Renewable/Sustainable Product Development: Green Chemistry vs. Energy-Curing Blues

By Michael L. Gould

In technology-driven market segments that employ energy-curable coatings, adhesives and composites, “sustainable” and/or “renewable” product character has taken on greater potential value, both from a marketing and cost/performance standpoint. However, in a challenging paradox, it is also widely assumed that bio-renewable (e.g., vegetable-based) raw materials utilized in the development of sustainable (i.e., non-petroleum based) products will deliver acceptable performance at *LOWER* cost than current raw materials. This paper will highlight product development features of the oversimplified puzzle that is “sustainability.”

General product marketability has gained momentum in recent years by employing labels or definitions such as “green,” “renewable,” “sustainable” and “eco-friendly.” Whether or not new products and technologies are truly any of these things, they are recognized more widely with each passing year as being “desirable.”

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In the UV/EB energy-curing submarket of the broader coatings, adhesives and composites markets, sustainability has taken on a greater measure of attractiveness as product manufacturers seek to differentiate their products from one another. While the debate is shaped over how to best define “sustainability” or to quantify “renewable” product content, both raw material producers and converters must examine and modify their product lines to accommodate the growing demand for building block raw materials derived from renewable (i.e., non-petroleum) resources.

Across several competitive raw material suppliers, renewable product offerings have been grouped and re-marketed to appeal to those seeking non-petroleum based monomers and oligomers. Examples of this include re-defining standard products—epoxidized soy oil acrylates, isobornyl and stearyl acrylates, THFFA, fatty acid-modified epoxy acrylates, dimer acid polyesters, etc.—as part of a specifically "renewable" portfolio.

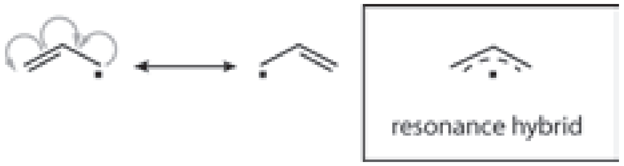
In late 2008, Rahn decided to tackle this opportunity from both a traditional marketing approach (defining renewable content in current products) and from the perspective of bringing unique, cost-effective, acceptably performing bio-renewable products to the marketplace. In this portfolio of products, renewable content is quantified by the percentage of product carbon that comes from oleo-based sources (e.g., natural plant oils and glycerine) rather than from petroleum refining. No attempt has been made to assess the total carbon efficiency and/or footprint by comparing the amount of energy and process chemicals (e.g., fertilizer) used in one type of product versus another. This in-depth quantitative analysis of total environmental balance is best left to those looking at the bigger picture. For now, the working assumption is that oleo-based products will inevitably prove to have a smaller net carbon footprint once all factors are considered.

High Renewable Content: Curing Woes with Natural Oils

Molecule design for energy-cure applications is relatively straightforward. A wealth of knowledge and experience published during four decades of UV/EB technology growth provides a good starting point for any new oligomer, provided that its intended end-use parameters are clear. For example, the introduction of polyacrylate functionality into an oligomer molecule is likely to produce a product with acceptable "cure response." A hard substrate needing a scratch-resistant topcoat that cures at low line speeds will drive molecule design in the opposite direction from a soft, flexible, low-energy substrate that needs high cure response at very high line speeds. Little by little, the end-use and performance parameters shape the design of a new product to the point where its efficacy can be measured.

FIGURE 1

Allylic radicals—"standing on the brake"



When dealing with oleo-based starting materials, there are some significant limitations that are encountered in many cases. Natural oils and rosin esters, for instance, have unsaturation that makes them unique in their properties. Some unsaturated oils have very good drying properties in air; others don't dry at all. In the case of free-radical cure, promoted by UV light and photoinitiator, natural unsaturation tends to form very stable allylic radicals that participate very little in the traditional "fast UV cure" paradigm as shown in Figure 1.

Over time, these allylic radicals oxidize to form peroxy compounds that can subsequently crosslink with other unsaturated chains. Thus, UV-cure response with these materials is typically "sluggish" at best, and film or cured article properties may change significantly over a period of hours or days. This does not have to be problematic, but it must be understood and anticipated in order to make effective use of materials in this class.

Another practical limitation of plant-based oils and esters is their inherent "softness." High molecular weight oligomer oils and fatty acids with high hydrocarbon content tend to form soft or plasticized matrices even after full cure. Thus, attaining the necessary hardness for a robust, scratch-resistant surface is challenging. Such limitations, however, are possible to overcome with adequate product design and formulation.

A World Awash in Glycerine: Process Limitations?

