

# The Benefits of UV Curable Materials in Additive Manufacturing

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## Abstract

Additive Manufacturing (AM) is the process by which successive layers of material are laid down on top of one another and bonded together to form a three dimensional object. UV curable formulations are uniquely suited for use in AM due to their rapid cure, range of properties, and dimensional accuracy. This paper will describe the physical properties of liquid and cured UV formulations, where they are being used today and the areas for potential use in the future.

## Introduction

Conventional manufacturing methods are often comprised of subtractive processes. That is, a large piece of metal, wood, or other substrate has material removed from it until the desired form takes shape. In contrast, additive manufacturing builds products “layer by layer”, or additively to reach the desired goal. To accomplish this, a virtual 3D model of the object is created, usually by computer aided design (CAD). The 3D model is then broken up into a series of individual slices, creating the computer file that is sent to the AM machine. The AM machine then creates the object by forming each layer via the selective placement of material. While the object is being formed, it is supported on a build platform which provides support, and can move in the z direction to assist with placement of fresh material.

The method by which different materials are added to the structure depends on whether the AM material is a liquid or a solid. For polymeric solids, such as ABS, polycarbonate, or their blends, fused deposition modeling (FDM) is often used. In this technique, a thin thread of thermoplastic material is heated to allow it to flow and then deposited onto the growing structure. The speed of build up and the resultant strength of the object can be dependent on the orientation of successive layers of material (e.g. 0/90, 0/45/90 or 0/0). Another technique involves solid powders. These powders can be either metal or organic in nature. Once the powder layer has been laid down, it can be bound in place using a liquid binder followed by another layer of powder, or fixed in place using a variety of thermal methods. In selective laser sintering (SLS), layers of powder (e.g. wax, nylon, aluminum) are fused together. Selective laser melting (SLM) melts the layers together, while selective heat sintering (SHS) uses a thermal print head to heat the powder being melted.

Liquid systems are most often polymerized using UV energy. The liquid formulation may be deposited via material jetting, in which the liquid is applied using a multi-nozzle print head, followed by UV curing, and the pattern is repeated until the object is complete. In stereolithography (SLA), the formulation is selectively cured using a laser beam that traces a cross-section of the part pattern on the surface of a liquid, UV curable resin. After each layer is cured, the build platform is lowered fractionally into the reservoir of liquid so that a new layer can be cured onto the object. Finally, in DLP projection, a

series of controllable micromirrors to project an image onto the surface of a pool of UV curable liquid, curing the entire layer at once.

UV curable liquid systems are prone to shrinkage when cured and this shrinkage can lead to undesirable stresses being built up in the object. One manifestation of the stress build up is that the article will be prone to curling. In addition, the cured formulation must have the proper glass transition (T<sub>g</sub>), viscosity and the right toughness/hardness balance.

Figure 1 summarizes the advantages and disadvantages of the methods described above.

**Figure 1. Advantages and limitations of different AM technologies**

	Advantages	Limitations
Light-polymerized	Accuracy Good surface finish	Limited raw materials May require post-curing Shrinkage and curl
Powders	Variety of materials No post curing required Fast build times Mechanical properties of Nylon & Polycarbonate parts	Rough surface finish Weak mechanical properties Material changeover difficult
FDM	No post curing Variety of materials Easy material changeover Office environment friendly Low end, economical machines	Rough surface finish Slow on large / dense parts

Several UV curable chemistries were evaluated for viscosity, T<sub>g</sub>, and shrinkage to demonstrate their suitability for use in AM.

## Experimental

### Formulations

High viscosity materials were placed in an oven at 60°C prior to use. The formulations were made by adding the constituents to a glass container and mixing until homogeneous. Additional heating (60°C) was used where necessary. The photoinitiator concentration was 2 phr of a  $\alpha$ -hydroxyketone plus 0.5 phr of a phosphine oxide type photoinitiator. Some properties of the resins and diluents used in the experiments are shown in Table 1.

