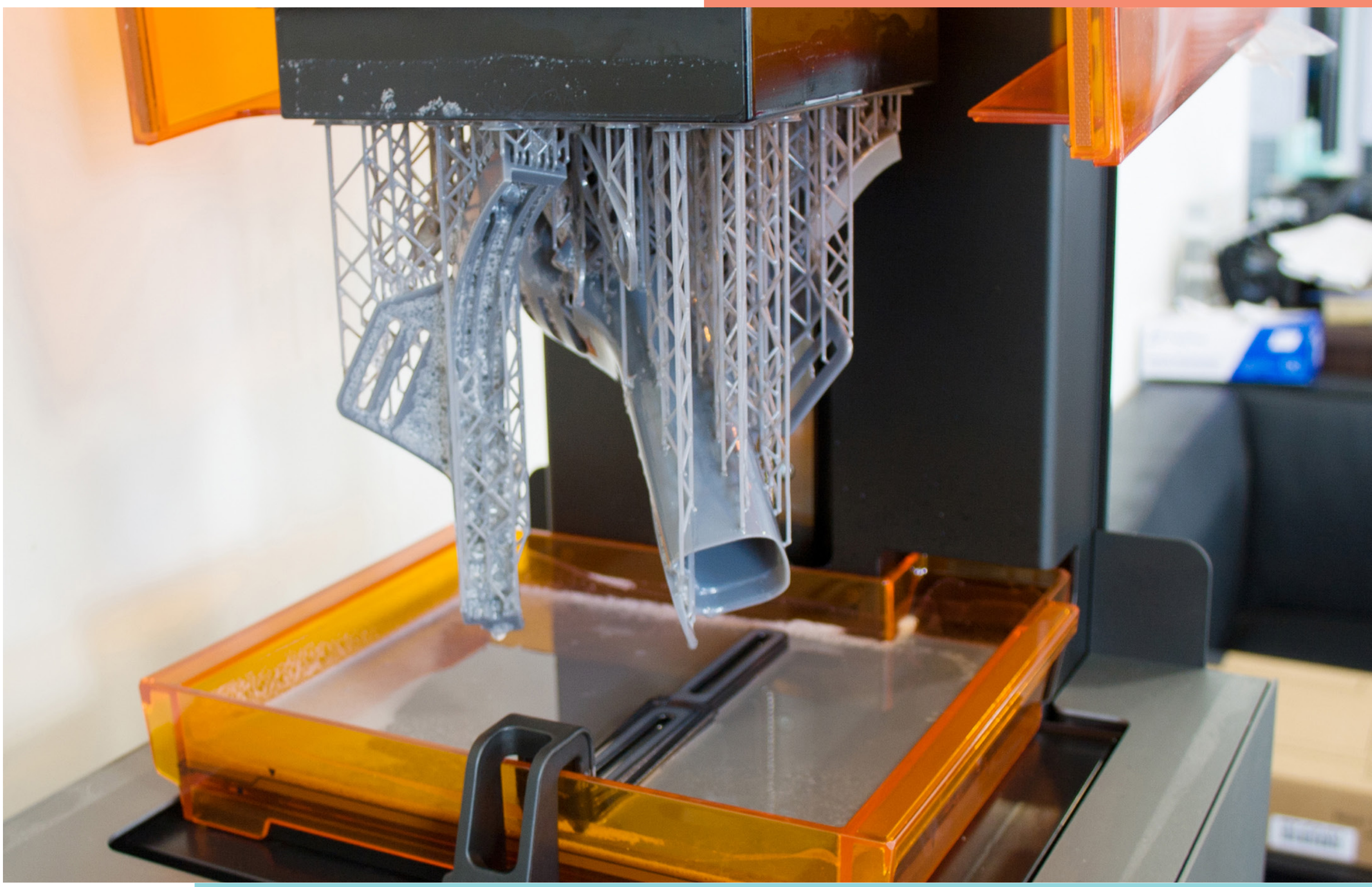
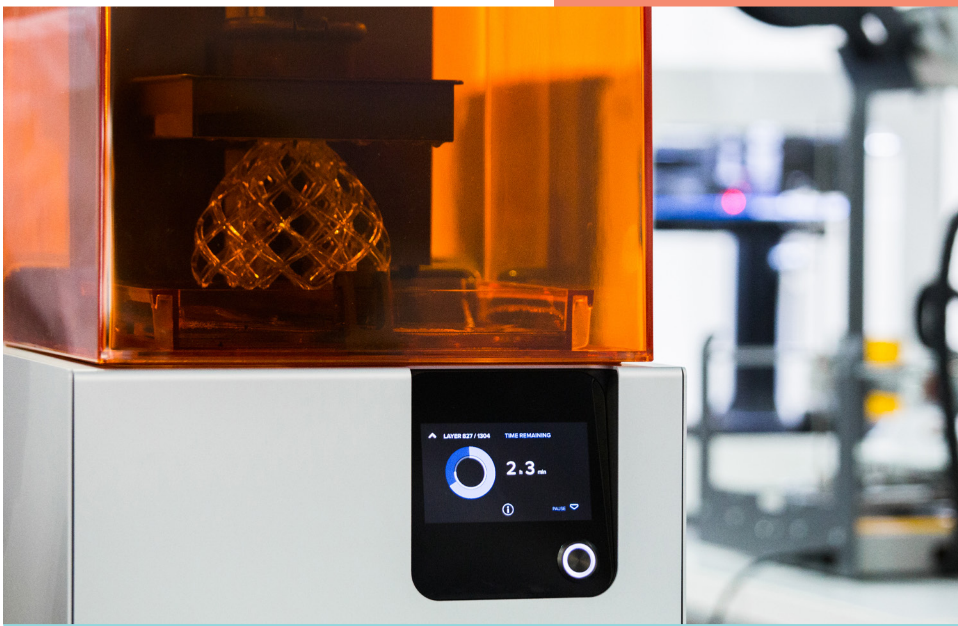
BOMAR® OLIGOMERS FOR 3D PRINTING RESINS

