The Effect of Newly Developed (Meth)acrylate Resins on Impact Strength in 3D Printing

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Abstract

The present work explores formulation concepts targeting high-impact strength UV-curable urethane (meth)acrylate-based 3D printing resins. A variety of hard backbone structures are formulated in combination with several impact modifying materials, including newly developed tri-, di-, and mono-functional oligomers. Mechanical properties and impact strength are reported.

Introduction

In the area of photopolymer based 3D printing, there is a continual push to develop materials matching the physical properties of thermoplastic materials used in extrusion based 3D printing processes.[1] Some of these thermoplastics, such as polycarbonate or ABS, are well known for their impact and temperature resistance properties, with heat distortion temperatures (HDT) in excess of 100°C and impact resistances measured in the hundreds of J/m.[2] Unfortunately, most UV-curable resins used in 3D printing that have similar HDTs are quite brittle with little impact resistance or fractural toughness.[1,3] This is primarily due to the high degree of cross-linking that is typically necessary to achieve high HDTs. Higher cross-link densities, while increasing the strength and HDT, also tend to impart a brittleness that is not easily overcome.[4,5] Thus, to expand the reach of light-curing 3D-printing processes, new materials, or combinations of materials, need to be developed that better balance impact and temperature resistance properties.

In this work, we broadly screen a variety of UV-curable (meth)acrylate resin materials for their impact and temperature resistance capabilities. Three hard resins (HR) were tested both alone and together with several impact modifying (IM) materials in a model 3D printing formulation. The purpose of the screening was to identify candidate materials that could be used in high impact strength, high HDT 3D printing formulations and to identify any basic structure-performance relationships to be used in future material development.

Experimental

The model 3D printing formulations used in this work are provided in Table 1. All formulations contain the same basic package of monomers, photoinitiator, and light absorber with the oligomer components varying. The No IM formulation, where the oligomer portion is only HR, was used as a control for the purposes of comparison with the impact modified formulations. Aside from the Isobornyl Acrylate, Tricyclodecanedimethanol Diacrylate (CAS# 42594-17-2, DCPDA), was also included as a monomer to improve HDT. The light absorber used was 2,2'-(2,5-thiophenediyl)bis[5-(1,1-dimethylethyl)-benzoxazole (CAS# 7128-64-5, BBOT). Light absorbers are commonly used in 3D printing formulations to better control depth of cure, reduce light scattering, and generally improve on print resolution.

Table 1. Model 3D Printing Formulas

		No IM	Modified
Oligomers	HR	52.00 %	37.00 %
	IM	-	15.00 %
Monomers	IBOA*	42.00 %	
	DCPDA	5.00 %	
Photoinitiator	TPO	0.99 %	
Light Absorber	BBOT	0.01 %	

* For resins that include IBOA as a reactive diluent, the added IBOA content was adjusted to normalize IBOA content to 42.00% across all formulations

All formulations were mixed until all solid components were dissolved and the mixture was homogenous. Formulation viscosities were measured using a Brookfield CAP 2000+ viscometer at 25°C. Test specimens of each formulation were prepared according to the relevant test methods identified below and cured with a broad spectrum Dymax 2000-EC flood curing unit for 2 minutes per side. The irradiance was measured at approximately 50 mW/cm^2. Specimens were allowed to rest for at least 18 hours at ambient temperature before testing.

Impact resistance was tested according to ASTM D256A using an analogue IZOD Pendulum Impact Tester. A 45 notch with a 0.25-mm notch radius was cut into each test specimen using a Qualitest QuickNotch II Impact Speciman V-Notcher. In this study, the impact resistance is reported in J/m which can be roughly converted to kJ/m^2 by dividing the result by 10.

