

# Quality & Durability Improvements of 3D Printed Parts via Bio-Based Modification of Photocurable Resins

Nathan Noyes/Croda/New Castle, DE, USA  
Wouter Vogel, PhD/Croda/Gouda, NL

## Abstract

Within polymer-based additive manufacturing, photocurable resin-based processes have gained acceptance due to advantages in printing time, surface finish, and interlayer adhesion relative to filament or powder fusion techniques. Still, serial production of functional parts via these 3D printing processes is isolated due to material limitations. Through modification of benchmark photocurable resins with bio-based (meth)acrylate derivatives based on dimer fatty acid technology, improvements in dimensional stability, water absorption, and toughness have been demonstrated which enable greater functionality and durability of printed parts.

## Introduction

3D Printing, or Additive Manufacturing, is experiencing continuing growth as an alternative to conventional injection molding and subtractive manufacturing processes, in part because the technique allows finely detailed articles of complex geometry to be created and redesigned if necessary without the costly and time-consuming manufacturing of molds and with minimal wasted material. For these reasons, 3D printing has been adopted readily for rapid prototyping (e.g. design for automotive parts and consumer goods) and where customization is of high value (e.g. dental molds, orthopedic aids, personalized footwear or athletic gear, and reproduction of non-stocked replacement parts). Continual advancements in printing processes and machinery push applications steadily from custom, short run production closer to serial manufacturing. Of the major printing techniques, including metal sintering, filament deposition, powder sintering, and photopolymer processing, the latter accounts for the largest share of material sales to date and is also one of the more useful techniques for creating fully functional articles<sup>1</sup>. The ability of the energy source in photopolymerization, or vat polymerization, processes stereolithography (SLA), digital light processing (DLP), and multi-jet systems (MJF/MJM) to penetrate through multiple layers of polymer leads to a matrix with greater crosslinking across the build direction than can be achieved with melt fusion alone.

Still, 3D photopolymerization comes with its own set of material-related limitations. Articles printed via SLA/DLP typically require post processing to remove excess or incompletely reacted resin as well as support structures. Additionally, the acrylate resins available are typically rigid and brittle and control over the crosslink density and flexibility is desired. Additionally, the advancement of plastic manufacturing of this kind is affected by sustainability considerations related to circularity or renewability of the raw materials and final polymers.

Infusing of bio-based resins have gain considerable interest over de last years with acrylated soybean oil as an example. Also, bio-based (meth)acrylate functional derivatives of specialty dimerized fatty acids have arisen as a platform technology capable of improving on these limiting performance factors. The underlying building block is a branched C<sub>36</sub> diacid which, when incorporated into a resin, introduces flexibility, improves melt flow and wetting for interlayer adhesion, and increases durability through reduction in water/chemical absorption. A series of dimer diacrylates have also shown exceptional conversion rates and dimensional stability in 3D printing and post-curing.

### Cure Conversion and Dimensional Stability

A variety of acrylate and methacrylate monomers and oligomers may be utilized in photopolymer printing. It is generally observed that acrylate components are quick to react<sup>2</sup>, but that methacrylate components result in polymers with improved mechanical and tensile proprieties, comparatively<sup>3</sup>. For this reason, dimethacrylates are typical components of a resin formula. High molecular weight dimethacrylates or lesser functional monomers have been shown to reduce shrinkage – a factor critical in additive manufacturing - during photopolymerization due to a lower relative concentration of reactive sites, but may contribute to incomplete conversion to polymer. Unreacted monomer is both an occupational risk to users and detrimental to the aesthetics, durability, and biocompatibility of printed articles<sup>4</sup>. Additionally, traditional high molecular weight dimethacrylates are often of a high viscosity, which impedes on printability, as conventional printing with UV resins have a viscosity range of 1-10 Pa s.

Irregularly structured C<sub>36</sub> dimer acid derived diacrylates with their aliphatic hydrocarbon core and low crystallinity maintain a low monomer viscosity, high conversion rate, and minimal shrinkage. Such dimer diacrylates can and have been prepared by several synthetic routes, including the series described in Figure 2, prepared by Trujillo-Lemon, et al from hydrogenated dimer acid<sup>5</sup>. The dimer acid may be additionally functionalized or polymerized prior to acrylation to enable formulation versatility.