**Table 1. Resins and Diluents**

Resin ID	Type	Functionality	Viscosity (cPs, 25C)
EA 1	Epoxy acrylate	2	700 - 800K
EA 2	Modified epoxy acrylate	2	15 - 20 K
EMA 1	Epoxy methacrylate	2	650-750 K
UA 1	Urethane acrylate	2	5 - 10 K

Diluent ID	Type	Functionality	Viscosity (25C)
Diluent 1	Diacrylate	2	5 - 10
Diluent 2	Triacrylate	3	100 - 200
Diluent 3	Alicyclic diacrylate	2	100 - 250
Diluent 4	Cyclic diacrylate	2	1000 - 1500

## Characterization

Viscosities were obtained using a Brookfield DV II+ viscometer at 25°C and 60°C using a #21 spindle.

The Tg of the cured materials (5 mil film) was determined using DMA 2980 (TA Instruments) in oscillatory 3-point bending mode at a frequency of 1 Hz and an amplitude of 50um. The temperature profile involved heating the sample from -20 to 200 °C at 3°C/min.

The degree of shrinkage was determined by determining the ratio of the liquid density to the solid (cured) density.

## Results and Discussion

While the benefits of the process of AM make it an attractive option for prototyping or manufacturing, the properties of the finishes article must also meet the requirements of the task. These requirements may include properties like high tensile strength with toughness (elongation), hardness, appropriate viscosity, good reactivity, low shrinkage and high Tg. Limiting the shrinkage during cure is especially critical for an AM process, since shrinkage leads to increases in internal stresses, curling and possible distortion of the final article being produced.

Two epoxy acrylates, one epoxy methacrylate, and one urethane acrylate were blended with one of four diluents, cured and evaluated for viscosity (25C and 60C), shrinkage and Tg. The results appear in Table 2 (see end of paper).

Figure 2 below shows the shrinkage (blue bars), Tg (orange dots) and viscosity at 25C and 60 C (black text, 25C/60C) for blends with 60% oligomer content and 40 % of diluent 1. The shrinkage values for these blends range from ~10 – 14%, with the epoxy methacrylate (EMA) having the highest shrinkage and the epoxy acrylate having the least amount of shrinkage. There does not appear to be any significant difference between the epoxy based oligomers and the urethane acrylates (UA). The Tg

values for these blends range from ~45 – 150C. The EMA has the highest Tg and the modified EA, designed to be flexible, has the lowest Tg. The UA has a lower Tg than the unmodified EA systems, as expected. The viscosity of the UA blend is lower than any of the EA or EMA blends.

