Biobased Routes to UV Curable Materials

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Abstract

Global environmental concerns are driving efforts to reduce greenhouse gas emissions. Increasing demand for fossil fuel-based resources has escalated chemical costs. As a result of these and other market pressures, many companies are developing products and manufacturing processes that are more environmentally sustainable. This paper reviews progress in biobased routes to make UV curable materials and describes new alternative, sustainable methods of producing polyester polyols and acrylated polyester polyols.

Introduction

Research, development and manufacturing activities in various industries are focusing on reducing carbon footprints. Sustainability, eco-efficiency, industrial ecology and green chemistry have become the new principles guiding the development of next-generation processes and products. Reduction of carbon footprints can be achieved by minimizing energy use and increasing reliance on renewable resources (biobased materials originating from biomass). Some examples include developing environmental friendly processes that use less energy and more sustainable processes and producing chemicals from renewable feedstocks. Meanwhile, using renewable resources reduces our reliance on fossil fuels. A root cause of global warming is excess carbon dioxide release. Carbon is a major fundamental element upon which modern civilization is built. The entire coating industry, most of the chemical industry, all petroleum-based products, biobased products, fuels and even life itself are based on carbon. Ecosystems manage carbon through a biological carbon cycle. As a result, it is necessary to first review how carbon-based industries and materials fit into the natural global carbon cycle, then address environmental issues related to carbon management.

Natural Carbon Cycle

Carbon is present in the atmosphere as carbon dioxide (CO_2). Plants, algae and certain bacteria produce organic carbon in the form of sugars and carbohydrates by rearranging the atoms of CO_2 and water in a chemical process known as photosynthesis (Eq. 1). Sunlight enables this chemical transformation, and oxygen is a byproduct. Humans and other animals ultimately depend on photosynthesis for food—as energy stored in organic carbon—and oxygen for respiration. Humans and animals, in turn, convert oxygen and food into carbon dioxide, which is taken up by plants and algae.

$$6nCO_2 + 6nH_2O \xrightarrow{\text{Sunlight}} (C_6H_{12}O_6)_n + 3nO_2 \qquad \text{Eq. 1}$$
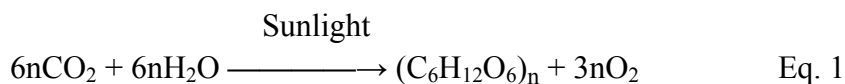
Over a million years the biomass–organic carbon from plants and animals has fossilized to become today's fossil-based feedstocks such as natural gas, petroleum and coal. For the last hundred

years, humans have consumed these fossil-based resources to make coatings, chemicals, plastics and fuel, releasing vast quantities of CO_2 into atmosphere. Clearly the reintroduction of a million years' worth of stored carbon into the atmosphere will affect the balance of the global carbon cycle. Evidence suggests that global warming is a result of these carbon emissions. Our reliance on fossil-based feedstocks is a root cause of global greenhouse gas issues, an unsustainable way to manage carbon.

Sustainable carbon management uses biomass from renewable feedstocks (e.g., crops, plants and trees), instead of fossil fuel resources to make coatings, chemicals, plastics and fuel. For example, some "bioenergy" fuels include bioethanol and biodiesel. Furthermore, an increase in the cultivation of crops and plants could begin to reverse the CO_2 release rate and realize a Zero Carbon Footprint—a net balance between CO_2 fixation and release—or even start restoring carbon in nature.

Low- and zero-VOC coatings and inks cannot contribute to a Zero Carbon Footprint unless they are made from biobased materials derived from renewable resources. This includes using non-fossil fuel based energy sources in their manufacture and transportation as well.

The remainder of this paper reviews biobased materials and their use in the coatings industry, with the goal of increasing awareness of the capabilities for such materials.

Definitions: Biomass, Biobased Products, Biobased Material and Biobased Content

In order to properly discuss "low-carbon footprint" coating materials, it is necessary to define commonly used terms set forth by concerned national and international agencies. Biomass, Biobased Products, Biobased Material and Biobased Content refer to different aspects of incorporating renewable resources into modern products.

The United States Farm Security and Rural Investment Act of 2002 (FSRIA) defines **Biomass** as:

> Any organic material that is available on a renewable or recurring [basis], including (i) agricultural crops; (ii) trees grown for energy production; (iii) wood waste and wood residues; (iv) plants (including aquatic plants and grasses); (v) residues; (vi) fibers; (vii) animal wastes and other waste materials; and (viii) fats, oils, and greases (including recycled fats, oils, and greases), but exclusion of (i) paper that is commonly recycled; or (ii) unsegregated solid waste.

More simply, the International Union of Pure and Applied Chemistry (IUPAC) definition is "a material produced by the growth of microorganisms, plants or animals." In both definitions biomass is a material wholly derived from living things. Inorganic materials not obtained from living things, like metals and stone, are clearly not considered biomass. Fossil fuels are also not considered biomass because they take millions of years to form and they cannot be rapidly renewed. Biomass is a general term for the materials sourced from currently or recently living things.

Biobased Products are products made from biomass. FSRIA defines a Biobased Product as "a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal and marine materials) or forestry materials." From this definition, it is important to note that a biobased

product partly consists of a material derived from biomass, but may also contain fossil-based and/or inorganic materials.

The organic materials used to make biobased products containing non-fossil carbon are **Biobased Materials**. In chemistry, organic materials are compounds in which carbon is bound to other carbon atoms, oxygen, hydrogen and/or other elements in a chain, ring or three-dimensional structure. Because a Biobased Material is organic and contains a certain amount of carbon sourced from biomass, the percentage of biobased carbon is of interest to evaluate the carbon footprint. In other words, a Biobased Material is not necessarily derived 100% from biomass, and this biobased content is quantifiable.

