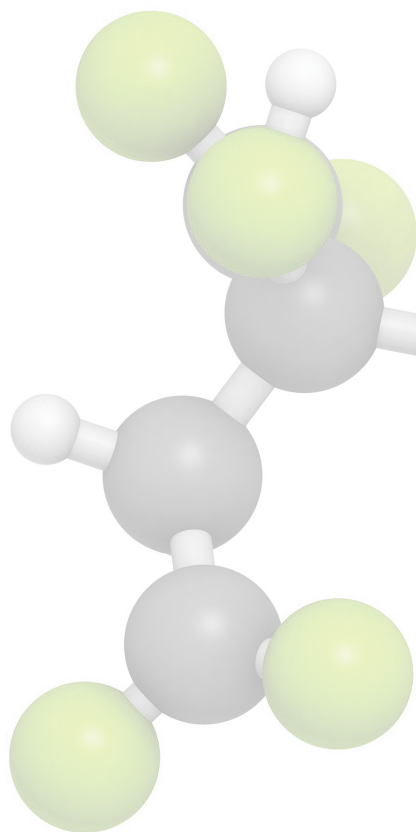


Biobased Materials for UV Coatings

By Mary Kate Davies and
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As finite resources dwindle in supply, chemical production is shifting from petroleum materials to sustainable materials, particularly biobased materials. Hurdles exist that dampen the development of biobased materials, including supply of raw starting materials; competitive production processes; and acceptance of drop-in alternatives. After decades of work and hurdles are overcome, industry is beginning to see commercialization of biobased materials. With that, the UV/EB-curable industry stands to benefit from these materials. This paper will focus on the progress and future opportunities of biobased materials for UV coatings.

Introduction

In the last decade, production of industrial chemicals has seen a shift from petroleum-based to biobased.^{1,2} The shift is being driven by the cost of petroleum; concern over greenhouse gas emissions; new abilities to bioengineer and genome sequence; and pressure from consumers to have more environmentally friendly products. Armstrong World Industries has a long-standing history of using biomaterials—from recycling cork dust and manufacturing linoleum to designing biobased polyesters for use in floor tiles.³ Our researchers believe it is essential to develop more sustainable products and methods to maintain those products. The next effort is to focus on UV-curable materials that come from sustainable biobased sources.

Elemental Life Cycle

Carbon, oxygen and nitrogen are important elements for life and provide key starting materials for commodity chemicals. Existing as carbon dioxide and diatomic gases (CO_2 , O_2 and N_2), the conversion of these compounds to critical primary metabolites by bacteria, fungi and plants creates the terrestrial beginnings of the elemental life cycle.

The elemental life cycle begins with nitrogen fixation. N_2 is relatively inert and requires microorganisms to combine hydrogen (H^+) with N_2 (Equation 1) to create ammonia and hydrogen gas (H_2), which are commercially important starting materials. Ammonia is an important nucleophile for production of amines and amides—two functional groups that are highly important and used in materials for UV-curable coatings.

Equation 1



Oxygen and carbon are closely tied together in the elemental life cycle. Through photosynthesis, plants, algae and cyanobacteria take CO_2 , water and sunlight and convert them to O_2 and liberate the carbon for incorporation into metabolites for cellular function. In turn, humans and animals take oxygen and metabolites and turn them into CO_2 (Equation 2 simplified). This cycle creates a loop that can be neutral, if the amount of CO_2 stays the same; negative, if the amount of CO_2 decreases; or positive if the amount of CO_2 increases.

Equation 2

More than a million years ago, plant and algae mass sank to the bottom of lakes or oceans and mixed with sediments under anoxic conditions. Pressure and heat turned this mass into current-day petroleum, coal and natural gas. Over the last 200 years, CO₂ in the atmosphere has increased due to the use of petroleum products. A global warming trend has also been established and may be due to the increase of atmospheric CO₂—a known greenhouse gas. This was the determination of the Intergovernmental Panel on Climate Change in 1990, which became the framework for the Kyoto Protocol established in 1997.⁴ The Kyoto Protocol is a treaty between industrialized nations that sets binding obligations on greenhouse gas emissions. The treaty was signed by the U.S. in 2001, but was never ratified.