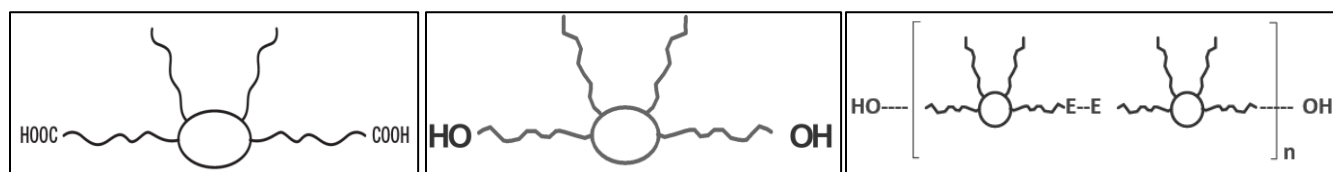


Figure 1. Generalized structure of dimer acid, dimer diol, and polyester polyol

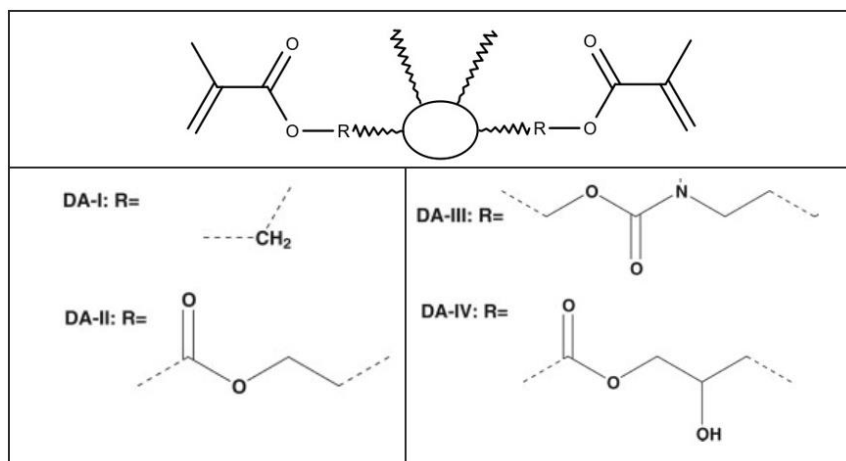


Figure 2. Dimer dimethacrylate structures

Monomer	Molecular Weight (g/mol)	Viscosity (Pa.s)	Double Bond conc. (g/mol)	Conversion (%)	Shrinkage at Conversion (%)	Shrinkage Normalized to Full Conversion	Polymer Water Sorption (%)
<b>EBDMA</b>	554	1	4.0	84 ± 2	6.0	7.1	0.7 ± 0.03
<b>TEGDMA</b>	286	0.008	7.5	83 ± 1	13.0	15.7	5.15 ± 0.06
<b>Bis-GMA</b>	512	700	4.5	65 ± 2	6.6	10.2	3.5
<b>UDMA</b>	571	10	3.9	80 ± 2	5.6	7.0	2.9 ± 0.4
<b>HDDMA</b>	254	0.007	7.8	76	10.7	14.1	0.58 ± 0.02
<b>TDDMA</b>	366	-	5.1	94	10.1	10.7	0.11
<b>DA-I</b>	673	0.61	2.7	100 ± 0	4.4	4.4	0.005 ± 0.002
<b>DA-II</b>	786	0.72	2.5	94 ± 2	2.4	2.6	0.010 ± 0.002
<b>DA-III</b>	843	2.2	2.4	98 ± 2	5.6	5.7	0.009 ± 0.002
<b>DA-IV</b>	849	2.7	2.4	92 ± 2	3.7	4.0	1.80 ± 0.03

Table 1. Monomer Properties and Conversion Characteristics of Dimer Diacrylates and Common Monomers (Trujillo-Lemon, 2006)

In the homopolymerization of the traditional monomers (carried out with visible light activation and camphorquinone and ethyl 4-N,N-dimethylaminobenzoate catalysts), higher conversion rates correlated roughly with greater shrinkage. Despite all the tested dimer diacrylates polymerizing to a greater degree than the other monomers, shrinkage remained low due in part to lower initial double bond concentrations.