Biobased Content is the amount of biobased carbon derived from biomass in a material/product as fraction weight or percent weight of total organic carbon in the material/product (Eq. 2).

$$\text{Biobased Content} = \frac{\text{Amount of biobased carbon}}{\text{Amount of biobased carbon} + \text{Amount of fossil-based carbon}} \times 100 \quad \text{Eq. 2}$$

In practical situations, biobased content can be determined by testing to ASTM Method D6866.[1] This method, using the principles of radiocarbon dating, compares the amount of a decaying carbon isotope in a sample relative to the amount in the same sample if it were made entirely from biomass. Specifically ASTM D6866-05 is a method used to measure carbon-14 (^{14}C) content and calculate the quantity of the material or product derived from biomass versus petroleum-based components.

Scientific Background of ASTM D6866-05 Method

^{14}C is known as "radiocarbon" or radioactive carbon. It is present in all living things in minute amounts. Since it is radioactive, it gradually decays by radioactive β-emission. ^{14}C originates in the upper atmosphere of the earth, created when neutrons from solar radiation collide with nitrogen in the air. Occasionally a reaction occurs in these collisions, converting nitrogen-14 (^{14}N) to ^{14}C. The unstable ^{14}C immediately begins radioactive decay, but more is constantly re-created. The net effect is that the amount of ^{14}C in the air remains relatively constant. In addition to being subject to radiodecay, ^{14}C immediately reacts with oxygen in the air, forming CO_2. CO_2 rapidly mixes throughout the atmosphere, where, at ground level, it is absorbed by plants during photosynthesis. As this process is continuous, the percentage of ^{14}C in living plants is the same as the percentage of ^{14}C in the surrounding air. The consumption of plants by animals, and the consequent movement of this biomass through the food chain, including to humans, ensures that all living plants, animals and humans have the same percentage of ^{14}C in their bodies at any given time. These living bodies are said to be in "equilibrium" with the ^{14}C in the air. Although the ^{14}C is radioactively decaying in a living thing, it is constantly replaced through carbon exchange processes, such as photosynthesis or the ingestion of food, leaving the percentage relatively constant. When a plant stops photosynthesizing carbon dioxide, or when an animal dies, the incorporation of ^{14}C also stops, and the equilibrium is disrupted. From that time forward, the only ^{14}C process at work in the organism is radioactive decay. Eventually all the ^{14}C in the body will disappear. This principle applies equally to a deceased person, a cut corn stalk, or an uprooted soybean plant. When these things stop living, they no longer take in ^{14}C from their surroundings, and the ^{14}C in the remains gradually decays.

Radiocarbon dating measures the ^{14}C content to determine when something was last alive, using the known "half-life" of [14]C. The half-life of ^{14}C is the amount of time it takes for ½ of the original amount to disappear by radioactive decay, and is about 5,730 years. This means that every 5,730 years, the amount of ^{14}C in a fossil is only ½ of what it was 5,730 years ago. For example, if a radiocarbon dating lab measures that a dead plant has 50% as much ^{14}C in it than in a living plant, the dead plant was last living about 5,730 years ago. Petroleum and dinosaur bones are examples of fossil materials that don't have a significant ^{14}C signature, because they date back more than 50 million years ago. ASTM D6866 is a test method to quantify biobased content using a radio dating approach.

Enzyme Catalysis - More Environmentally Sustainable Manufacturing Process

Saturated and unsaturated polyols have wide applications in the coating industry. Currently, heavy metal compounds (e.g., cerium trioxide, lead borate, stannous octanoate, zinc borate), or strong acid catalysts (e.g., halogen-activated carboxylic acids or sulfonic acids) are used to prepare these polyols under elevated temperatures and long reaction times.[2] Moreover, the residues of these conventional catalysts remain in the final products. Enzymes have been recognized as environmentally sustainable catalysts, useful in a wide range of reactions and under mild conditions.[3] For the coating industry, enzymes can be used to prepare saturated and unsaturated polyols.[4] As an example, lipase catalyzes the synthesis of unsaturated polyester polyols from ε-caprolactone and 2-hydroxyethyl acrylate (Fig. 1). Given sufficient time, the development of industrial biotechnology will produce an abundance of applications in the coating industry. Enzymatic catalysis is a more sustainable and eco-efficient process that will change traditional chemical manufacturing processes.
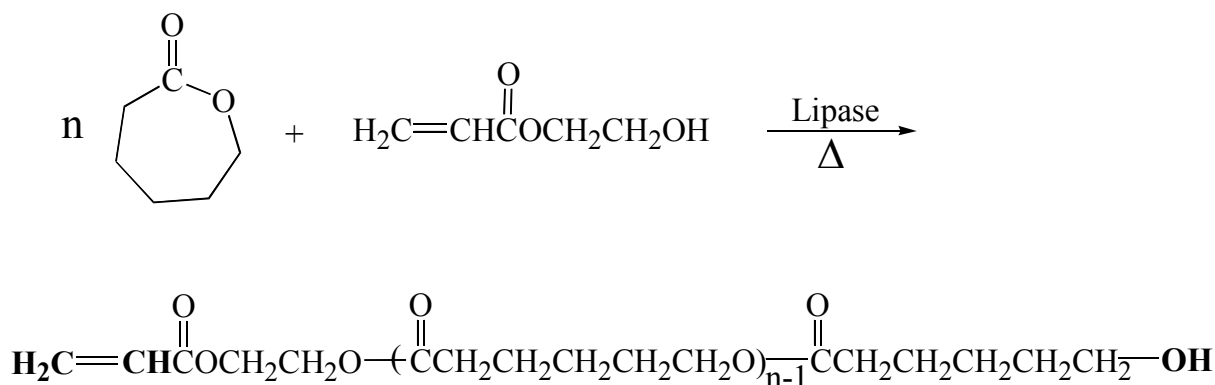

Figure 1. Lipase-catalyzed synthesis of an unsaturated polyester polyol.