With the focus today on global warming, governments, companies and individuals are focusing on using products and processes that cut down on CO₂ emissions or that may even have a negative impact on the CO₂ cycle. This is known as a “sustainable practice” or sustainable carbon management.

Sustainable Carbon Practice

Government and industry are working on implementing sustainable operating practices. This entails being conscious of the use of energy and materials that go into any process and working toward using them as efficiently as possible. One way to do this is to use renewable materials to make products. Renewable materials that are derived from living or recently living organisms (most commonly plants), are known as biomass. Biobased products are products that contain biomass or materials that originate from biomass.

Biomass, however, does not contain 100 percent biobased content. Biobased content is defined as the

weight of the biobased carbon divided by the total biomass weight times 100.⁵ The reason the carbon content is used to determine biobased material is because organic life is based on carbon and the isotopic profile of carbon provides a way to quantify the age of a material. ASTM Method D6866 is currently used to determine the biobased content. This method compares the amount of decaying carbon isotope in a sample relative to the amount in the same sample if it were made from current biomass. Specifically, ASTM D6866-05 is a technique used to quantify the carbon-14 (¹⁴C) content and calculate the percent of the material or product derived from biomass versus petroleum-based components. Products that contain a defined amount of biobased content are eligible under the U.S. Department of Agriculture’s BioPreferred® program for certification. This program is a way to certify product claims regarding the amount of biobased content it contains.

TABLE 1**12 top sugar-derived building blocks determined by the U.S. Department of Energy**

Building Blocks
1,4 Diacids (succinic, fumaric and malic)
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
Aspartic Acid
Glucaric Acid
Glutamic Acid
Itaconic Acid
Levulinic Acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol/Arabinitol

Raw Starting Materials

In 2004, the U.S. Department of Energy (DOE) released a list of 30 top value-added chemicals that could be made from biomass.⁶ The DOE broke that list down further into 12 sugar-derived building blocks. (Table 1) The criteria for ruling other chemicals out included known uses and usefulness as a starting material. Several important alcohols were left off the list and are being used to create bio-alternatives, including methanol, ethanol and butanol. In addition to that, the DOE did not list any other known biomaterials such as triglycerides, cellulose, PHA starting materials, glucose and fructose. Not all of these materials may be useful for coatings alone, but, when combined with acrylates and other functional linkers, these materials yield a library

of alternative functional opportunities for coatings.

Competitive Production Processes

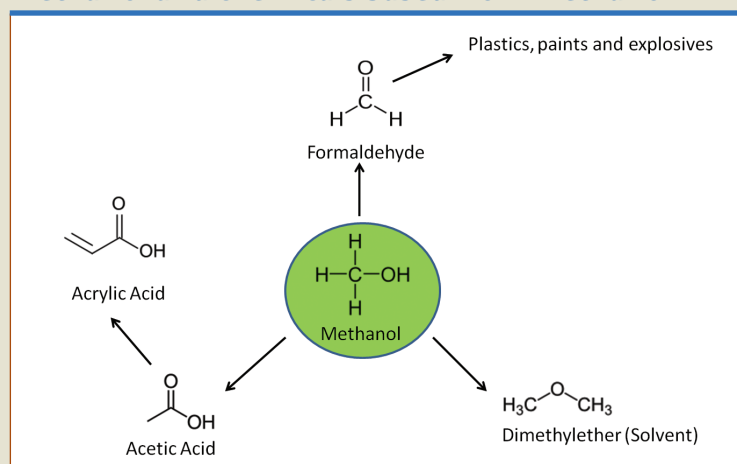
C1 Carbon Starting Materials (Methanol)

Methanol or “wood alcohol” is the simplest of alcohol groups. The term “wood alcohol” comes from the fact it was first made through pyrolysis of wood. In 1923, the conversion of syngas to methanol was achieved and methanol has been produced this way for the past 90 years.⁷ Work has been conducted by multiple groups over the last 30 years to determine the feasibility of a biosyngas-to-methanol facility. Indications are that the methanol would be cost-comparative with current syngas methanol, but a high capital cost would deter new investment in an established reliable industry.

