

Design and Performance of Radiation Curable Acrylates with High Renewable Carbon Content

*Jeffrey Klang, PhD
Sartomer USA, LLC
Exton, Pa USA*

Abstract

Radiation curing technology is widely recognized as a “green” or sustainable technology because of the avoidance of VOC emissions and low energy use compared to solvent or water based coating and printing technologies. The use of radiation curable materials based at least partially on renewable raw materials brings another level of sustainability. While renewable based radiation curable materials are currently being used commercially (primarily in printing inks), there are many opportunities to design new materials with higher renewable content and enhanced performance. The properties of new materials with high renewable content in targeted coating and ink applications will be discussed.

Introduction

Chemicals derived from renewable resources have long been widely used in a variety of industrial, household and cosmetic applications. Nearly all of the renewable raw materials used are plant based and are all ultimately derived from plant sugars formed by conversion of CO₂ by photosynthesis (Figure 1). These raw materials are converted to final products using a range of chemical processes such as esterification, epoxidation, hydrogenation, fermentation, hydrolysis, dehydration or polymerization.

Like the general chemical industry radiation cure applications have also long used renewable raw materials in a variety of ways. Materials like rosin esters, sucrose esters, and vegetable oil derivatives are used as inert ingredients for pigment wetting, thickening or plasticization. There are also a significant number of reactive acrylate monomers and oligomers on the market that are at least partially based on renewable raw materials. Some examples are shown in Figure 2 along with their biorenewable carbon content¹.

While there are several different ways to express the renewable content of a chemical product this paper will use the biorenewable carbon content or %BRC. The %BRC has the advantages of being easy to understand and calculate, of being reasonably

widely accepted and being verifiable by analytical testing^{2,3}. The %BRC can be calculated by the equation:

$$\%BRC = 100 \times (\# \text{ of Biorenewable Carbon Atoms} / \# \text{ of Total Carbon Atoms})$$

Figure 1.

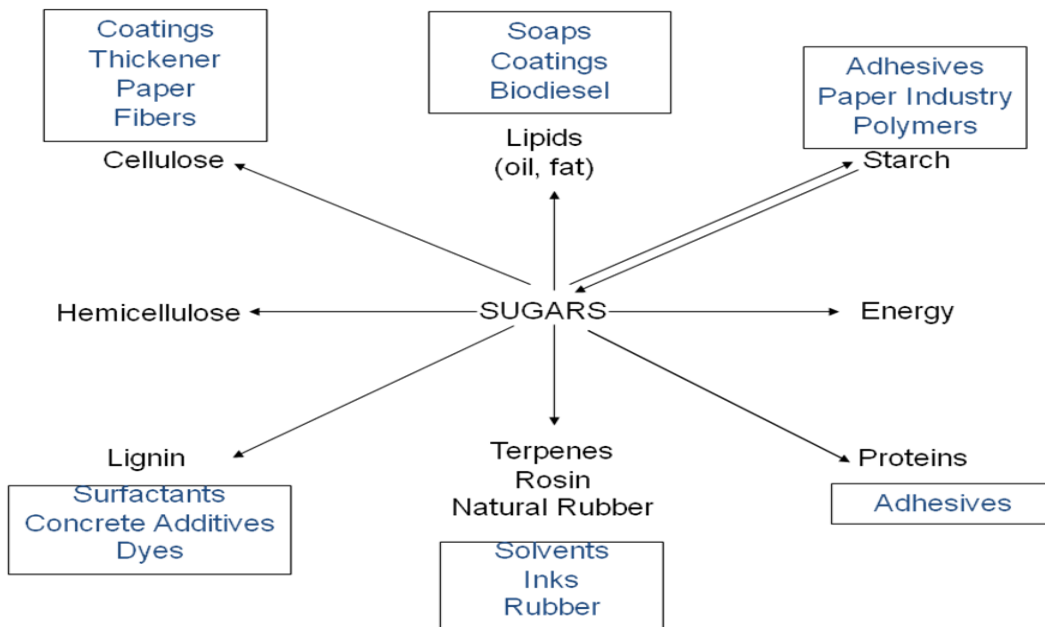
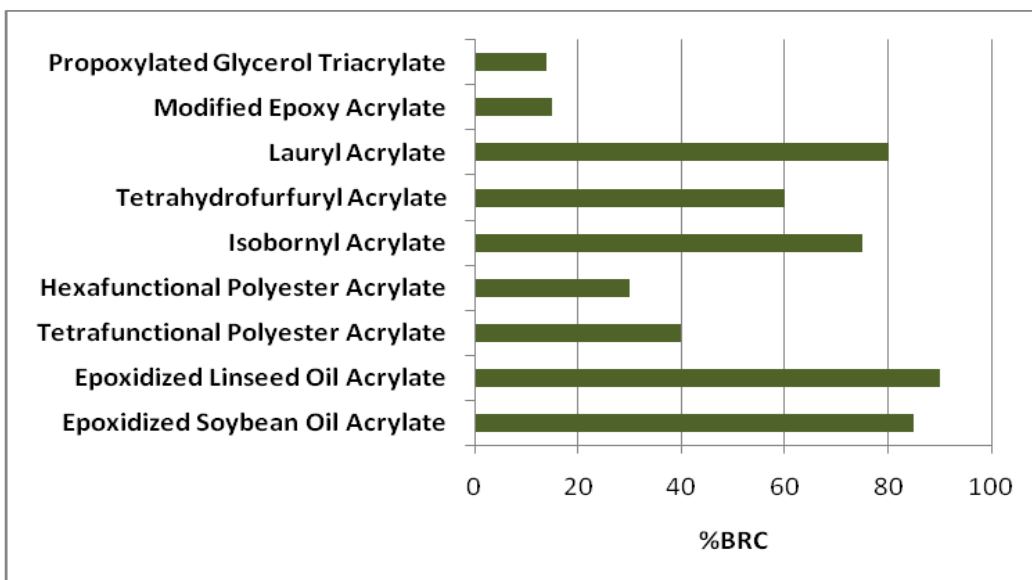