Biobased Material for UV/EB Coating Application

In 2005, a joint report by U.S. Department of Energy (DOE) and U.S. Department of Agriculture (USDA) concluded that U.S. agricultural and forest sources can renewably supply one billion dry tons of biomass annually, while continuing to meet food, feed and export demands.[5] This amount of biomass would not satisfy U.S. fuel demands but could theoretically replace petrochemical feedstocks for chemical production. The DOE also identified twelve high-volume chemicals that could be produced from biomass and can serve as starting chemicals for many industries through biotechnical processes.[6] Some of these top candidates (Figs. 2, 3, and 5) show great potential in the coating industry.

C3 Building Blocks: 3-Hydroxypropionic Acid

Biomass fermentation has been used to produce the three-carbon (C3) material 3-Hydroxypropionic acid (3-HPA). A variety of simple chemical reactions of 3-HPA yield its primary derivatives. (Fig. 2). Among these derivatives, acrylic acid and methyl acrylate are major chemicals in the UV coating industry, and polyether polyols, derived from 1,3-propanediol, are used today in coating applications.
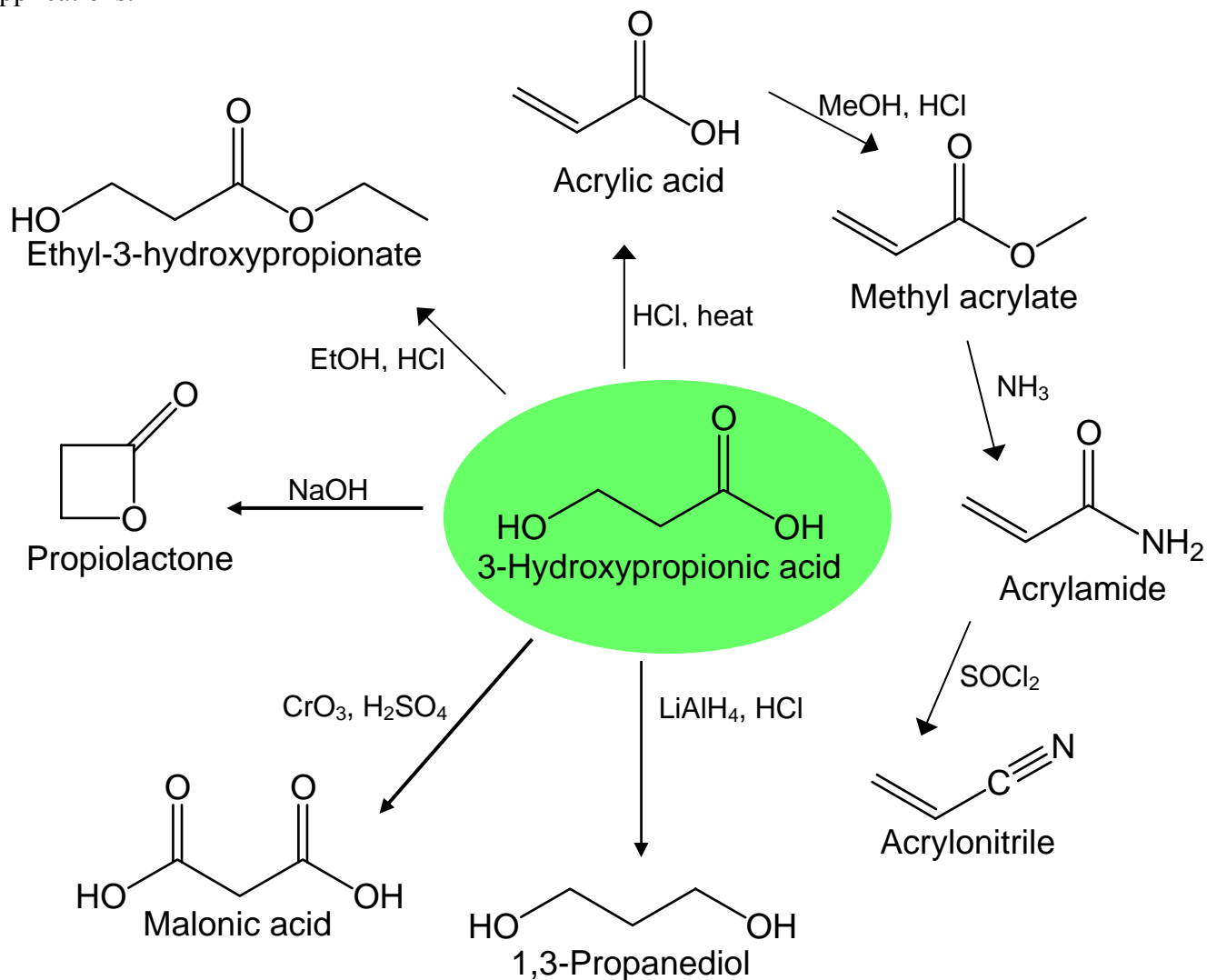

Figure 2. 3-HPA and its derivatives.