Methanol is used for methyl-esters in biodiesel, plastics and food flavors. Methanol can also be chemically modified to produce formaldehyde, acetic acid or dimethylether. (Figure 1) Even though 27 to 29 million metric tons of methanol are produced annually, most of that methanol gets transformed into other products that have larger carbon profiles. With

FIGURE 1

Methanol and chemicals based from methanol



the economic hurdles that exist in biomethanol production, C2 materials may provide better footing into market entry.

C2 Carbon Starting Materials (Ethanol and Acetic Acid)

Ethanol is produced industrially by fermentation of corn syrup and sugar with yeast. In 2010, nearly 13.2 billion gallons of ethanol were produced in the U.S.⁸ If industry adopts bioethanol as a starting material for other chemical platforms, production is expected to continue to increase. The ability

to oxidize ethanol to acetic acid or dehydrate it to ethylene makes ethanol a versatile starting material for many other chemical platforms. (Figure 2) These chemicals can be used to create polyesters, plastics and diacids. The acrylated secondary chemicals from bioethanol can add characteristics to coatings and films such as low volatility, flexibility, soft surfaces and hydrophilic or hydrophobic properties. The benefits of using ethanol as a starting material include centuries of experience conducting fermentation;

FIGURE 2

Ethanol and chemicals based from ethanol

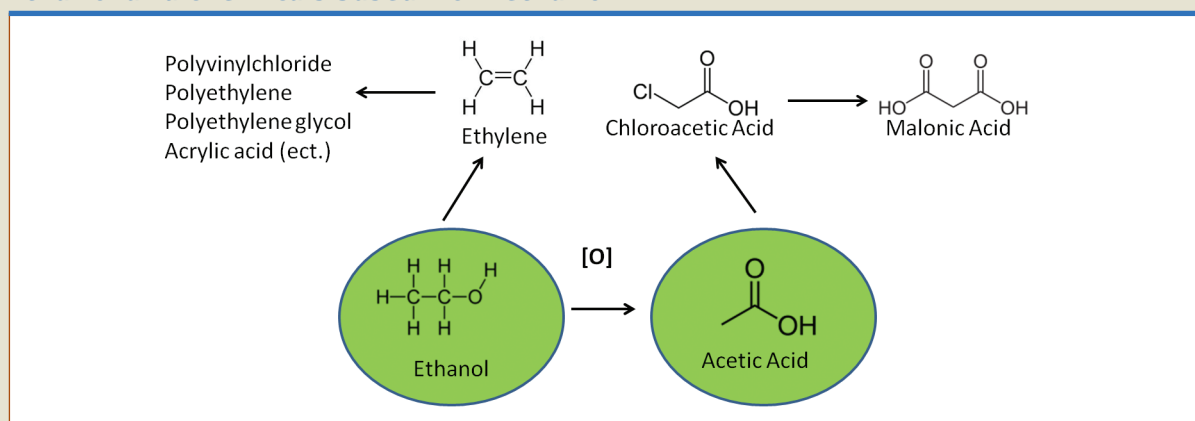
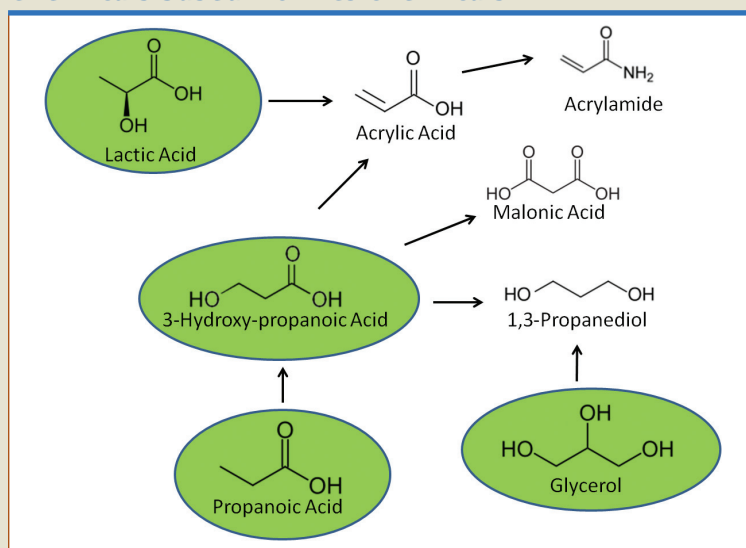