**Figure 2. Physical Properties – 60 % Resin**

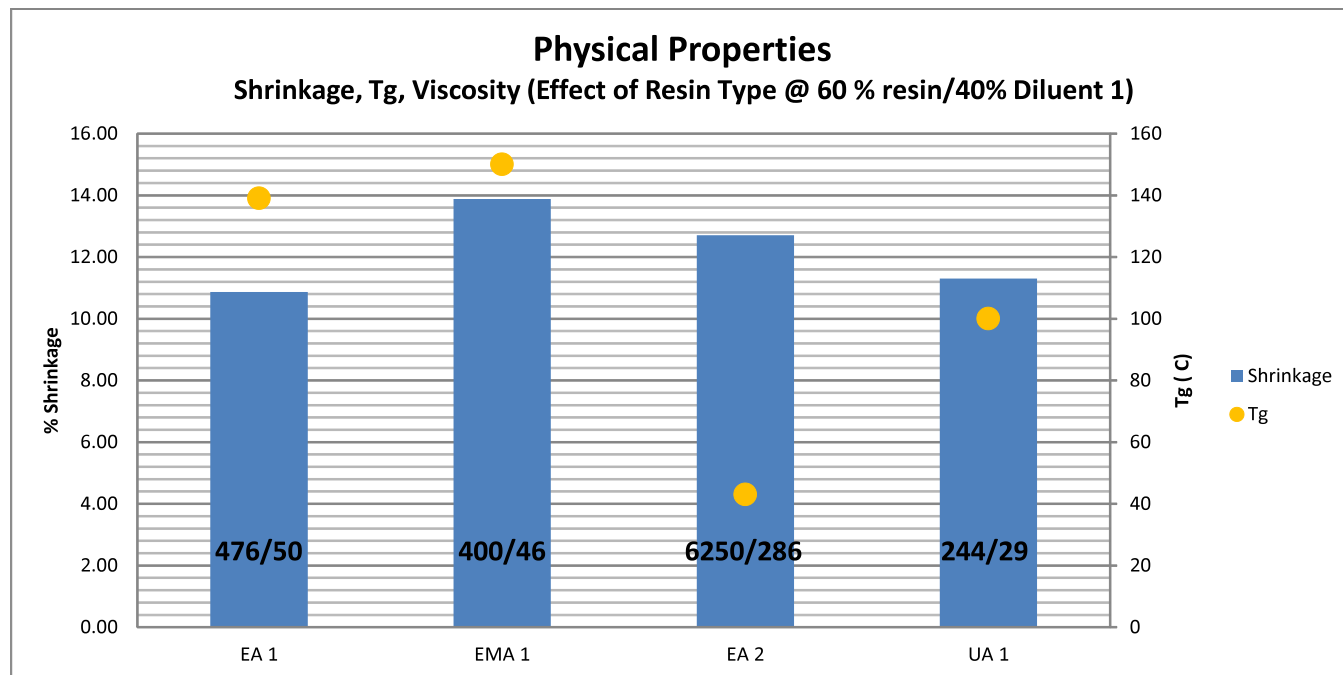
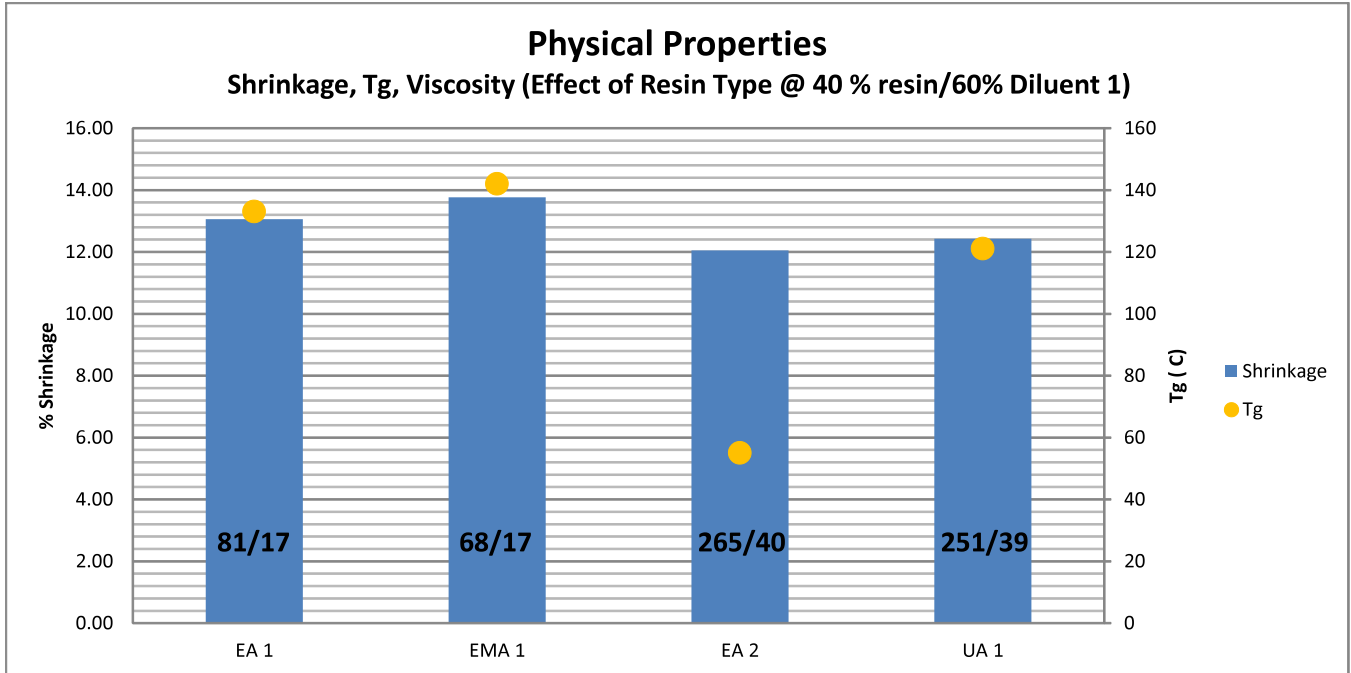