## Mechanical Improvements

For analysis of dimer diacrylates in a formulated resin, a high bio-based content resin derived from epoxidized soybean oil was selected. Specifically, the chosen resin (referred to here as Bio-Resin) is a 76% bio-based a mixture of acrylates and methacrylates, determined to meet viscosity requirements for 3D printing, and possess a higher deformation energy than some industrial standard SLA resins<sup>6</sup>. One such standard commercially available clear prototyping resin (StdPR48) is included for comparison. To this resin, fractions of two dimer acrylates were compounded. The first, an acrylate of high purity, fully amorphous dimer diol

(DDA). The second, an acrylate of a bio-based amorphous polyester polyol dimer-based diacrylate (pre-polymer, named PPDA).

Printed tensile bars were tested in the z-direction for mechanical properties.

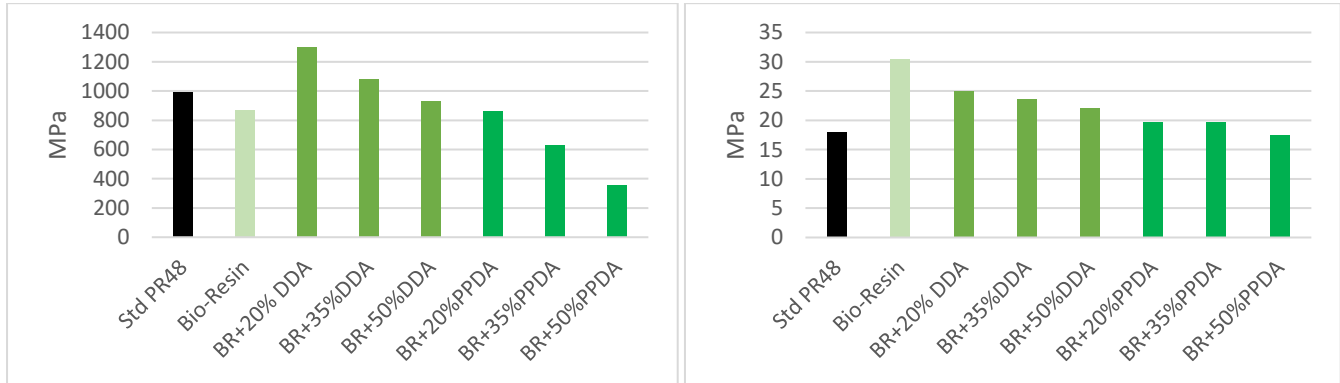


Figure 3 Left) Modulus

Right) Strain at Break

A minority addition of dimer diol acrylate improved the modulus of the bio-resin, to greater than that of the standard reference acrylic resin, with reductions in modulus observed with the amorphous variant of higher molecular weight. Strain at break also decreased with addition of the bio-based building block. Elongation at break increases in all cases, with the most dramatic increases observed with larger fractions of polyester polyol acrylate.

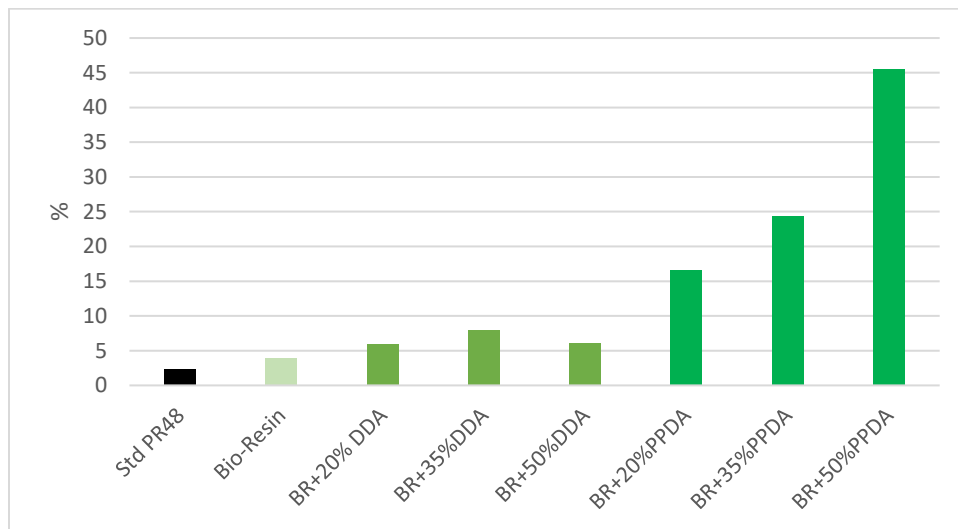


Figure 4. Elongation at Break

The combination of improved modulus and flexibility indicates improved toughness of the printed part, which is to be further validated in pending impact testing.