Figure 2: Examples of Current Commercial Acrylates with Renewable Raw Material Content



Some of the current commercial examples have impressively high %BRC values, but until there is a viable commercial supply of bio-sourced acrylic acid it will be impossible to make 100% renewable acrylates. While there is development activity in this area availability at reasonable prices is still likely several years away⁴. Despite the commercial availability of radiation curable acrylates with partial biorenewable carbon content and their widespread use in some applications there is still a need for new offerings with higher %BRC and improved properties. In particular there are needs for multifunctional low viscosity diluents and for oligomers with low color and properties suitable for general coatings applications.

Results and Discussion

Table 1 introduces a series of six new radiation curable acrylates with BRC contents of 50 to almost 90% and functionalities of 2 to 12 acrylate groups per molecule. The products are all derived from readily available renewable raw materials and were converted to acrylates using standard techniques such as esterification, epoxy addition and urethane formation. The properties of each will be discussed in more detail below.

Table 1: Experimental Monomers and Oligomers

	Description	%BRC	Acrylate Functionality	Color	Viscosity (cPs)
Monomer 1	Low Viscosity Hydrophobic Monomer	62.5	2	50 APHA	10*
Oligomer 1	Vegetable Oil Urethane Acrylate	55.9	3	2G	18,800
Oligomer 2	Hydrophobic Oligomer	74.7	2	300 APHA	40
Oligomer 3	Modified Vegetable Oil Epoxy Acrylate	88.5	6	1G	5800
Oligomer 4	Modified Vegetable Oil Epoxy Acrylate	79.3	12	1G	24,000
Oligomer 5	Low Viscosity Oligomer	50.0	2	50 APHA	45

*At 25°C, all others at 60°C.

As noted above there is a need for low viscosity, multifunctional monomer diluents with high BRC. Monomer 1 is a higher molecular weight analogue of 1,6-hexanediol diacrylate (HDDA) made by conventional acrylate processing techniques using a raw material derived from a common vegetable oil. Table 2 shows a comparison of the basic properties of Monomer 1 to HDDA. Monomer 1 has liquid properties similar to HDDA with the benefits of reduced volatility, less skin irritancy, higher Tg and better flexibility. Diluency power, cure efficiency and weathering performance have been found to be nearly identical to HDDA. Its balance of properties make Monomer 1 well suited for applications such as ink jet, screen and flexo inks and exterior coatings.

The performance of Monomer 1 as a diluent in simple high BRC formulations will be discussed below.