C3 Building Blocks: Glycerol

Glycerol is a byproduct of biodiesel production. If the United States displaced 2% of the on-road diesel with biodiesel by 2012, almost 800 million pounds of new glycerol supplies would be produced.[7] The three hydroxy groups of glycerol enable the production of industrially useful derivatives (Fig. 3). In the coating industry, glycerol, 1,3-propanediol and propylene glycol are used to make surfactants, polyester polyols and polyether polyols.
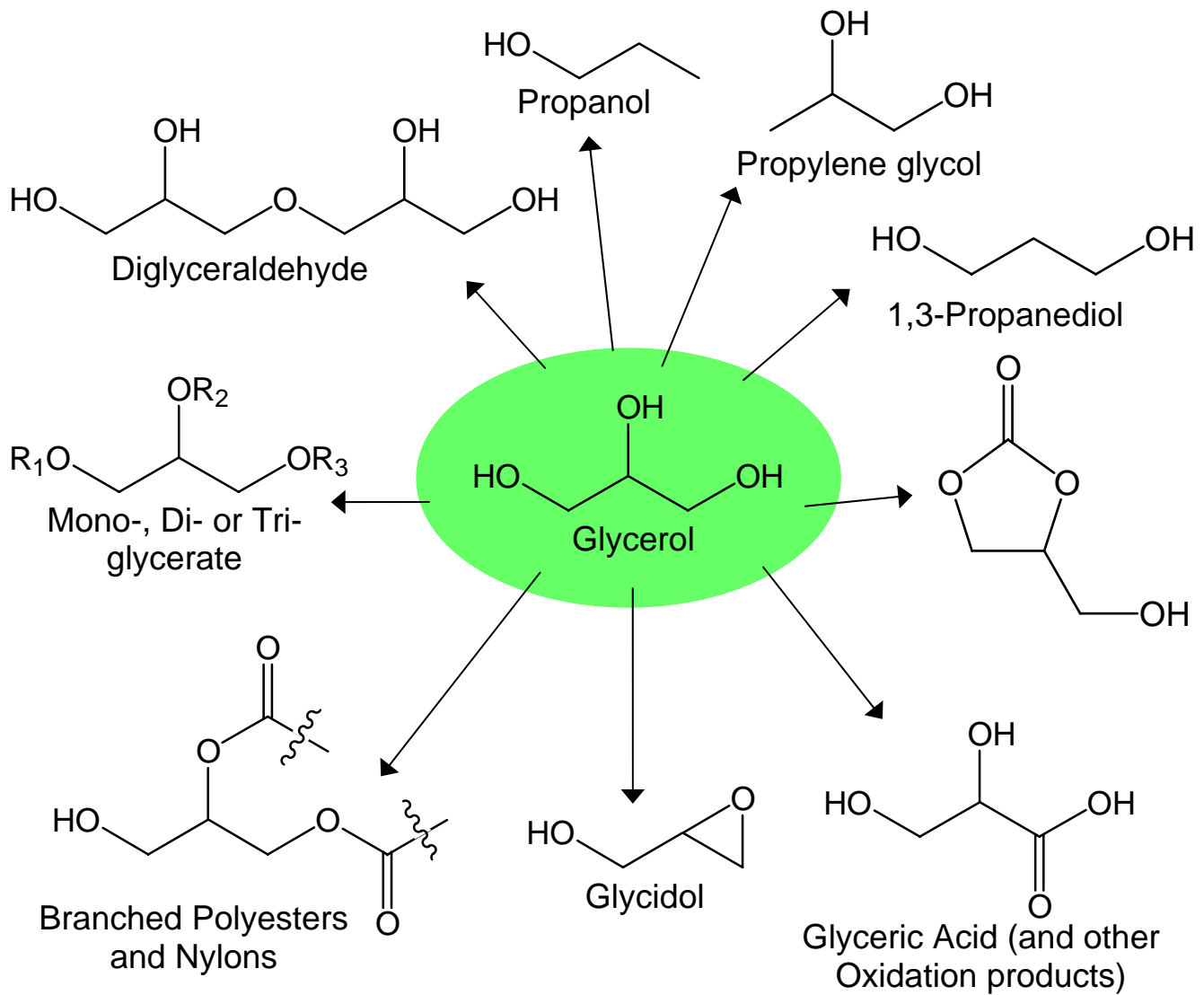
Figure 3. Glycerol and its derivatives.