Figure 1. Dymax 2000–EC Curing System
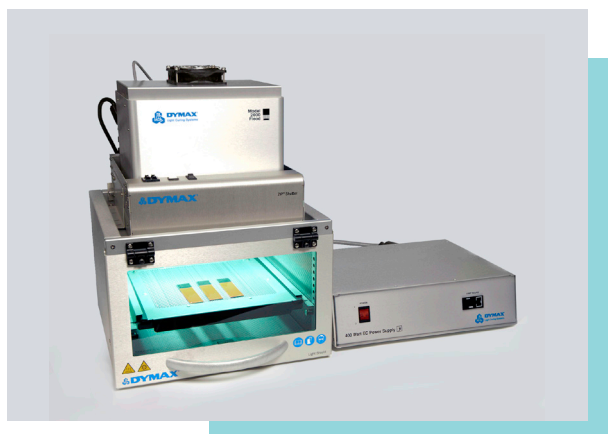
This factor reflects the approximate 10 mm of material depth remaining in the specimen behind the notch.

The HDT for each formulation was assessed using DMA methods per ASTM D648. Specimens were tested using a Thermal Analysis DMA Q800 with dual cantilever geometry and the data output analyzed using the TA Universal Analysis software. For HDT determination, the instrument's Controlled Force test parameters were used to apply a constant stress of 0.445 MPa and the temperature was increased at a rate of 5°C/minute.

Type IV "dogbone" specimens of each formulation were cast for tensile mechanical testing. Tensile properties of all specimens were obtained using an Instron tensile tester and related software according to ASTM D638. Specimens were extended at a strain rate of 25 mm/minute.

Results and Discussion

Material Characterization

Table 2 provides a relative comparison of two key structural characteristics for each material that often affect physical properties: functionality and molecular weight. For multifunctional materials, higher functionality and/or lower molecular weight are typically associated with greater cross–link density leading to increased stiffness and possible brittleness. On the other hand, lower functionality and/or higher molecular weight tend to reduce cross link density and increase flexibility, but possibly reducing strength and temperature resistance.[4] The molecular weights reported were normalized to aid in comparability and further analysis.

For the hard resins, HR1, HR2, and HR3, both functionality and molecular weight increase simultaneously such that the functionality of HR3 is almost double and molecular weight almost triple that of HR1. For the impact modifiers, IM1 and IM2 are both reduced functionality materials with the most significant difference being their molecular weights. IM1 is higher molecular weight and would qualify as a polymer under most regulatory definitions. IM2 is the lowest molec–ular weight material used in this study and might technically be classified as a monomer. IM3 through IM7 are more traditional difunctional urethane (meth)acrylate oligomers of varying molecular weights. The unique substructural ele–ments within these materials are not the focus of this work.

Table 2. Material Functionality and Relative Molecular Weight

Material Reference	Product Name	Functionality	Relative MW
HR1	BR-952	2.0	2.2
HR2	Exp. Olig. 1	2.2	4.5
HR3	Exp. Olig. 2	3.8	7.9
IM1	Exp. Olig. 3	1.3	3.5
IM2	Competitive Impact Modifier	1.0	1.0
IM3	BR-344	2.0	21.9
IM4	BR-5541M	2.0	28.4
IM5	BR-543	2.0	11.6
IM6	BR-7432GB	2.0	24.2
IM7	BRC-4421	2.0	13.9

Formulation Viscosity

Formulation viscosity is an important parameter in 3D printing not only due its effect on ease of use, but also on printability. The viscosity of the material being printed can sometimes make the difference between print success and failure. Unfortunately, the ideal viscosity or the maximum allowable viscosity for a given 3D printing process will vary depending on unique characteristics of that printing process and the 3D printer being used. Generally, formulations that are near
1,000 cP at 25°C or less work with most 3D printers. However, there are some formulations currently on the market where the viscosity is as high as 5,000 cP at 25°C and are still being used successfully.

The formulation viscosities for all the HR and IM combinations can be found in Table 3. Only a few formulations deviate significantly from the 1,000 cP maximum and the highest viscosity, found with the HR2–IM4 combination, is still well within the range of commercially available, higher viscosity formulations. As would be expected, formulation viscosity is positively correlated with molecular weight as illustrated in Figure 5. A notable exception to the trend is between HR2 and HR3, which is likely indicative of a substructural difference that has more of an effect on viscosity than the overall molecular weight. Based on the apparent slopes of the linear trends in Figure 5, HR1 formulations are the least sensitive to changes in IM molecular weight and HR2 the most sensitive.

Table 3. Formulation Viscosity at 25°C. All Values in cP.