Table 2: Comparison of High %BRC Monomer to HDDA

	APHA Color	Viscosity @ 25 °C	Surface Tension (dynes/cm)	Volatility**	Tg (°C by DSC)
Monomer 1	< 50	10 cPs	33.4	1.8%	91
HDDA*	20	9 cPs	35.7	12.5%	43

*Sartomer SR238

** Measured by TGA as weight loss at 80°C over 240 minutes.

The basic physical properties of Oligomers 1 through 5 are shown in Table 3. Each oligomer will be discussed separately in more detail below.

Table 3: Physical Properties of Experimental Oligomers

	Tg by DMA, °C		Tensile Properties			
	Loss Modulus	Tan Δ	Strength (psi)	Elong. (%)	Modulus (psi)	Energy @ max Load (ft-lb)
Oligomer 1	31	63	3350	51	75,119	0.4582
Oligomer 2	-3	11	150	5	3314	0.0008
Oligomer 3	-30	16	470	6	8783	0.0033
Oligomer 4	4	76	1000	1.8	65205	0.0022
Oligomer 5	-27	63	Too brittle to be tested.			

Cure Conditions: 1880 mJ/cm² energy as measured by Power Puck II radiometer with 3% Esacure KIP100F ((70:30 blend of oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone] and 2-hydroxy-2-methyl-1-phenyl propan-1-one) and 1% Esacure TZT (2,4,6-trimethylbenzophenone) photoinitiators.

Oligomer 1 is one of several urethane acrylates that have been made from hydroxyl functional vegetable oils or derivatives. In addition to varying the vegetable oil portion of the product the use of urethane chemistry allows for adjustment of properties by choice of isocyanate and acrylating agent. Oligomer 1 exhibits the high flexibility and toughness typical of many urethane acrylates. Other urethane acrylates with modified structures are being tested.

Oligomer 2 and Oligomer 5 are both made from raw materials that have undergone one or more chemical processing steps and are quite chemically pure. One result of this is that the color of resulting acrylates is low compared to most acrylated oligomers with high renewable carbon content. In addition, chemical processing provides structures and resulting properties that are not available directly from nature or from petrochemical sources.

Oligomers 3 and 4 can be considered higher functionality versions of conventional epoxidized oil acrylates such as epoxy soybean oil (ESO) and epoxy linseed oil (ELO) acrylates. They are made by reaction of a well defined fatty acid stream with a high functionality naturally derived polyol core followed by epoxidation and acrylation using standard methods. Oligomer 3 differs from Oligomer 4 in that only about 50% of the available epoxy groups are converted to acrylate. So in addition to 6 acrylates/molecule Oligomer 3 also contains about 6 epoxies/molecule offering opportunities for dual cure uses. As they are based on a raw material that is chemically processed with relatively pure and well defined precursors Oligomers 3 and 4 should exhibit less of the year-to-year and regional variations seen with products that use vegetable oil precursors more directly.

All of the experimental oligomers were tested for basic coating properties as neat materials and in a simple high BRC formulation consisting of 50% Oligomer, 23% Monomer 1, 23% IBOA, 3% Esacure KIP100F (70:30 blend of oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl)phenyl] propanone] and 2-hydroxy-2-methyl-1-phenyl propan-1-one) and 1% Esacure TZT (2,4,6-trimethylbenezophenone). All samples were cured with a Fusion 600W/in H bulb at 861 mJ/cm² total UV energy as measured by a Power Puck II radiometer.

Oligomers 1, 3 and 4, which are all vegetable oil derived, were compared to a commercial ESO acrylate (Sartomer CN111US). Neat oligomer results are summarized in Table 4 and formulation results in Table 5.

Table 4: Neat Oligomer 1, 3 and 4 Coating Properties vs ESO Acrylate

	Hardness		MEK Rubs	Rub Resistance	Adhesion			
	Pencil	PersoZ			PET	PLA	Glass	Aluminum
Oligomer 1	8B	35	200+	+	--	+++	--	+
Oligomer 3	8B	40	195	+	++	+++	--	+
Oligomer 4	3B	90	200+	++	--	+	+	--
ESO Acrylate	6B	50	60	+	--	--	--	--

Key to symbols for all tables: -- poor/fail, + fair, ++ good, +++ very good.
Rub resistance measured by change in gloss after Sutherland rub test.