C4 Building Blocks: Succinic Acid

Four-carbon (C4) diacids, including succinic, fumaric, and malic acids, have similar biochemical production paths. As an example, succinic acid is discussed. The biobased process used to make succinic acid from sugar (glucose) originates from biomass or renewable resources (Fig. 4). Succinic acid is easily transformed to numerous primary families of derivatives (Fig. 5). Among succinic acid and its derivatives, 1,4-butanediol and succinic acid are currently used to make polyester polyols and polyether polyols in the coating industry.
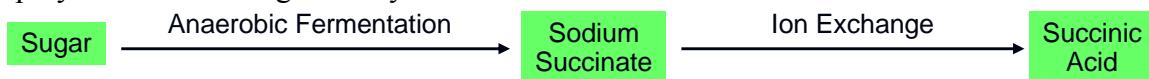
Figure 4. Biobased production of succinic acid from glucose.
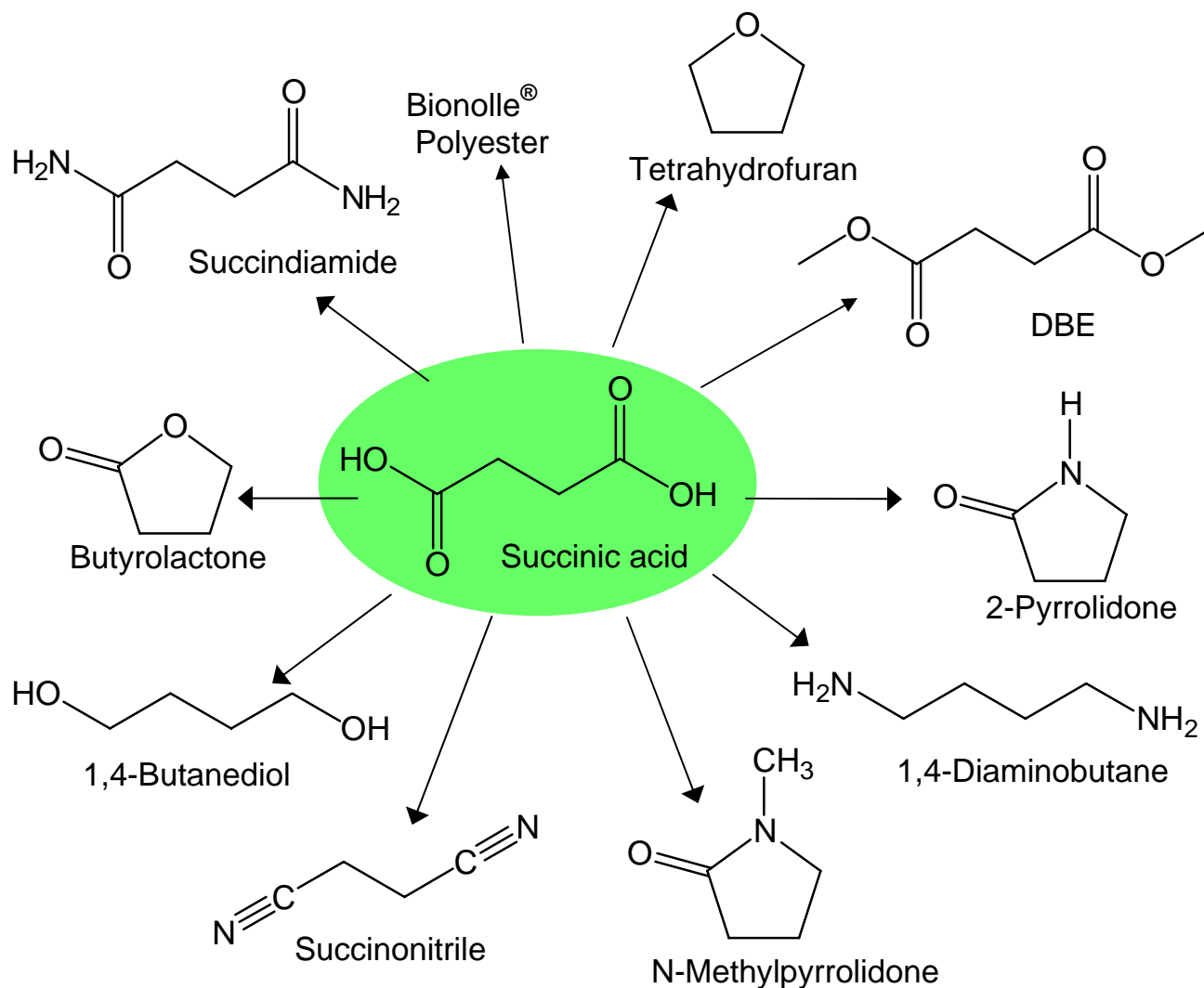
Figure 5. Succinic acid and its derivatives.

C16-C22 Materials: Plant Oils

Plant oils extracted from plant seeds are composed of triglycerides and generally comprise saturated and unsaturated fatty acids. The triglycerides are esters formed from glycerol and fatty acids. A typical structure of an unsaturated fat triglyceride contains three fatty acids, esterified to the three hydroxy groups of glycerol (Fig. 6).
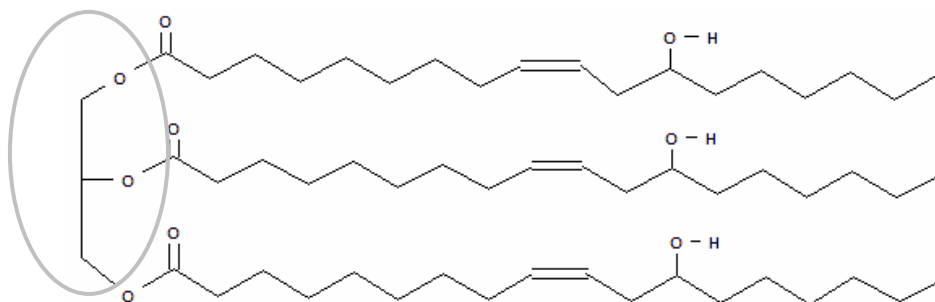
Figure 6. Example of an unsaturated fat triglyceride. The backbone on the left is formed from glycerol (circled), and the long chains are ricinoleic acid esters.