Technology Bulletin



BOMAR

DEVELOPMENTS IN 3D PRINTING



Photopolymer resin development for 3D printing continues to be a key area of focus for the additive manufacturing industry, either to achieve better mechanical properties or to meet new requirements for various emerging applications in areas like dental, aerospace, and automotive. Although new equipment developments continue to expand the formulation window, formulators continue to seek materials with a variety of mechanical properties while also achieving low formulation viscosities, appropriate cure speeds, and long–term UV and environmental stability. Proper selection of the oligomeric backbone structure is key in formulating a quality 3D printing resin in order to simultaneously attain all properties in one formula.

While each application may require slightly different properties, resins in the 3D printing industry tend to fall into three groups of resins that can be applied to numerous applications: rigid, tough, and flexible. These basic categories can give customers an easier way to choose the type of oligomer necessary for their formulation based on what properties they desire.

The following Bomar® oligomers were selected as top suggestions for each general category of 3D printing resins. Using these oligomers, customers will have the capability to formulate 3D printing resins that have desired mechanical properties relating to their specific application. These oligomers have been tested to determine their suitability for 3D printing. A summarized list of oligomers is available below, along with a recommended starting point formula for each resin type.

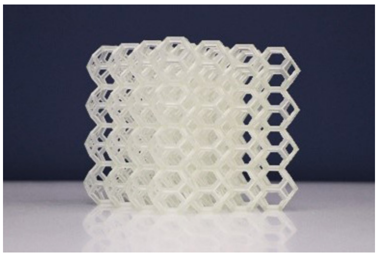
Table 1. Summarized List of Oligomers

Formula Type	Suggested Oligomers
Rigid	BR-741, BR-371MS, BR-952, BR-970H
Tough	BR-541MB, BR-571MB, BRC-4421, BR-970BT, BR-990
Flexible	BR-345, BR-543, BR-5541M, BRC-4421, BR-744BT, BR-7432GB, BRS-14320S

STARTING FORMULAS

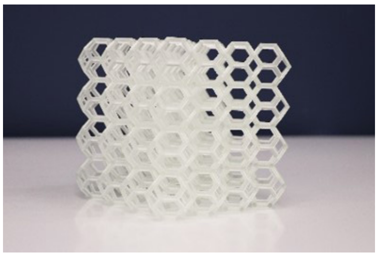
Table 2. 3D Printing Starting Point Formulas