FIGURE 3

Chemicals based from C3 chemicals



high yields by new strains of yeast; and future production via cellulosic starting materials.

Acetic acid is another C2 biobased material. Acetic acid is produced industrially from syngas methanol by methanol carbonylation, but methanol carbonylation only accounts for 75 percent of the annual production of acetic acid.⁹ Another historic route to acetic acid production accounts for the other 25% and occurs via starch fermentation with *Clostridium* or *Acetobacter* bacteria. Globally, 5 million tons of bio-acetic acid are produced annually. Acetic acid is often chlorinated to chloroacetic acid which can be further transformed to other chemicals such

as malonic acid, thioglycolic acid or chloroacetylchloride. Malonic acid stands to be the most useful product of acetic acid, as it can be further reacted and decarboxylated.

C3 Carbon Starting Materials (Propanoic Acid, 3-Hydroxypropanoic acid, Glycerol and Lactic Acid)

Glycerol is a byproduct of biodiesel production. More than 1 million tons of glycerol is produced in the U.S. and Europe each year.¹⁰ The three hydroxy groups of glycerol enable the production of industrially useful derivatives. (Figure 3) In the coating industry, glycerol is used to make surfactants and trifunctional additives. The most recent noteworthy use of glycerol was developed by DuPont and

Tate and Lyle with their conversion of glycerol to 1,3-propanediol.

1,3-Propanediol is chemically synthesized by the hydration of acrolein, which is produced by the oxidation of propylene. Two current methods exist to produce bio-1,3-propanediol—the above mentioned DuPont and Tate and Lyle method using *E. coli* or *Clostridium*. Only the *E. coli* method is being used commercially, with 120,000 tons being produced in 2007.¹ 1,3-Propanediol can undergo condensation with acrylic acid or other acids to be difunctional or create polyesters for oligomers acrylates.

A company called Polymer Phases has taken a different perspective on glycerol and designed renewable UV-curable, drop-in additives that are 75 to 100 percent sustainable. Two products they developed are GreenPhase™ UV-101 and GreenPhase™ UV-201. These two products are hydrophilic and compatible with Sartomer SR454. They provide flexibility and some solvent resistance.¹¹

Propanoic acid, lactic acid and 3-hydroxy-propanoic acid are currently being pursued by companies as possible starting materials for biobased acrylic acid. The leading competitors are OPX/DOW, Myriant Technologies and Cargill/Novozyme.¹² Currently, biobased acrylic acid is not available commercially, which is likely due to cell toxicity, purification and low yields in the fermentation and subsequent conversion to acrylic acid.