Table 5: Properties of a High BRC Formulation Containing Oligomers 1, 3 and 4.

Formulation		Hardness		MEK Rubs	Rub Resistance	Adhesion			
Oligomer	%BRC	Pencil	PersoZ			PET	PLA	Glass	Al
1	57.2	4B	30	30	+	--	+++	--	--
3	72.8	8B	40	<10	+	--	+	+	--
4	68.4	2B	120	200+	++	--	--	--	+
ESO Acrylate	71.2	3B	80	40	--	--	--	--	--

As they are all based on vegetable oils and contain long chain fatty acids Oligomers 1,3 and 4 as well as ESO acrylate all cure to relatively soft films as measured

by pencil and Persoz hardness tests. Within the series the higher functionality Oligomer 4 does show higher hardness compared to the others. All of the experimental oligomers do show quite good MEK resistance and are much improved over ESO acrylate in this regard. Interestingly, Oligomers 1 and 3 both provide very good adhesion to PLA (polylactic acid) which is an increasingly popular choice for packaging because of its renewability⁵. Test results on the high BRC formulations are somewhat disappointing given the fairly encouraging neat oligomer results. However, no attempt was made to adjust or optimize the formulations and it seems likely that much better results could be achieved.

Analogous studies to those above were carried out on Oligomers 2 and 5. Although the two materials are based on quite different raw materials they do have some similarities: both are at least partially cyclic in structure, have low viscosity and are diacrylate functional. In this case a standard bisphenol A epoxy acrylate oligomer (Sartomer CN120) which shares the cyclic structure and difunctionality was used as the comparison.

Table 6: Neat Oligomer 2 and 5 Coating Properties vs Bisphenol A Epoxy Acrylate

	Hardness		MEK Rubs	Rub Resistance	Adhesion			
	Pencil	Persoz			PET	PLA	Glass	Aluminum
Oligomer 2	5B	84	33	+++	+++	+++	+	+++
Oligomer 5	7H	Not tested	200+	+++	--	+++	--	+
BPA EA	2H	319	200+	+++	--	+	--	--

Table 7: Properties of a High BRC Formulation Containing Oligomers 2 and 5.

Formulation		Hardness		MEK Rubs	Rub Resistance	Adhesion			
Oligomer	%BRC	Pencil	Persoz			PET	PLA	Glass	Al
2	66.2	6B	22	134	++	--	+++	--	+++
5	54.4	3H		200+	+++	--	+++	+	--
BPA EA	30.4	F	258	162	++	+	+++	--	+

In these tests the performance of Oligomers 2 and 5 equals or exceeds that of the epoxy acrylate oligomer in some respects. In particular, Oligomer 5 has very good hardness, chemical resistance and rub resistance both as a neat material and in the high BRC formulation. In other work that is being reported on separately, Oligomer 2 has shown very good performance as a moisture vapor barrier material⁶.

Conclusion

A series of new acrylate monomers and oligomers with high renewable carbon content and differentiated physical properties has been developed. Some of these products may help address performance needs that cannot be met by high %BRC acrylates currently on the market. Work is ongoing to further explore the properties of

these new materials in a range of applications and new materials with high renewable carbon content and enhanced properties continue to be developed.

References

- 1) <http://www.sartomer.com/techlit/3062.pdf>; Sartomer Bulletin “Naturally Derived Products”.
- 2) <http://www.happi.com/articles/2009/07/biorenewable-carbon-index-for-green-formulations>
<http://www.ciras.iastate.edu/bioindustry/biobasedproducts/content.asp>
- 3) ASTM D6866 - 08 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis
- 4) http://www.biomassmagazine.com/article.jsp?article_id=1407
US patent application US2007219390
World patent publication WO2009128555
- 5) Royte, Elizabeth (August 2006). "Corn Plastic to the Rescue". *Smithsonian Magazine*.
<http://www.smithsonianmag.com/science-nature/plastic.html>.
<http://www.ptonline.com/articles/200209fa3.html>
- 6) “Influences on Barrier Performance of UV/EB Cured Polymers”; Josh Oliver, Sartomer USA LLC; UV&EB 2010 Technology Expo and Conference

Acknowledgements

The author would like to thank James Goodrich and Sarah Cotts of Sartomer’s UV/EB Applications group for formulation and physical properties testing and all members of Sartomer’s Product Development team for synthesis work.