	Hard Resin		
Modifier	HR1	HR2	HR3
None	155	650	340
IM1	160	465	380
IM2	70	185	150
IM3	335	940	670
IM4	1190	2250	1860
IM5	520	1220	950
IM6	700	1750	1145
IM7	750	1880	1230

Figure 2. Relationship between IM Molecular Weight and Formulation Viscosity. R^2 Value for all linear trends is 0.66 ± 0.01.
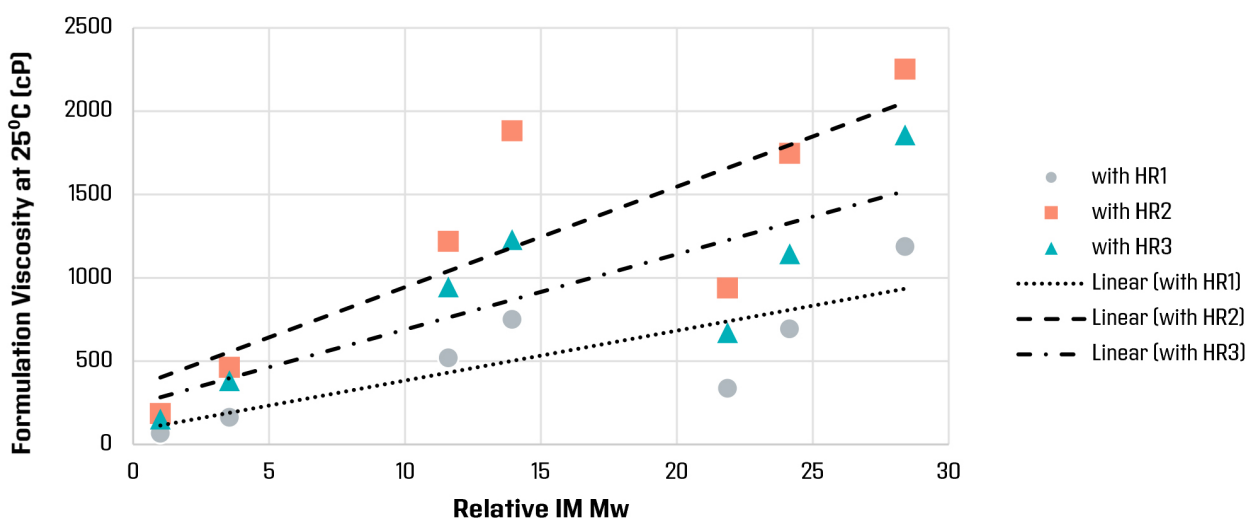
Impact Resistance

Figure 3 summarizes the impact resistance measurements for all formulations. The "All HR Average" is the average impact resistance of an IM containing formulation across all three HR. To better compare the effect that each IM had on impact resistance, the change in impact resistance relative to the No IM control formulation is presented in Figure 4.