FIGURE 4

Biobased production of succinic acid from glucose

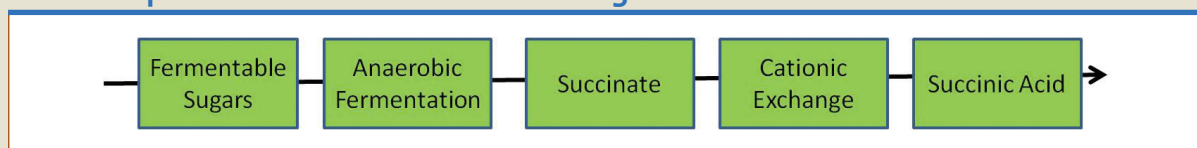
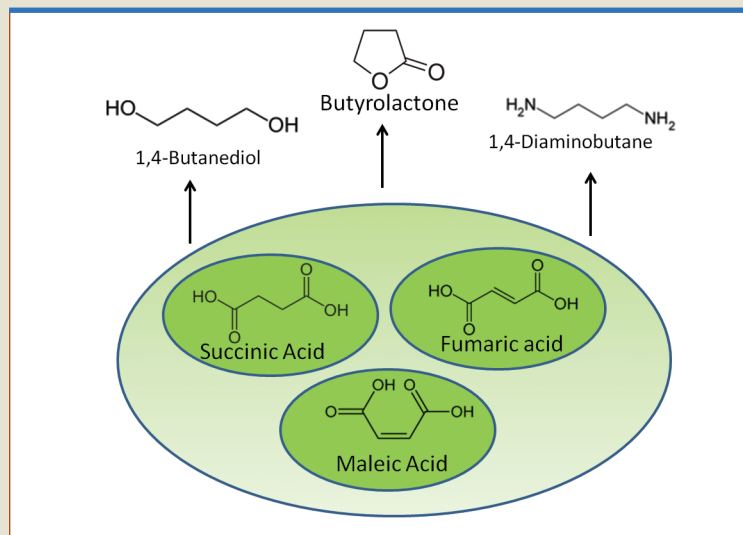


FIGURE 5

C4 Diacids succinic acid, maleic acid and fumaric acid



C4 Carbon Diacids (Succinic, Fumaric, and Malic Acid)

The C4 diacids (succinic, fumaric and malic acid) are very similar in structure and can be readily used to produce the others. Most succinic acid is synthesized through three industrial routes—carbonylation of ethylene glycol; hydrogenation of maleic acid; and oxidation of 1,4-butanediol. The current industrial routes use petroleum-based starting platforms to create succinic acid, but biobased succinic acid is currently being manufactured or investigated by several companies—Bioamber, Myriant Technologies, BASF and Lanxess.¹¹ Biosuccinic acid is produced by fermentation with *E. coli* or yeasts using simple sugars or starches. (Figure 4) Succinic acid is easily transformed to several useful primary derivatives for coatings and polyesters. (Figure 5) 1,4-Butanediol diacrylate offers high solvency and low viscosity as an additive to coatings.

C4 Other Carbon Starting Materials (Butanol, 3-Hydroxybutyric acid)

Two biobased materials are of interest as building blocks for coatings—

butanol and 3-hydroxybutyric acid. Butanol (Figure 6) is produced by the hydroformylation and hydrogenation of propylene. Before the 1950s, biobutanol was produced as a byproduct of the acetone, butanol and ethanol fermentation of starch using *Clostridium acetobutylicum*.¹³ When petroleum became readily available, fermentation was no longer commercially feasible to produce these commodity chemicals. Recently, Gevo has produced bio-isobutanol using yeast and a novel pathway not found in nature.¹⁴ Butamax (a company created by DuPont/BP) is also commercializing the production of biobutanol.¹⁵

FIGURE 6

Butanol and 3-hydroxybutyric acid



Although chemically similar, isobutanol and butanol will offer different starting points for chemical platforms due to isobutanol containing the tertiary carbon structure instead of the linear structure. 3-Hydroxybutyric acid is also being explored for polybutyric acid production for plastics, but also as a potential alternative to acrylic acid.