Triglycerides from natural sources are converted to the individual fatty acids and glycerol by acid or base-catalyzed transesterification. Useful derivatives of glycerol have been described earlier in this paper. Saturated fatty acids are not of interest as precursor chemicals for polyol synthesis as they lack the functionality for satisfactory derivitization. Examples of sources rich in unsaturated fatty acids include soy, linseed, tung, tall and castor oils. The typical composition of soy bean oil contains approximately 81% unsaturated oils (Table 1).
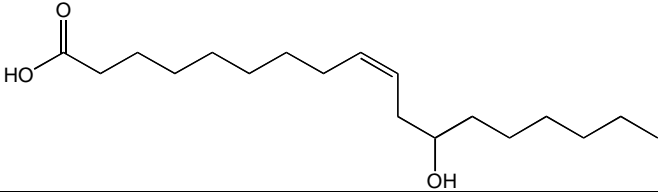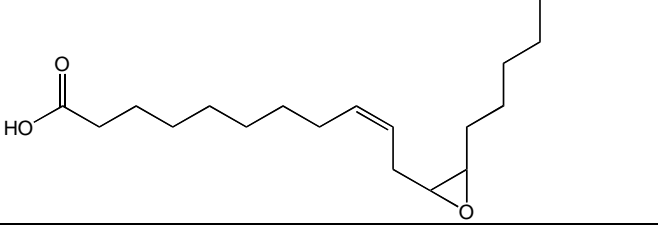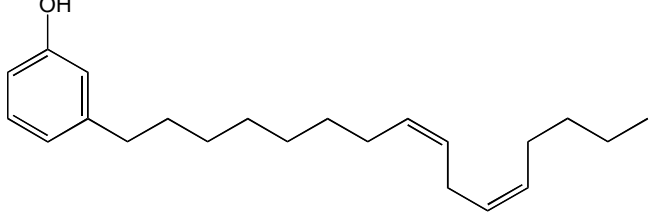
Table 1. Composition of soy bean oil.[8]

Component name	Composition	Chemical Structure
Linoleic acid	51%	
Oleic acid	23%	
Palmitic acid	10%	
Linolenic acid	7%	
Stearic acid	4%	

Castor and lesquerella oils have an additional chemical advantage of a pendant hydroxyl group. Vernonia oil naturally contains an epoxy group, which provides numerous options for functionality and

applications. Another natural oil of interest is the cashew nut shell liquid (CNSL), cardanol, an unsaturated phenolic compound (Table 2).

Table 2. Unusual components naturally found in certain oils.

Source	Component name	Composition	Chemical Structure
Castor oil	Ricinoleic acid	90%[9]	
Vernonia oil	Vernolic acid	80%[10]	
Cashew nut shell liquid	Cardanol	92%[11]	

As seen in the chemical structures above, unsaturated fatty acids contain functional groups such as olefinic, hydroxyl and epoxy, on a long carbon (C16-22) chain. Also, fatty acids contain terminal carboxylic acids. The functional groups enable direct UV cross-linking or chemical modifications toward polyol synthesis.

Today, several commercially available biobased polyols from plant oils are available. Castor oil polyols include Polycin (Vertellus) and Albodur (Alberdingk Boley). Soy bean oil-based polyols include Soyol (produced by Urethane Soy Systems Company), Renuva Polyol (Dow) and BiOH (Cargill). Given current interests in developing biobased coatings, other plant-oil polyols will certainly follow. To give an example of the simplicity of developing a fatty acid-based polyol, Dow reported a four step reaction to prepare its soy bean oil-based polyols,[12] including: (1) a methanolysis step, where a fatty acid methyl ester and glycerol are formed from transesterification of triglyceride and methanol (Fig. 7A); (2) a hydroformylation step, where the olefinic groups in the fatty acid methyl ester are converted to aldhyde groups through a catalyzed hydroformylation reaction with carbon monoxide and hydrogen (Fig. 7B); (3) a hydrogenation step, where the aldehydes are reduced to hydroxyl groups in the presence of catalyst under hydrogen pressure (Fig. 7C); and (4) a final polymerization step, where the product is transesterified with a selected glycol to form the polyol structure (Fig. 7D).
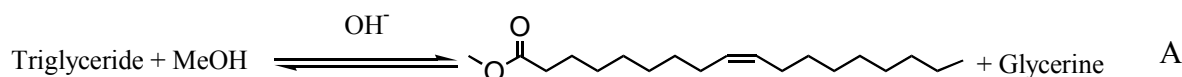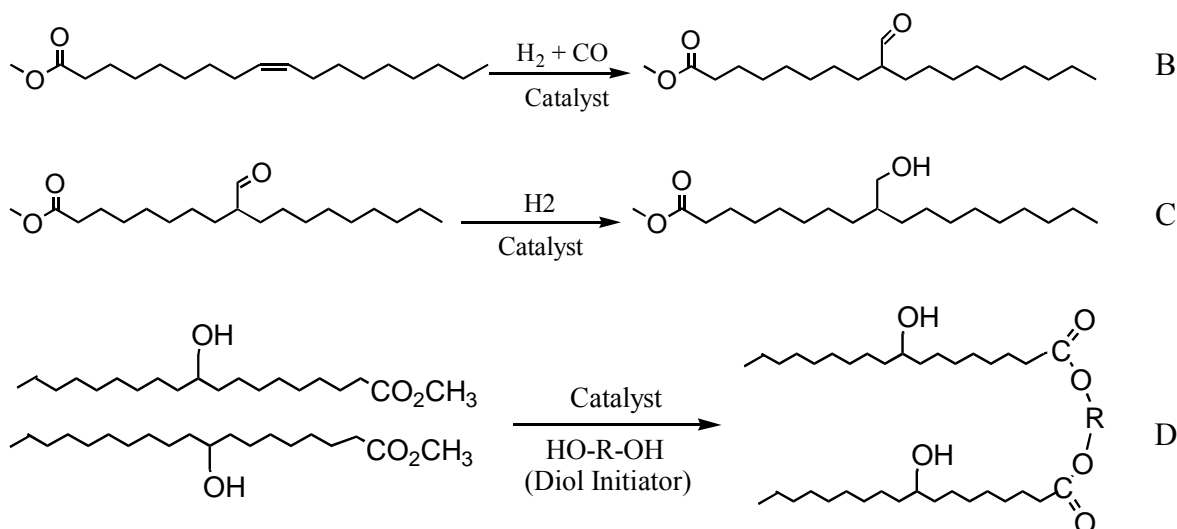
Figure 7. Dow's four step polyol synthesis, based on soy feedstocks. Example shown for oleic acid conversion.