Ridgid



Product	Weight %
BR-952	67.00%
BR-371MS	7.00%
HEMA	26.00%
TPO	1.00%
OB	0.06%

Tough



Product	Weight %
BR-541MB	50.00%
IBOA	40.00%
EOEOEA	10.00%
TPO	2.00%
OB	0.01%

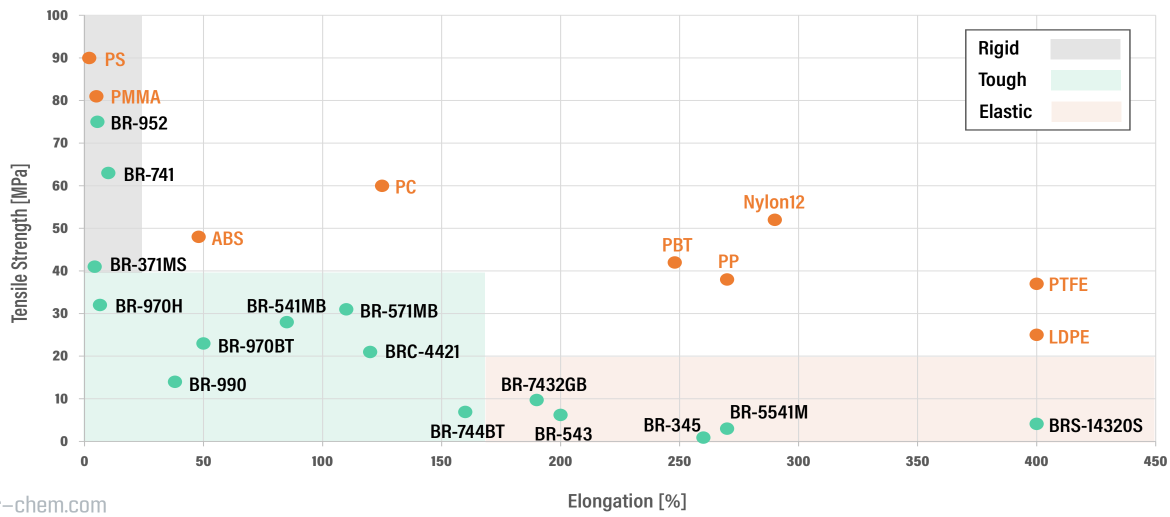
Flexible/Elastic Resin

Product	Weight %
BRC-4421	50.00%
IBOA	17.50%
EOEOEA	32.50%
TPO	2.00%
OB	0.01%

Table 3. Test Results from Rigid, Tough, and Flexible Starting Point Formulas

	Rigid Resin	Tough Resin	Flexible Resin
Viscosity, cP @ 25°C	400	600	500
Tensile, psi [MPa]	12,300 [85]	2,700 [19]	170 [1.2]
Elongation, %	3.7	75	80
Modulus, ksi [MPa]	450 [3,130]	110 [765]	0.38 [2.6]
Notched Izod Impact resistance, J/m	15	150	N/A
Durometer Hardness	91D	72D	45A
Water Absorption, %	0.33	0.43	0.75
Tg, °C	149	74	12
HDT, °C	177	58	11

Figure 1. Tensile vs. Elongation Applied to Rigid, Tough, and Flexible Materials



TESTING & RESULTS

Viscosity and Glass Transition Tempera–ture

Low viscosity is a critical parameter for most photopolymer–based 3D printing applications. The oligomer itself does not need to be low in viscosity; however, it is essential for the fully blended product to be flowable in the printer to allow for a good resolution of the 3D printed part and achieve reasonable print speeds. While initial oligomer viscosity is usually a good indicator of final viscosity, the viscosity reduction rate can be much faster for some oligomers for an equivalent amount of diluent. For example, some low molecular weight urethane acrylates such as BR–371MS and BR–741 have strong urethane hydrogen bonding that can be broken up through monomer dilution to achieve a low formulation viscosity. Dilution rate curves in a variety of monomers for each Bomar oligomer can be found on the oligomer's product data sheet.

An additional key parameter for oligomers is the glass transition temperature (Tg) as this provides a good basic indicator of material hardness. Formulators seeking to produce a hard, rigid material should look for higher glass transition temperature oligomers while those targeting a soft, or more flexible material should look for oligomers with a lower glass transition temperature. However, blending a low Tg material such as BR–7432GB with a high Tg material like BR–952 can help to improve the overall impact strength of the formula.

Table 4. Viscosity and Glass Transition Temperature of Se–lected Oligomers

Oligomers	Viscosity (cP)	Glass Transition Temperature, Tg
BRS-14320S	16,400 @ 60°C	-112°C
BR-345	46,000 @ 25°C	-57°C
BR-543	13,000 @ 60°C	-52°C
BR-5541M	24,000 @ 60°C	-45°C
BR-7432GB	88,000 @ 60°C	-4°C
BR-744BT	46,000 @ 60°C	8°C
BR-990	33,800 @ 60°C	22°C
BR-970BT	13,000 @ 25°C	40°C
BRC-4421	6,600 @ 60°C	48°C
BR-571MB	28,000 @ 60°C	50°C
BR-541MB	6,430 @ 60°C	60°C
BR-970H	24,000 @ 25°C	70°C
BR-741	74,000 @ 60°C	79°C
BR-371MS	65,000 @ 60°C	110°C
BR-952	9,300 @ 25°C	153°C

Tensile Data

Tensile data for each oligomer provides a good basic understanding of the mechanical performance of the materials. It is important to view these properties alongside one another, as some applications that require good flexibility may also desire higher modulus than other applications.