Without the addition of an IM, HR3 provides the highest degree of impact resistance and HR1 the least. This trend is seen in all the modified formulations except those with IM4, IM5, and IM6 suggesting that there may be a synergistic effect between these IM's and HR2 resulting in a greater resistance to impact. Interestingly, the reduced functionality materials, IM1 and IM2, did not significantly increase the impact resistance of the formulation and in some cases reduced it. Of these two, IM1 may be marginally better likely due its slightly higher functionality and bulkier, polymeric structure, both of which should contribute to the formulation's toughness and resistance properties. Taken as a whole, the impact resistance testing indicates that there is a positive relationship between impact resistance and molecular weight with the higher molecular weight materials, such as HR2, HR3, IM4 and IM6, providing the best results.
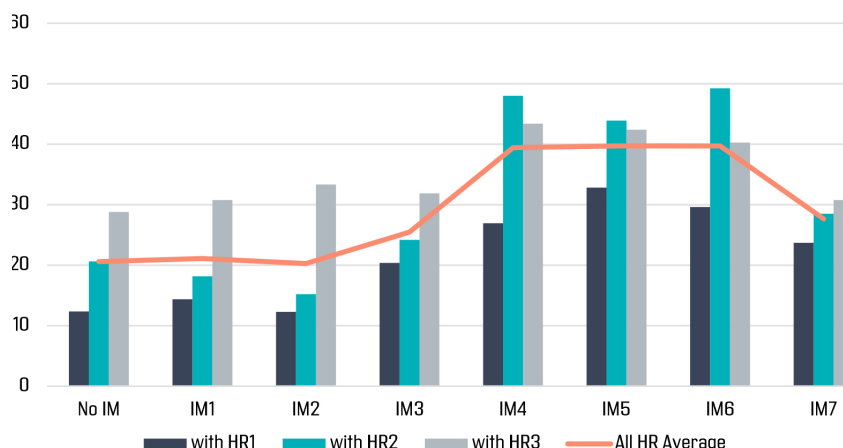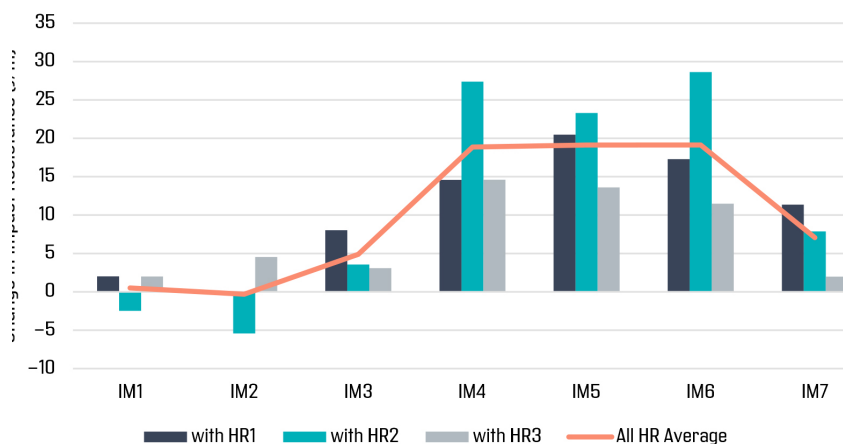
Figure 3. Formulation Impact Resistance

Figure 4. Effect of IM on Impact Resistance Heat Distortion Temperature

The HDT for all formulations is shown in Figure 5 and the change in HDT for each IM relative to the No IM formulation is in Figure 6. The HDT shows a consistent decreasing trend between HR formulations with HR1 based formulations giving the highest HDT and HR3 the lowest. This is to be expected based on the estimated level of crosslinking provided by the HR materials. Even though HR1 has a lower nominal functionality, it is a much smaller molecule leading to a tighter and stiffer cross-linked network.

Among the IM materials, the monofunctional IM2 had the greatest negative effect on HDT overall. IM1, with its structural characteristics leading to more restricted molecular motions, performed better than IM1. The trend between the HDT and IM molecular weight does not appear to be as strong as the trend seen with the HR. Formulations containing IM6 in combination with any of the HR showed the highest HDTs of the IM containing formulas despite having the second highest molecular weight. In contrast, IM7, which has the second lowest molecular weight, also performed well on average thereby fitting with the expected trend. Likely, HDT has a high sensitivity to rigid intramolecular substructures which can overcome the effect of molecular weight.
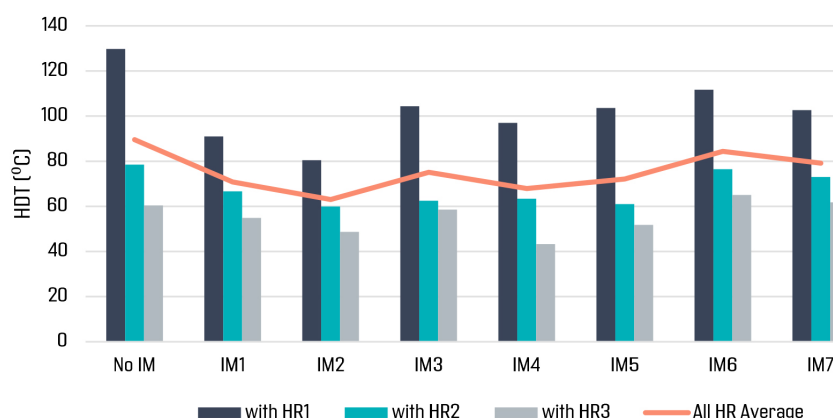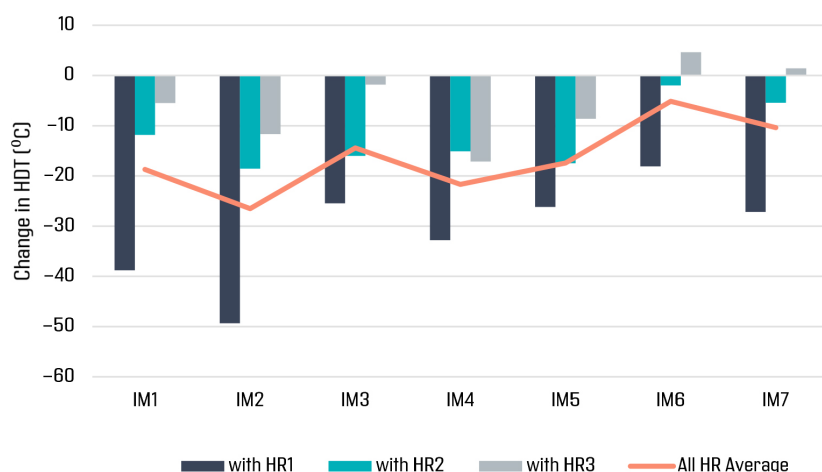
Figure 5. Formulation HDT