Cerenol: A Commercially Available Biobased Polyol, Based on a C3 Building Block

Cerenol is poly(trimethylene ether glycol) made from Bio-PDO. Bio-PDO is 1,3-propanediol originating from corn sugar *via* aerobic fermentation. Conventional poly(trimethylene ether glycol) is made by ring-opening polymerization of oxetane (1,3-propylene oxide), derived from petrochemicals (Fig. 8).
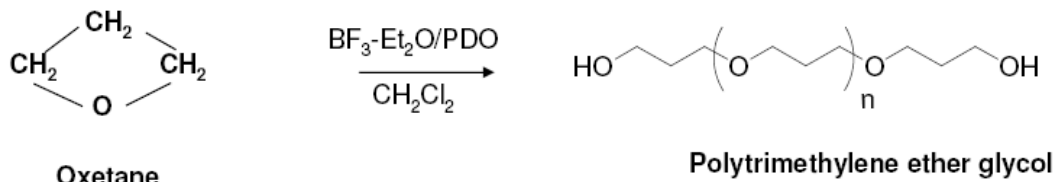

Figure 8. Conventional synthesis of poly(trimethylene ether glycol).

The biobased content of poly(trimethylene ether glycol) made from polycondensation of Bio-PDO is 100%. Clearly, biobased copolyether polyols, such as poly(trimethylene-co-ethylene ether) glycol, and biobased polyester polyols can be made by using Bio-PDO as a building block (Fig. 9).
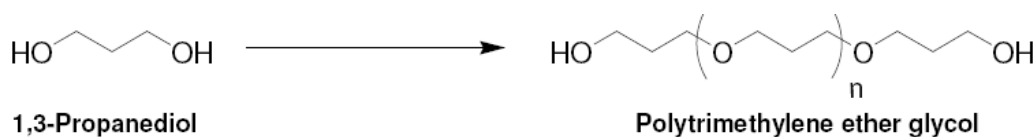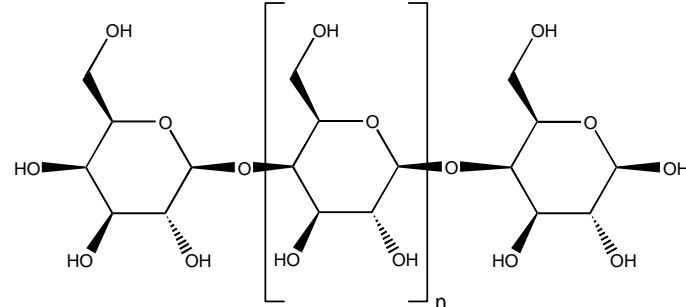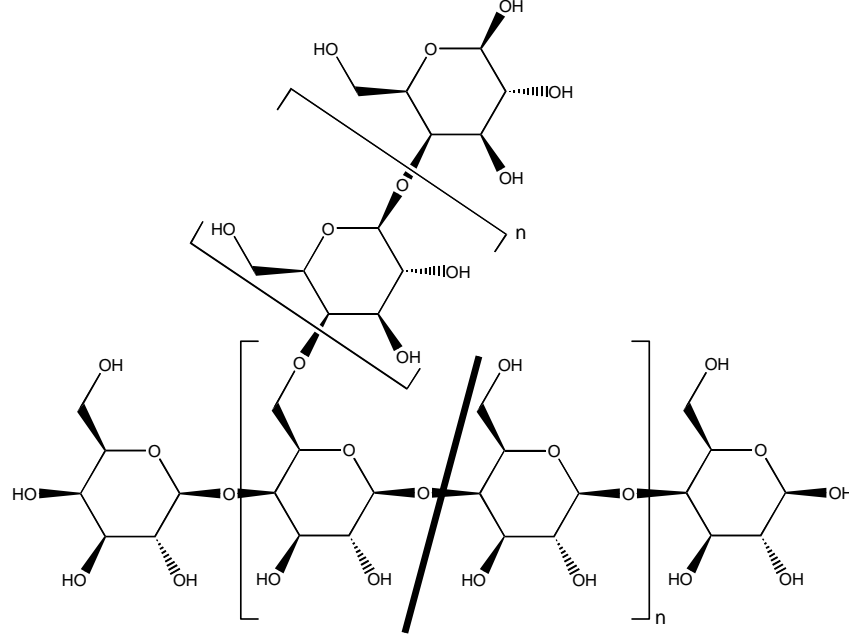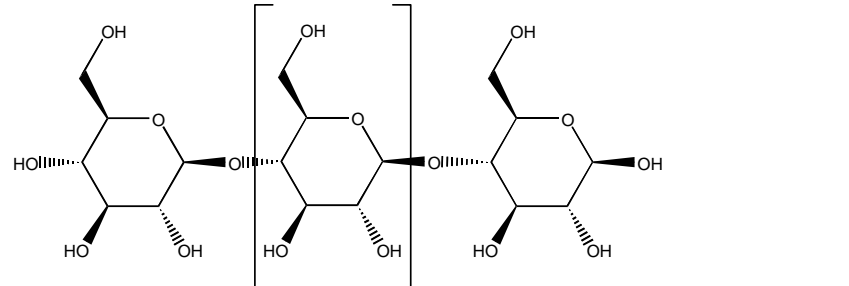

Figure 9. Synthesis of 100% biobased poly(trimethylene ether glycol).

