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# Plantics-GX: a biodegradable and cost-effective thermoset plastic that is 100% plant-based

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We recount here the story of the discovery and invention of a family of thermoset resins that are fully biodegradable and plant-based. The resin is prepared by polymerising glycerol, the simplest triol, with citric acid, the simplest abundantly available triacid. Mixing these two chemicals at moderate temperatures begins a multi-step esterification that results in a network-like resin foam. The hardness, brittleness, and toughness of this resin can be controlled by changing the alcohol : acid ratio, the temperature, and the presence of additives. Remarkably, this resin is fully biodegradable, breaking down to its molecular components in water. The degradation period can be varied from a few days to a few months, depending on the degree of polymerisation. We have prepared over 800 different formulations of this new material, which is now being produced on the ton scale by Plantics BV in The Netherlands under the trade names Glycix and Plantics-GX. This resin is made from inexpensive and widely available starting materials. It is 100% biobased, non-toxic and biodegradable. Thus, it has the potential to replace petro-based thermoset polymers and foams in a variety of real-life applications.

## Introduction

In the early 19<sup>th</sup> century, the Swedish chemist Berzelius reacted tartaric acid with “sweet oil” (now known as glycerol), obtaining a material that could neither be crystallized nor distilled. About 100 years later, the Belgian-American inventor Baekeland obtained foams from the polymerization of phenol and formaldehyde in aqueous media. The reaction was developed further to make a coherent moldable thermoset (the famous Bakelite<sup>1,2</sup>) and the foam was left behind. Nonetheless, phenol-formaldehyde foams became a profitable business after WW II.

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Foam processing as we know it now, in construction, marine applications, and furniture, came of age when Otto Bayer discovered in 1937 the fast reaction of isocyanates with alcohols at room temperature to give so-called urethanes.<sup>3</sup> By manipulating the ratios of bifunctional isocyanates and polyalcohols, chemists could suddenly make closed-cell and open-cell polyurethane (PUR) foams with controlled resilience and density on an enormous scale. Isocyanates are “spring-loaded” reagents,<sup>4</sup> giving the advantage of fast reaction kinetics. But this comes at a price: isocyanate chemistry involves highly hazardous substances, and the resulting foams are a nightmare to work with.<sup>5</sup> Moreover, their end-of-life is problematic.<sup>6</sup> They are not biodegradable on any human time scale, and their incineration produces suffocating and poisonous smoke.<sup>7</sup> The global polyurethane market demand was nearly 16M tons in 2013 and is expected to reach 22M tons by 2020, growing at a CAGR of 5% from 2014 to 2020.<sup>8</sup> Flexible and rigid foams accounted for over 38% and 26% of the market volume in 2013, respectively. Considering their enormous quantities, PUR and PIR-type foams incur an immense environmental burden.

Other foams can be produced from various petro-based thermoplastics, notably polyvinylchloride (PVC), styreneacrylonitrile (SAN), ethylvinylalcohol (EVA) and the ubiquitous polystyrene (PS) used in packaging. All of these can be used as core materials in sandwich panels in marine applications, aviation and construction. But all of them come with a similar trade-off: they are easy to process and relatively cheap, but they are not biodegradable and in many cases cause environmental problems. Foams are among the greatest environmental pollutants. Most of them are not recycled, and end up in landfills.

Because the environmental problems with these foams are usually incurred at the end of the products' life cycles, they are seen as less critical by many manufacturers and users. This view will have to change if we want to become a sustainable society. The chemical industry can change it by adopting alternative foams that are biobased and biodegradable,<sup>9</sup> but these must also be cheap enough to compete in tomorrow's market.<sup>10</sup> The transition to biobased materials is especially problematic in the case of the thermoset sector, because thermosets' complex structures are not as easy to imitate compared to thermoplastics (this is true also for the biomass starting materials: lignin is much more difficult to process into chemicals than cellulose/hemicellulose<sup>11,12</sup>). In this short paper, we present our (admittedly accidental) invention of such a foam: a thermoset resin made from glycerol and citric acid. Here, with the editor's kind consent, we tell the story as it happened. Although some of the technical details of the invention have been described in patents,<sup>13–17</sup> this is the first time that the full story appears in a scientific journal.