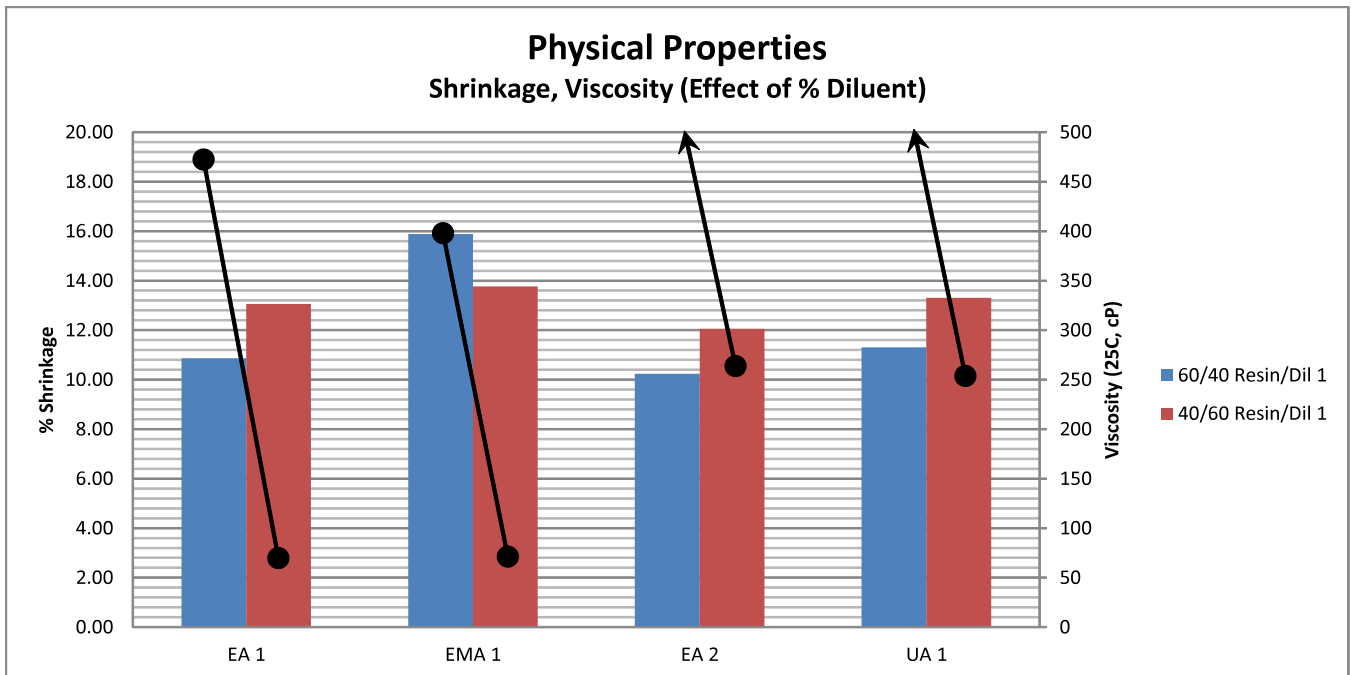
Figure 3 below shows the same information for blends with 40 % oligomer content and 60% diluent 1. The same trends are apparent for these 40/60 blends; the EMA has the highest shrinkage and the EA2 has the lowest. However the overall range for the shrinkage values has narrowed a bit to, showing that the diluent is starting to dominate the shrinkage properties. Surprisingly, the absolute % shrinkage values do not change much on going from 40 to 60% diluent. The effect of increasing the diluent also results in much lower viscosities and somewhat lower Tg values.