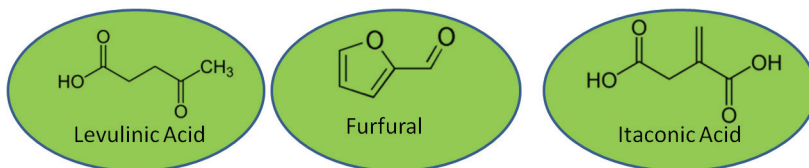
C5 Carbon Starting Materials (Itaconic Acid, Furfural and Levulinic Acid)

Several C5 starting materials are available from biobased sources. Itaconic acid is produced industrially by the fermentation of sugar by *Aspergillus*. Itaconic acid is mainly produced by China and imported into the United States. Roughly 15,000 tons of itaconic acid are produced annually, and the market is expected to continue to grow due to itaconic acid's natural antimicrobial properties.¹⁶ The conjugated system in itaconic acid allows polymerization to occur. However, homopolymerization can be difficult to achieve and the resulting structure is complex.

Furfural is another biobased material that is produced by the acid treatment of sugar or hemicellulose. China is the main producer of furfural, producing 800,000 tons each year. Furfural can be oxidized to create furoic acid; hydrogenated to produce furfural alcohol; or decomposed to produce furan. Levulinic acid, a third starting material, is produced by heat treating sucrose with sulfuric acid. Sucrose

FIGURE 7

C5 starting platforms



converts to hydroxymethylfurfural, which hydrolyzes to produce formic acid and levulinic acid. Itaconic acid, furfural and levulinic acid are potential starting materials for coating additives and oligomers, but more research is needed into their potential usefulness. (Figure 7)

C6 Carbon Starting Materials: Citric Acid

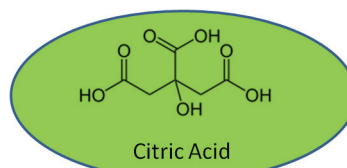
Citric acid (Figure 8) is produced via fermentation of sugars by *Aspergillus niger*. Global production of citric acid was 1.6 million tons in 2007, with most of the citric acid going to consumption in the food industry.¹⁷ Citric acid is unique in that it provides three functional carboxylic acids for polyester formation. Reduction of those carboxylic acids to alcohols can provide a quaternary building block for acrylation, which may be a biobased alternative to trimethylolpropane in trimethylolpropane triacrylate.

C6 Carbon Starting Materials: Triglycerides

Triglycerides are esters containing three fatty acids and glycerol. Triglycerides may be saturated or unsaturated in nature, with unsaturated fatty acids having the greatest implications for coatings. Saturated fatty acids and monounsaturated fats are typically not of interest as precursor chemicals because they lack the functionality to undergo chemical modifications

FIGURE 8

Citric acid



such as epoxidation. Oils that are rich in polyunsaturated fatty acids are more desirable. Some of these oils include cottonseed, wheat germ, soy, corn, sunflower and safflower oil.

Soy oil is the most abundant of these oils as it is the least typically used for food or health care products. The typical composition of soy oil contains approximately 81 percent unsaturated

TABLE 2

Unsaturated fatty acids in soy oil

Fatty Acid	Fatty Acid Structure
Linoleic	
Alpha-Linolenic	
Oleic	

oils, with the main unsaturated fatty acids being linoleic acid, alpha-linolenic acid and oleic acid. (Table 2) Castor oils have a pendant hydroxyl group, which adds additional functionality. The functional groups enable direct UV crosslinking or chemical modifications toward polyol synthesis.

Today, several commercially available biobased polyols from plant oils are available. A few of the commercially available polyols are Agrol from Biobased Technologies, Cargill BiOH polyols and Renuva from DOW. Using fatty acids, modifications can be made that allow for polyol polymerization. Alberdingk Boley produces a castor oil-based polyol. This polyol is not marketed as such but can be used as an additive to UV-curable coatings to increase hydrophobicity and chemical resistance.¹⁸

Conclusion

Before the wide acceptance of petroleum, many commodity chemicals were produced from biobased materials. As the price of petroleum continues to increase due to global demand, the door to reinvesting and reinventing biobased chemicals is being reopened. Many companies such as Armstrong World Industries consider this to be an essential investment in our future. With companies developing many different platforms for petroleum-based chemicals, the UV/EB industry can take advantage of these opportunities and create materials based on these platforms for incorporation into coatings, inks and films.

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