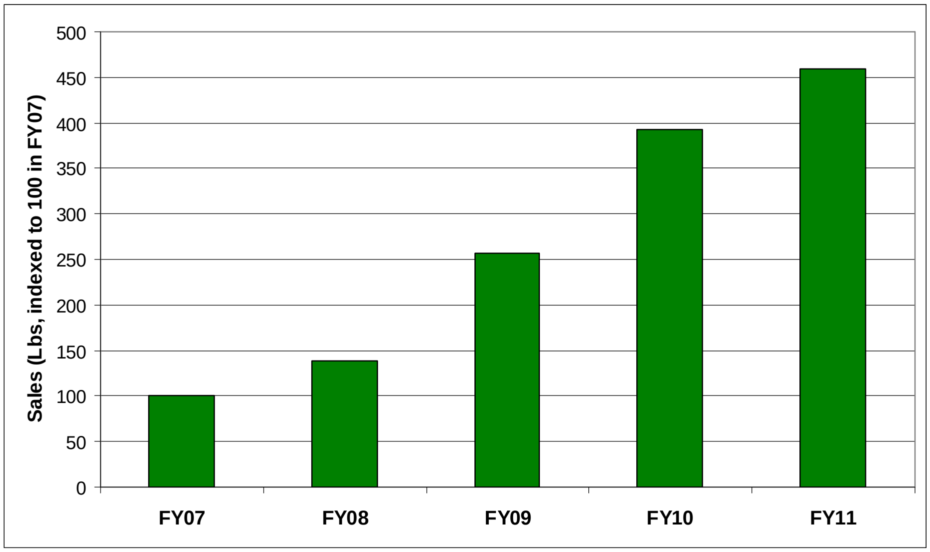
At the same, the CompositeBuild.com website was launched to further increase awareness and to educate the building industry about composite materials and how they can be used to meet green building goals. The CompositeBuild.com website contains an expanded electronic showcase of composite materials used in the residential and commercial building industry. The focus is on the environmentally-considerate attributes of these materials, such as renewable or recycled content, insulation value, durability and air quality certification. The launch of this innovative approach has significantly increased awareness and use of Envirez-containing building products in the green building community.

III. Commercial Impact

The technology development that has enabled the production of resins with a higher percentage and wider assortment of renewable and/or recycled feedstocks as well as expanded the number of possible fabrication methods has resulted in a dramatic increase in the sales of Envirez resins in recent years. Although detailed sales information for Envirez resins is proprietary, Envirez resin sales are now on the order of millions of pounds. Technology for the next generation of Envirez products (Envirez Low Styrene resins) has cleared the TSCA review process and field trials at numerous composite fabricators are underway.

Chart 1 shows that Envirez sales in North America have increased by more than 350% in the last 4 years as a result of this new technology development, with growth rates of 17-85 percent in a given year. This growth is in sharp contrast to the dramatic decreases in industry sales volumes observed during a similar time period. For example, the American Composites Manufacturers Association has reported that the number of pounds of unsaturated polyester resins sold in 2008 and 2009 decreased by 19 and 40 percent, respectively.[1] This counter-current growth for Envirez is clear and compelling evidence of the increased market penetration and impact of this green chemistry technology.

Chart 1. Envirez sales volume in North America for fiscal years 2007-11



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