Table 5. Tensile Data for Selected Oligomers, 30% IBOA dilution

	Oligomer	Tensile, psi [MPa]	Modulus, ksi [MPa]	Elongation, %
Rigid	**BR-741**	9,200 [63]	390 [2,700]	10
	BR-371MS	6,000 [41]	370 [2,600]	4.3
	BR-952	10,800 [75]	380 [2,600]	5.4
	BR-970H	4,600 [32]	210 [1,500]	6.5
Tough	**BR-541MB**	4,100 [28]	80 [570]	85
	BR-571MB	4,500 [31]	140 [970]	110
	BRC-4421	3,000 [21]	90 [610]	120
	BR-970BT	3,400 [23]	40 [280]	50
	BR-990	2,050 [14]	9.5 [66]	38
Flexible	**BR-345**	130 [0.9]	0.06 [0.4]	260
	BR-543	900 [6.2]	0.9 [6.2]	200
	BR-5541M	440 [3]	0.4 [3]	270
	BR-744BT	1,000 [6.9]	2.4 [17]	160
	BR-7432GB	1,400 [9.7]	3.2 [22]	190
	BRS-14320S	600 [4.1]	1 [6.6]	400

Moisture Absorption

Low moisture absorption is an important parameter for several 3D printing applications, including dental applications. Materials with high moisture absorption can depolymerize over time, swell and distort detail in the part, or suffer from reduced mechanical properties. Water absorption is tested by curing 8-gram samples of oligomer and 2% Irgacure 184 in an aluminum pan mold through a Fusion D-bulb conveyor, then placing them in an oven for a minimum of 24 hours at 50°C to ensure complete dryness. After drying, the pucks are weighed to get a dry tare weight, and then immersed in water for 24 hours and weighed again to determine how much water is retained in the material.

Table 6. Water Absorption Data for Selected Oligomers

Oligomer	Water Absorption (%)
BRS-14320S	0.05
BRC-4421	0.17
BR-952	0.23
BR-371MS	0.24
BR-741	0.28
BR-990	0.38
BR-970H	0.40
BR-744BT	0.44
BR-541MB	0.44
BR-970BT	0.50
BR-5541M	0.52
BR-571MB	0.85
BR-7432GB	1.04
BR-345	1.10
BR-543	1.58

Shrinkage

Shrinkage is another very important factor when developing 3D printing formulations. Materials with a high degree of shrinkage may lead to poor printing capability, poor resolution, or warpage in finished part. Shrinkage is a function of several factors, including molecular weight, reactive group type, and reactive group density. For the purposes of this study, a comparative test looking at z-directional shrinkage using TA Instrument's Discovery HR-2 photorheometer attached to a Dymax BlueWave MX-150 405 nm LED spot curing unit was used to assess comparative shrinkage. This data may not correlate exactly to ASTM standards for volumetric or linear shrinkage.

Table 7. Shrinkage Data

Oligomer	Comparative Shrinkage (%)
BRS-14320S	1.06
BRC-4421	4.10
BR-952	5.36
BR-371MS	2.56
BR-741	2.55
BR-990	4.23
BR-970H	4.85
BR-744BT	1.14
BR-541MB	3.02
BR-970BT	4.50
BR-5541M	3.18
BR-571MB	2.42
BR-7432GB	1.07
BR-345	1.21
BR-543	1.51

Post Curing Methods

During the 3D printing process, the laser or light source from the printer will typically only partially cure the printed part, leaving the model in a stage known as the green state. Therefore, when a part comes off the 3D printer, it must typically be post-cured to complete the cure and develop the final material properties. This post-curing process can be conducted under either broadband or LED light source, although a resin formula will typically be optimized to a certain type of post-curing equipment.

Prior to post-curing a part, a part must be rinsed with a solvent such as isopropyl alcohol in order to remove any unreacted resin from the surface. This washing step is crucial because it prevents small holes or parts in a detailed assembly from being filled in. Solvent resistance and solubility parameters of a material affect how well isopropyl alcohol can wash the part in its green state.

OTHER OLIGOMER RECOMMENDATIONS FOR PRINTING

3D Inkjet

Due to a target viscosity of 10–20 cP at print temperatures of 40°C - 50°C, oligomer content in Inkjet formulas is relatively low. In addition to viscosity limitations, the inkjet process does not work well with crystalline materials or high molecular weight materials as these are not able to pass smoothly through the inkjet system. However, the benefits of full color printing, excellent resolution, and multimaterial prints still make 3D inkjet a significant area of development with targets of improved toughness, better flexibility, and other unique needs.