**Figure 3. Physical Properties – 40% Resin**



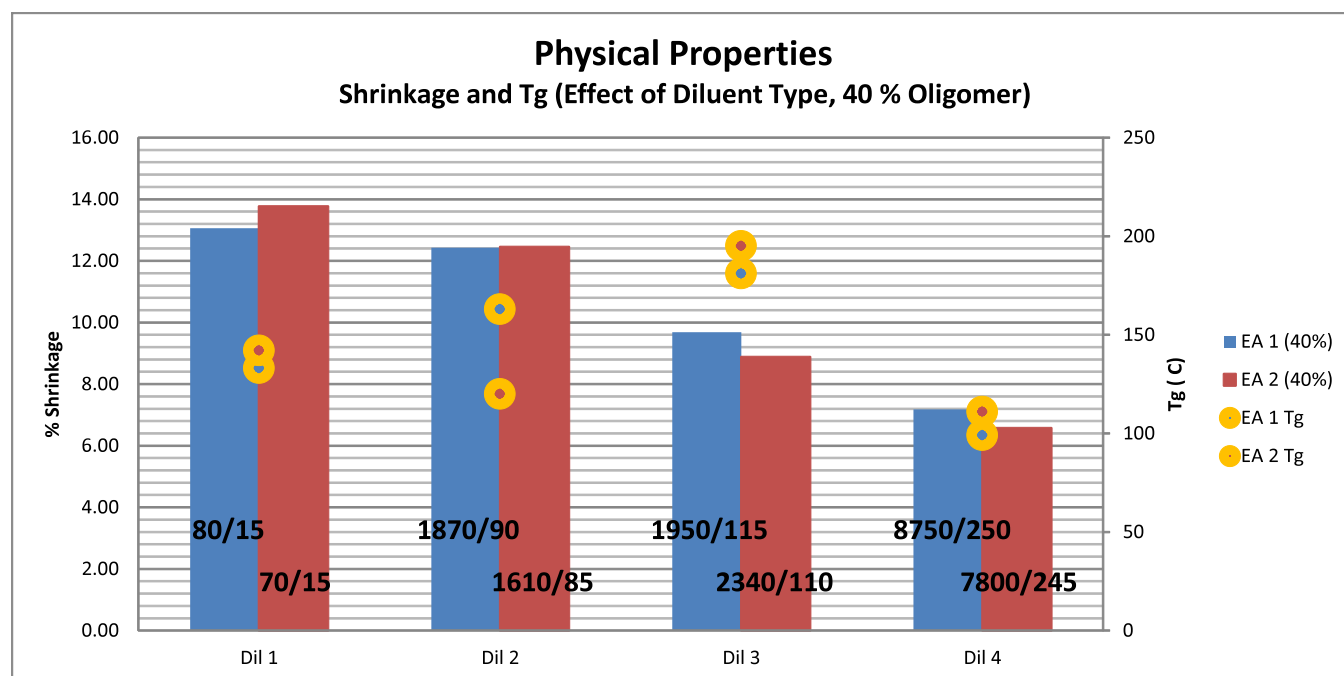
In Figure 4, the effect of dilution on all of the oligomers studied is shown as seen below. As expected there is a significant reduction in the formulation viscosity as the diluent 1 concentration is increased from 40 to 60%. At the same time, the % shrinkage values increase by 2-3% regardless of the type of oligomer present in the formulation. Reducing the viscosity through increased diluent 1 content to achieve application viscosity has the undesirable effect of increasing the shrinkage of the system.