## Results and discussion

In March 2010, while at the ORCS meeting in Monterey, we heard several uplifting lectures regarding the wish list of the US Department of Energy for reactions of so-called platform molecules. This gave us the idea for a new kind of bio-kerosene, basically trying to connect some of these molecules together. But about two weeks later, we found that mixing glycerol and citric acid at medium temperatures yielded a solid foam that was impossible to remove from the glass vessel. In fact, it bound so strong to the glass that when it cooled down and contracted, the glass



with a smooth glossy polyester sheet, which turned out to be important for the elastic foams (see below for the details).

Incidentally, adding acid catalysts to the prepolymerized liquid resin does not accelerate the foaming process much, because the rate of evaporation of water vapor is the practical limiting factor. We tried a variety of acids, including HCl, H<sub>2</sub>SO<sub>4</sub> (which tans the white foam), H<sub>3</sub>PO<sub>4</sub>, HClO<sub>4</sub> and H<sub>3</sub>BO<sub>3</sub> (the latter is incorporated in the final foam, resulting in larger cells).

The prepolymerized glycerol/citric acid resin is an excellent adhesive, most probably due to the numerous –OH and –COOH groups on its surface. It binds strongly to practically any hydrophilic material, including wood, oxidised metal, glass and paper to name just a few examples. Conversely, it does not adhere well to strongly hydrophobic materials such as Teflon, polysilicone or polypropene. This strong binding to surfaces opens the possibility of glueing these surfaces to a machined piece of foam as the core in a sandwich panel construction. For example, aluminum/foam/aluminum sandwiches are easily obtained with heating under light pressure in an oven, using the prepolymerized resin as the adhesive. Using this approach, we constructed 100% biobased sandwich panels with nonwoven hemp, paper/cardboard and plywood (see Fig. 2). This avoids the use of petro-based epoxy or polyester resins. Similarly, three-layer to six-layer plywood can be glued under light pressure, without any phenol-formaldehyde or urea-formaldehyde resins.

Observing the adhesive properties of the resin, we reasoned that it would serve as an excellent matrix for composite materials. Composites made with synthetic fibres often have as their weak point the interface between the fibre and the matrix. For this reason, the glass fibres in so-called fibreglass composites are often coated with a special “sizing”, which is often kept as a trade secret.<sup>19,20</sup> But since the surfaces of glass fibres are covered with –OH groups, these can bind exceptionally well to Glycix, with its multiple –OH and –COOH functional groups.<sup>16</sup> Similarly, the polymer also adheres excellently to a variety of biobased fibres and materials, because these also have large numbers of –OH groups on their surfaces.<sup>17</sup> We ran experiments on adding a host of different filler materials, including gelatin, sugar, methylcellulose, wood dust, paper, cotton, regenerated cellulose, glass fibres, metallic fibres, titania, alumina and silica. In total, we



Fig. 2 The foam can be polymerised between layers of wood, paper or metal, giving biobased sandwich materials.

prepared over 800 different composites, using the resin as a matrix and also using its fibres or platelets as the reinforcer. A full description of these composite materials and their applications is out of the scope of this short paper. Detailed technical descriptions are included in the patents.<sup>16,17</sup>

Cellular foams have many applications in various industrial sectors, which depend in turn on the type of cells and on their size. In general, the cell shape and size in these foams and the density depend on the temperature range and processing time (Table 1). Foaming for 48 h at 110–120 °C gives closed-cell foams (0.6 g cm<sup>-3</sup>), whereas foaming at 120–140 °C for 12–16 h yields robust open-cell reticular foams (see the Experimental section for details). At higher temperatures, the processing time reduces to minutes, giving low-density foams (0.1 g cm<sup>-3</sup>) with fragilities comparable commercial PUR foams. For comparison, the densities of PUR and PS can reach below 0.05 g cm<sup>-3</sup>, comparable to Balsa wood. At the other extreme we could suppress the foaming entirely: keeping a thin layer of prepolymerized resin below 100 °C during 5 days of heating on a PTFE tray yielded a colorless transparent PMMA-like sheet, with closed cells that were no longer visible to the naked eye. The material can be machined and polished to various shapes and sizes (Fig. 3).

Table 1 Synthesis and physical parameters of the foams<sup>13</sup>

Entry	Temperature, °C	Time, h	Appearance	Density, mg cm <sup>-3</sup>
1	90	100	Transparent sheet	800
2	100–120	60	Closed-cell foam	500–700
3	120–140	16	Open-cell foam	300–600
4 <sup>a</sup>	180	1	Fragile open-cell foam	100–200

<sup>a</sup> Above 150 °C, the citric acid undergoes decarboxylation to itaconic acid and therefore the network structure changes.