Table 8. Oligomer Recommendations for Inkjet Formulas

Oligomer	Viscosity, cP	Glass Transition Temperature, Tg	Comments
BR-741	74,000 @ 60°C	79°C	Tough resin, relatively low molecular weight
BR-771F	41,600 @ 60°C	69°C	Low molecular weight, good balance of high tensile strength and moderate elongation with excellent cure speed. Tough
BRC-841	13,000 @ 60°C	84°C	Hydrophobic backbone, low molecular weight
BR-952	9,300 @ 25°C	153°C	High Tg, UDMA structure, low viscosity
BR-970BT	13,000 @ 25°C	40°C	Low molecular weight and low viscosity with good flexibility

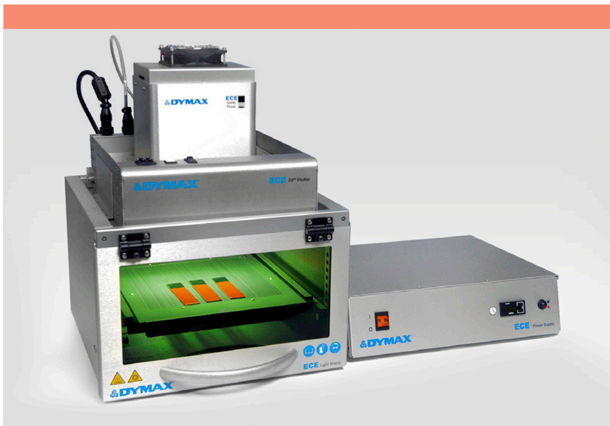
CONCLUSION

The Bomar oligomers discussed in this study offer many advantages to 3D printing resins. The organization of these oligomers into three groups: rigid, tough, and flexible allow for a customer to choose the appropriate product for their specific application. It is important for all 3D printing formulations to have low viscosity, fast cure speeds, and varying strengths and flexibility. Bomar oligomers can assist in obtaining these properties for whatever application necessary.

RECOMMENDED EQUIPMENT FOR POST CURE AND REWORK

After a 3D model is built, it may be necessary to supply additional curing energy to the part to ensure that optimized material properties are achieved. Dymax has several curing system configurations that are ideally suited for the post–cure process or rework.

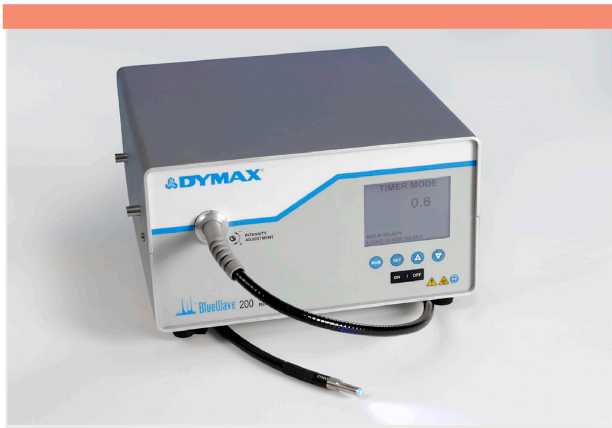
UV Light–Curing Flood Systems



Ideal for post cure

Dymax flood–lamp systems are designed for area curing or for curing multiple assemblies at once. These flood lamp models use a powerful UV light–curing lamp (up to 225 mW/cm^2 for fast curing over a 5" x 5" (12.7 cm x 12.7 cm) area. Typical flood–lamp curing systems are composed of three main components: a UV flood lamp, manual or automatic shutter, and a light shield. CE–marked systems are available.

BlueWave 200 3.0 Spot Lamp System



Ideal for rework or repair such as curing drain hole fills, assembling larger assemblies, or repairing cracked or broken models

The Dymax BlueWave 200 3.0 is a high–intensity, light–curing spot–lamp system. This spot–curing lamp emits energy in the UVA and visible portion of the spectrum (300–450 nm) and is ideally suited for either manual or automated processes. The unit contains an integral shutter which can be actuated by a foot pedal or PLC and a universal power input that provides consistent performance at any voltage. A wide range of lightguides in various materials and configurations are available for use with this unit, providing application flexibility. This unit is also CE–marked for distribution in Europe.

Global Headquarters: 51 Greenwoods Road | Torrington, CT 06790 | USA | +1 860–626–7006