However, these commercially available biobased polyols are not UV curable, though all of them can be acrylated or used as polyols in urethane acrylates.[13] The necessary steps to convert these commercially available biobased polyols to UV curable materials would decrease the biobased content as petrochemicals would be needed to perform such reactions. For example, neither acrylic acid nor isocyanate are made currently from biomass.

Polysaccharides

Polysaccharide feedstock sources primarily consist of starches and cellulose. Other polysaccharides, such as lignin, chitin and chitosan, are used less frequently due to their higher cost. Cellulose is a polymer of glucose with β(1→4) linkages (Table 3). Starch is a glucose-based polymer mixture of 20-30% amylose and 70-80% amylopectin. Amylose is a linear polymer with α(1→4)

Table 3. Chemical structures of amylase, amylopectin and cellulose.

	Amylose
	Amylopectin
	Cellulose

linkages, resulting in a helical structure. Amylopectin is a derivative of amylose, containing branch points at α(1→6) linkages, at the methoxy groups. The α and β designation refer to the orientation of the chemical bonds joining the monosaccharides, while the (1→4) or (1→6) designation refers to which carbon atoms are connected to ether bonds. These polymers contain many hydroxy groups that can be

modified directly. Alternatively, the polymer can be broken down into individual saccharide units (typically glucose/sugar) using heat and acid. Reactions of the monosaccharide units through chemical or enzymatic processes, as described above, yields numerous valuable feedstock materials.

Conclusion

The natural carbon cycle analysis indicates that the development and use of low- or zero-VOC coatings are not nearly enough to reduce the carbon footprint of a material or process. However, a Zero Carbon Footprint would be achievable if the raw materials and energy used in producing a coating are derived from biomass. Using enzymatic catalysis is a more sustainable and eco-efficient process that will continue to improve and exhibit a greater impact on traditional chemical manufacturing. Biobased content and its quantification standards are discussed. Today, commercially available biobased chemicals and materials are quite limited, but increasingly raw materials derived from biomass will become available, including acrylic acid, methyl acrylate, propylene glycol, 1,4-butanediol and succinic acid for coating applications. Biobased polyols, derived either from plant oils or cornstarch, are the only commercially available renewable feedstocks currently used in the coating industry and must be converted to acrylates for UV coating applications.

Acknowledgements

References

[1] "Method for Determining the Renewable/Biobased Content of Natural Range Materials;" ASTM International; ASTM D6866-05.

[2] (a) U.S. Patent 3,169,945; (b) U.S. Patent 3,655,631; (c) U.S. Patent 4,791,189; (d) U.S. Patent 4,683,287; (e) U.S. Patent 4,916,254; (f) U.S. Patent 5,731,406; (g) D. Tian, J. S. Ross and G. A. Sigel; "A Comparison of Caprolactone Based Polyols in Flooring Formulations;" RadTech; 2000.

[3] (a) K. Drauz, and H. Waldmann, Eds.; In "Enzyme Catalysis in Organic Synthesis;" VCH (Weinheim, Germany); 1995. (b) R. A. Gross, A. Kumar, and B. Kalra; "In-vitro Enzyme Catalyzed Polymer Synthesis;" Chemical Reviews; 101(7); 2097-2124; 2001.

[4] U.S. Patent Application 20040242831A1.

[5] "Biomass as Feedstock for a Bioenergy and Bioproducts Industry:The Technical Feasibility of a Billion-Ton Annual Supply;" DOE and USDA Report; April 2005.

[6] "Top Value Added Chemicals From Biomass - Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas;" DOE Report; August 2004.

[7] K. S. Tyson; "Biomass Oil Analysis: Research Needs and Recommendations;" NREL Report; 2004.

[8] M. N. Riaz; "Soy Applications in Food;" CRC Press (Boca Raton, FL); 2006.

[9] Vertellus Specialties, Inc.; product literature; <www.vertellus.com>.

[10] "The Development of Euphorbia lagascae as a new oil crop within the European Community;" results from Contract FAIR-CT98-4460; <www.biomatnet.org/secure/Fair/S822.htm>.

[11] P. Oghome, and A.J. Kehinde; "Separation of Cashew Nut Shell Liquid by Column Chromatography;" African Journal of Science and Technology; 5(2); 92-95; December 2004.

[12] J. Argyropoulos, P. Popa and G. Spilman; "Seed Oil Based Polyols for Coatings;" FutureCoat; Toronto; 2007.

[13] D. Tian, K. Quisenberry, M. K. Boggiano, L. W. Leininger, S. L. Scheuering and J. S. Ross; "Floor Coating Formulations Obtained from 100% Natural, Renewable or Bio-based Materials;" Submitted for Presentation at e|5: UV & EB Technology Expo & Conference 2008; Chicago, IL; May 5 - 8, 2008.