Fig. 3 Photo showing a transparent non-porous resin "wheel" prepared by slow controlled polymerisation followed by machining and polishing, together with a cubic block of one of the original foam pieces prepared by fast polymerisation.



ester oxygen atoms. Conversely, at lower degrees of polymerisation there are more  $-OH$  and  $-COOH$  groups available, and the 3D structure is also more open.

Note that unlike with chain polymers, we believe that this resin cannot reach 100% polymerisation. There is simply not the space to form a perfect crystalline structure. As the network grows, some of the groups will quickly become inaccessible to esterification. Indeed, thermogravimetric analysis confirms that this resin is glassy, with a  $T_g$  of *ca.* 70–80 °C. Controlling the reaction kinetics in larger volumes is tricky at best, and can lead to unhappy situations.<sup>22</sup> If the resin forms too quickly, it can cure inside the reaction vessel. Once this happens, there is no way of getting it out. Scaling up the reactions is challenging – in one case, we had to throw away a 50L reactor after the resin polymerised too quickly and formed what was essentially a reactor-sized and -shaped molecule. Eventually, we succeeded in scaling up the process to the ton scale, by careful control of the reaction parameters.

Interestingly, the rigid glycerol/citric acid foams are much stronger compared to PUR foams in the same density range (Fig. 4). This has implications for practical applications in construction and isolation, because one can save on the weight (and cost) of foam core laminates.

### Foam formation on metal surfaces

From the start, we observed that the prepolymerized resin adheres strongly to a variety of metal surfaces, particularly aluminum, iron, and copper, and alloys thereof. In hindsight we suggest that this adhesion reflects a chemical binding of surface hydroxyl and carboxyl groups in the resin to hydroxyl and other groups on the metal surface. In several cases we could see clearly that a small portion of the metal dissolved and reacted with the polymer. The most regular and robust foams were obtained from the vitrification of the viscous glycerol/citric acid resin catalyzed by  $HCl_{(aq)}$  in aluminum trays (we used disposable baking trays). We attribute this regularity to traces of hydrogen gas evolved by the metal, which act as an

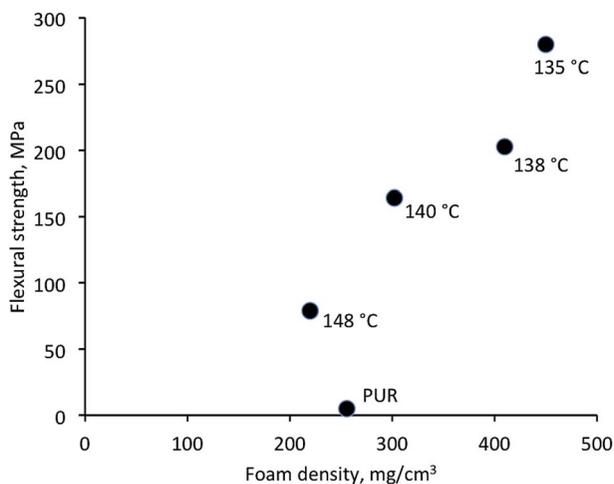


Fig. 4 Three-point test flexural strength as a function of the foam sample density.

assisting blowing agent. Indeed, we observed traces of aluminium salts incorporated in the foam, and contrasted the pale blue-grey color of the samples prepared on aluminum with the white foams prepared on Teflon or silicone rubber surfaces. The foams are free-standing upon peeling off the metal. Alternatively, an aluminum-foam-aluminum sandwich can be easily made by glueing on a top aluminum sheet with prepolymerized resin after the sample is machined to create a flat top surface (see Fig. 5).

### Elastic foams from the glycerol/citric acid resin

Inspired by polyurethane diisocyanate/polyalcohol chemistry we decided to vary the molar ratio of glycerol and citric acid. Starting from the original 1 : 1 mole ratio, we synthesised resins with an excess of glycerol of 1.2 : 1, 1.4 : 1, 1.6 : 1 and 1.8 : 1. These materials were synthesised using the same aluminum tray acid-catalyzed procedure as described above for the rigid foams. Our objective was to incorporate an excess of hydroxyl groups in the final foam, as well as to create regions with partial polymerisation. All the samples were rigid when dry, but the 1.8 : 1 glycerol : citric acid foam became elastic after absorbing water vapor under ambient conditions, as well as under controlled humidity conditions in a commercial humidifier. The result was a “memory foam”, which deforms under pressure and then slowly regains its original shape. Careful optimisation of the polymerisation showed that the best elastic foams had a density of *ca.* 300 mg cm<sup>-3</sup>. The densities of the foams prepared with glycerol : citric acid ratios of 1.4 : 1, 1.6 : 1 and 1.8 : 1 were 376, 282, and 317 mg cm<sup>-3</sup>, respectively. But while the first two samples remained rigid (flexural strength 155 and 191 MPa) the 1.8 : 1 sample was elastic.