## Extended Duration of Functional Part Usable Lifetime

The aliphatic nature of the bio-based dimethacrylates is also known to reduce water absorption, and improve resistance to degradation on the basis of exposure to chemicals and UV energy or weathering.

For example, a photocured thermoplastic urethane acrylate was prepared with several different polyols. Tensile bars were in this case molded, and cured before being submitted to a climate chamber for accelerated exposure testing. Only the urethane acrylate which included the dimer based polyester polyol retained tensile strength over 1000 hours, resisting thermo-oxidation, hydrolysis, and UV.

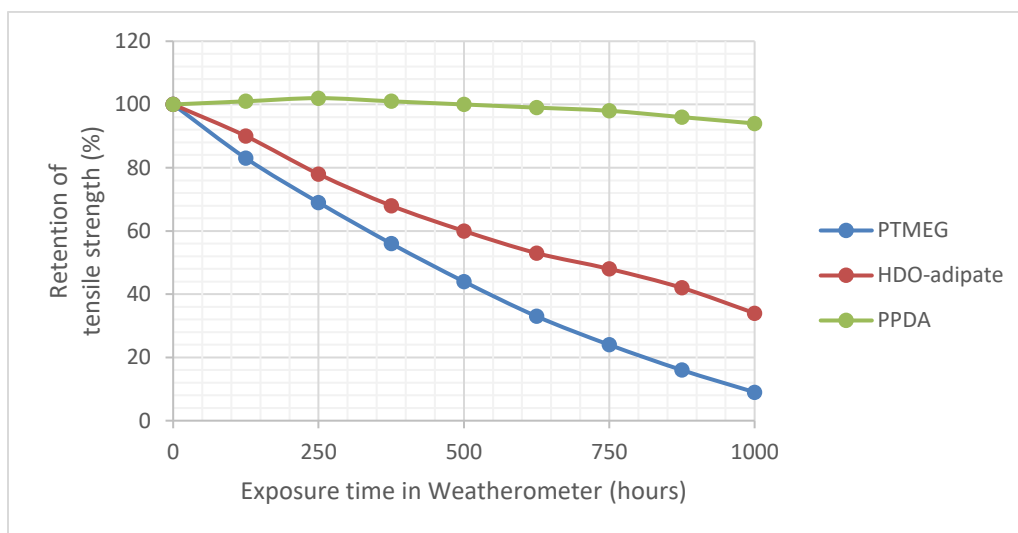


Figure 5. Durability under accelerated aging conditions

## Conclusion

Dimer acrylates offer a platform for improving increasing bio-based content, initial mechanical and aesthetic properties, and durability of photopolymerized 3D printed materials. Several monomers have been demonstrated and studied, prepared by a variety of different synthetic approaches. Further studies are ongoing, to allow optimization of the renewable photoreactive building block for a given application or resin system.

## References

1. Wohlers Associates. (2016). 3D Printing and Additive Manufacturing State of the Industry: Annual Worldwide Progress Report.
2. Ligon, S. C., Liska, R., Stampfl, J., Gurr, M., & Mülhaupt, R. (2017). Polymers for 3D-printing and Customized Additive Manufacturing. *Chemical Reviews Vol. 117*, 10212-10290.
3. deLombard-Watts, M., & Weissman, P. T. (2004). *Comparison of performance of acrylate and methacrylate aliphatic urethanes*. RadTech.
4. Lefeuvre, M.; Amjaad, W.; Goldberg, M.; Stanislawski, L. *Biomaterials* 2005, 26, 5130–5137.

5. Trujillo-Lemon, M., Ge, J., Lu, H., Tanaka, J., & Stansbury, J. (2006). Dimethacrylate Derivatives of Dimer Acid. *Journal of Polymer Science*, 44.  
<https://doi.org/10.1002/pola.21493>
6. Guit, J. (2019). Developing Biobased Photopolymer Resins for Stereolithography 3D Printing: Synthesis of Biobased Methacrylate Oligomers and 3D Printing of Formulated Photopolymer Resins. NHL Stenden University of Applied Sciences, GreenPAC, Emmen.