One of the largely overlooked potential workhorse materials in a biorenewable portfolio is glycerine. With a dramatic rise in the commercial efficacy of biodiesel fuels, and with global supplies accelerating to meet demand, by-product glycerine has literally flooded the market, taking glycerine prices down to an all-time low in recent years.[1] This factor adds additional intrigue to the prospective use of glycerine as a building block in new renewable products.

Glycerine—used widely in food, medicine and cosmetics—offers some significant benefits over other polyols, including low price, ease-of-handling and high functionality in a small package. Unfortunately, glycerine is not directly or easily made compatible with the traditional esterification chemistry by which so many acrylic monomers and oligomers are made. The molecule has a dramatic tendency to dehydrate and form polymeric tars under the conditions of acid-catalyzed esterification. Thus, glycerine must first be modified to enhance its stability in the presence of acid and heat, a step that adds cost and reduces renewable content in the ultimate product for which it is being used.

One strategy that was researched during this development program, one which would have an enormous upside given the likelihood of surplus glycerine supplies in the future, was sourcing propylene oxide made from glycerine. Commercial manufacturing to produce propylene glycol from glycerine is already a reality. With some slight modifications,[2] and given sufficient financial incentive, that process could be altered to yield propylene oxide. Unfortunately, the desirability of propylene glycol in the commodity chemicals market is very high. Propylene oxide, in largest measure, is used to make propylene glycol. Thus, a process to bypass a most desirable product for a lesser desirable one is unlikely to take root any time soon unless driven by significant profitability potential or environmental mandates.

Outside of the Box: Registration Woes

The year 2010 is upon us and with it comes the dawning of new REACH restrictions within Europe. One significant downside to a program that targets *NEW*, unique sustainable products is the difficulty in achieving easy market entry because of regulatory/inventory hurdles. The costs associated with registering new products under REACH are daunting. It would seem a logical strategy to first develop materials for markets outside of Europe, then, over time, to assess the efficacy of developing REACH-compliant versions of those materials for broader marketability.

Other countries may soon follow the lead of Europe and impose greater restrictions on the development and registration of new chemical substances as well. If that were to be the case, the likely mode of commercial entry for new renewable materials would be as polymers. Polymers have somewhat lesser utility as raw materials in traditional energy-curing applications because of limitations imposed by high viscosity, lower reactivity (in general) and difficult rheology. In a future where most or all new products brought to market are polymeric, we could see a significant shift toward waterborne UV/EB technology. When "sustainability" is a key target for new developmental products across the globe, it is hard to fathom regulatory trends that would actually increase the energy needed to cure workhorse products such as coatings.

Natural Product Basis: Pandora's Box?

In developing chemistry that interfaces directly with nature, some interesting questions come to mind that will inevitably need answers.

- Bioavailability—Will new reactive chemical materials based on natural products have significantly different "bioavailability" within people, animals and plants? And, if so, will there be issues of toxicity, allergies, irritation, etc., which will arise?
- Biodegradation?—Already the energy curing industry is hard at work to quantify recyclability versus biodegradability versus compostability, particularly for packaging materials. Will the incorporation of significant quantities of bio-sourced raw materials provide a more favorable life cycle for new products?
- With the sudden market shift toward biodiesel fuel in the past five years, the critical issue of global food supplies suddenly came to the fore.[3] Will a strategy to utilize potential foodstuffs (e.g., plant oils such as soybean, sunflower and coconut) as chemical raw materials exacerbate food shortages which will be felt most keenly by the Third World?

Conclusion

The incorporation of natural, biorenewable materials into the traditional energy curing raw material portfolio is not as straight forward as it might seem. Many issues, not the least of which are performance- and regulatory-related, complicate the landscape upon which the best of intentions cannot be easily translated into acceptable new products.

Sustainability, arguably a very broad concept with no exact definition, is a driving paradigm in the industrial world that is here to stay. The depletion of precious natural resources by a growing world population mandates that we all contribute to a sustainable future by "reducing, reusing and recycling" at a minimum. Consumerism is not the enemy; poor planning and inadequate infrastructure to minimize energy consumption and waste are the first "bogeys" on the green radar. As renewable and sustainable concepts are defined more quantitatively in the future, it is incumbent upon our industry to grow in those directions in order to ensure a sustainable future.

In the near term, we must work as an industry to clarify our goals, define our metrics and implement change through education. The efforts of vanguard groups such as the RadTech Sustainability Committee should not go unnoticed or unappreciated. These groups, working with academic and government resources, will ensure that we have a definitive pathway toward a greener, compliant future. ◗

References

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