The ease of synthesis of these foams is demonstrated by the simplicity of turning them into products. As we mentioned earlier, the pristine foams are covered with a smooth glossy polyester surface when the esterification is driven to completion. When one uses a circular silicone rubber pie tray with the 1.8 : 1 glycerol-citric acid stoichiometry, after humidification a ready-made circular resilient cushion with a spherical closed surface is produced in quantitative yield.



Fig. 5 Coffee table made from a metal frame and polished biobased resin foam. The inset shows how the metal surface reacts with the acid polymer, dissolving into the foam.

# Experimental

## Materials and instrumentation

Sandwich-type structures, composite sheets and other shapes were pressed using a Rondol Technology heated press (max. 20 tons per square inch, controlled heating up to 200 °C). Humidifying experiments were run using an Intertek G-BS300 humidifier. Thermal conductivity ( $\lambda$ ) values were measured following ASTM C-168-15. Three-point flexural strength tests were done following ASTM D-790. Unless stated otherwise, reagent-grade glycerol and citric acid (both monohydrate and dihydrate) were obtained from commercial sources and used as received. Raw waste glycerol from the biodiesel processing of waste oils (a brown smelly viscous mixture containing roughly 80% glycerol) was a gift sample from Petrotec Inc.

## Procedure for preparing the glycerol/citric acid foam on the kg scale

Glycerol (0.93 kg; 10.0 mol; reagent-grade) is poured into a 3 L glass beaker equipped with a magnetic stirrer and a hot plate. Then, 2.12 kg (10.0 mol) of citric acid monohydrate is dissolved by adding it in portions while stirring. After completion of the addition the temperature is increased to 130 °C with continued stirring until a colorless homogeneous syrupy liquid is obtained. 50 mL of conc.  $\text{HCl}_{(\text{aq})}$  is added and the stirring is continued for another 10 min. The liquid is transferred to a 30 × 60 × 5 cm aluminum tray and this tray is placed in a drying oven at 135 °C for 16 h. A small amount of hydrogen (30–40 ppm) will be released over the first 3 h. After cooling the tray down to ambient temperature, the process yields 2.30 kg of hard foam with an average height of 6 cm and a total volume of 7 liters (80.33% void, skeleton density 1.93 cm<sup>3</sup>, envelope density 0.38 g cm<sup>-3</sup>, pore volume 2.11 cm<sup>3</sup> g<sup>-1</sup>). The yield is >98% (the theoretical yield for 100% is 2.33 kg, allowing for a weight loss of 40 mol or 720 grams of water).

## Procedure for control experiments with itaconic acid<sup>13</sup>

Glycerol (13.2 gram) and itaconic acid (26 gram) were heated in an open beaker with stirring at 165 °C for 2 h. Then, 100 mg of *p*-toluene-sulfonic acid was added and the viscous liquid was poured in a silicone rubber mould and kept in an oven for 20 h. A yellow thick circular disc was obtained with a density exceeding 1 g cm<sup>-3</sup>. No foaming took place.

## Conclusions

Glycerol and citric acid are easily polymerised under moderate conditions, giving a resin solution which has strong adhesive properties, and ultimately robust macroporous thermoset resin foams. These resins have many advantages. Their synthesis process can be controlled, and they can be made rigid or elastic. They require no foaming agent, and the only byproduct of their synthesis is water. The resulting foams are strong and (depending on the degree of polymerisation) can retain their shapes and properties for years. Yet they also degrade in water in a straightforward hydrolysis, ultimately giving back the original starting materials. Both monomers are bio-based, cheap, and widely available. In its liquid state, the resin is an excellent adhesive matrix for a variety of composites with

practically any biobased fibre and many man-made fibres. Considering the above, we foresee bona fide industrial opportunities for these materials in the packaging, construction and agricultural sectors. The resin and its derivatives have been manufactured since 2015 on the ton scale by Plantics BV.<sup>23</sup>

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