**Figure 4. Physical Properties – Effect of Dilution**



Alternate diluents were evaluated to see if the shrinkage could be reduced while also maintaining high Tg and reasonable viscosity. The chart in Figure 5 below shows the effect of diluent type on shrinkage (blue bars), Tg (orange circles with appropriately colored centers) and viscosity (black text) in an EA and in an EMA blend, with the oligomer content held at 40%. Exchanging the difunctional diluent 1 for the trifunctional diluent 2 results in a slight decrease in shrinkage, a slight change in Tg and higher viscosity. When diluent 3, an alicyclic difunctional diluent is used, the shrinkage drops to ~ 9% with an increase in Tg and viscosities similar the diluent 2 viscosities. The shrinkage can be reduced to 6-7 % is diluent 4 s used, although the Tg is reduced and there is a significant rise in the formulation viscosity.

**Figure 5. Physical Properties – Effect of Diluent Type and %**



One cautionary note, while efforts were made to fully cure each sample prior to testing for % shrinkage or Tg, the % conversion was not measured, so that some of the changes in shrinkage may be partially due to differences in % conversion and not totally ascribed to differences in diluent or oligomer structure.

## Conclusions

In this limited study, 4 oligomers were blended with 4 diluents at either 60% or 40% oligomer level, cured and the % shrinkage, Tg and viscosity were measured. The effects of dilution, oligomer and diluent type on these properties were evaluated with an eye towards determining which factors could mitigate the degree of shrinkage while not adversely affecting the Tg or increasing the viscosity overly

much. At higher oligomer content, there is some variation in shrinkage as the oligomer type is varied, but the difference becomes less significant as the diluent content increases. The largest reduction in shrinkage appears to come when diluents containing cyclic structures are used. These types of diluents are not as good at reducing viscosity as the non-cyclic diluents. Heat can be used to reduce the viscosity of these formulations. The best combination of lowered shrinkage, high Tg and moderate viscosity seems to come from blends diluted with diluent 3. The bulky structure of this material helps control shrinkage, while maintaining good Tg. With heat, the viscosity is low.

As mentioned, this initial study is limited in scope and future work will investigate alternate strategies to achieve, low shrinkage, high Tg at good viscosities, such as inclusion of inert (non-UV active) materials or hybrid curing systems.

**Table 2. Summary of Results**

	Wt. % (resin and diluent only)																			
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
EA 1	60	40	60	40	60	40	60	40												
EMA 1									60	40	60	40	60	40	60	40				
EA 2																	60	40		
UA 1																			60	40
Diluent 1	40	60							40	60							40	60	40	
Diluent 2			40	60							40	60								
Diluent 3					40	60							40	60						60
Diluent 4							40	60							40	60				
Viscosity (cps, 25° C)	476	81	8452	1670	13350	1950	30000	8750	400	68	8300	1610	13000	2340	32900	7800	6240	265	760	257
Viscosity (cps, 60° C)	50	17	256	91	330	115	530	250	46	17	222	85	282	108	452	245	286	40	83	39
Shrinkage (%)	10.87	13.06	7.56	12.43	7.71	9.68	7.44	7.18	15.88	13.77	5.57	12.45	9.28	8.88	7.73	6.58	10.24	12.05	11.30	13.31
T <sub>g</sub> (tan δ <sub>max</sub> (°C))	139	133	162	163	166	181	110	99	150	142	165	86	171	195	121	111	43	55	100	97

PI added at 2 phr (α-hydroxy ketone) and 0.5 phr (phosphine oxide)



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