Figure 6. Effect of IM on HDT

Impact Resistance–HDT Relationship & Trade–Off Analysis

To explore any potential relationship between impact resistance and HDT, Figure 7 plots the impact resistance and HDT results for all higher functionality HR and IM combinations. Formulations containing the reduced functionality IM1 and IM2 were omitted as their structure and behavior appears to be different enough to warrant being separated. Unsurprisingly, there is an overall inverse relationship between impact resistance and HDT with HDT decreasing as impact resistance increases. This general relationship also holds for each subset of HR-based formulations, but to varying degrees. As the impact resistance increases, the HDT of HR1 formulations decreases at a higher rate than the other HR materials while the HR2 based formulations show very little change in HDT. The estimated slope of each trendline, reflecting the approximate change in HDT for each 1 J/m increase in impact resistance, is −1.1, −0.16, and −0.75 for HR1, HR2, and HR3 respectively.

Due to the inverse relationship between impact resistance and HDT there will usually be trade-offs between the two properties. Figure 8 illustrates the methods used to compare this trade-off between the IM materials and all the formulations. First, to compare

Figure 7. Relationship between HDT and Impact Resistance
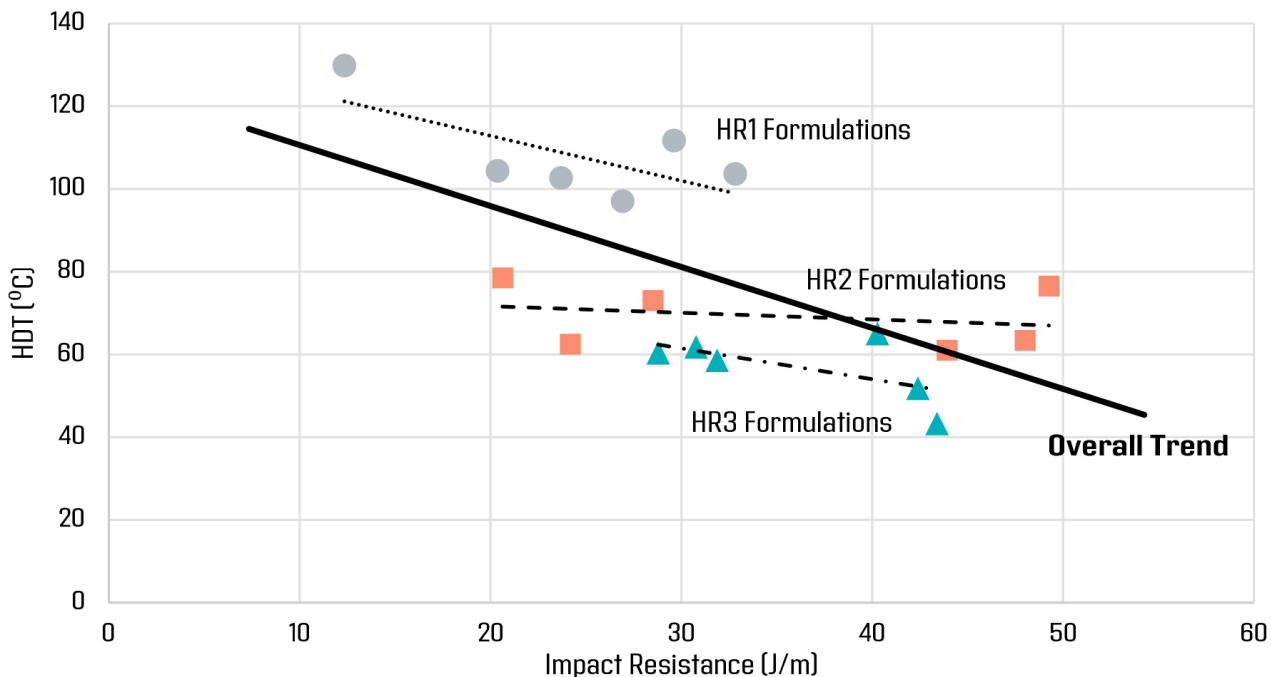
the effect of adding each IM, the slope between the No IM formulation and a IM modified formulation was calculated by:

$$\text{Slope} = \frac{\text{HDT}_{\text{No IM}} - \text{HDT}_{\text{IM}}}{\text{Impact Resistance}_{\text{No IM}} - \text{Impact Resistance}_{\text{IM}}} = \frac{\Delta\text{HDT}}{\Delta\text{Impact Resistance}} \quad (1)$$

Again, for each IM this slope reflects how much the HDT changed for each 1 J/m change in impact resistance. Second, for each formulation the triangular area under each result was calculated using the equation:

$$\text{Area} = \frac{(\text{HDT})(\text{Impace Resistance})}{2} \quad (2)$$

Like the area under a tensile stress–strain curve equating to a material's toughness, the triangular area created by a formulation's impact resistance and HDT provides a summary measure of the formulation's overall or combined capability to resist both impact fracture and distortion at high temperature. For example, under this construction a material with an excellent HDT and good impact resistance would be seen as similar to a material with excellent impact resistance and good HDT. In this case, the impact resistance and HDT balance out giving the two materials similar resistance profiles when looked at in total.

Figure 8. Impact Resistance–HDT Trade–Off Analysis Parameters
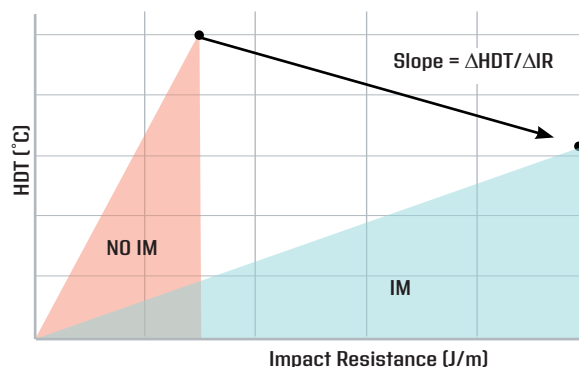
Figures 9 and 10 provide the results from Equations (1) and (2) respectively. The triangular areas in Figure 10 were normalized to the lowest value. IM6, especially when used in combination with HR2, provides the best balance of impact resistance and HDT. This is understandable given that IM6 shows the least negative effect on HDT for each gain in impact resistance of all the IM materials and HR2 had the most stable relationship between impact resistance–HDT, on average. Both IM4 and IM5 also show a favorable balance of properties in certain formulations with IM5 having the least drastic trade–off of the two. It is intriguing that the area of the No IM control formulations are very similar for all the HR materials. This would indicate that the difference in HDT between them is balanced out fairly equal by the increase in impact resistance. For the two reduced functionality IM materials, IM1 has a better balance of properties due to its better performance in both impact resistance and HDT.

Figure 9. Impact Resistance–HDT Trade–off for IM3–IM7
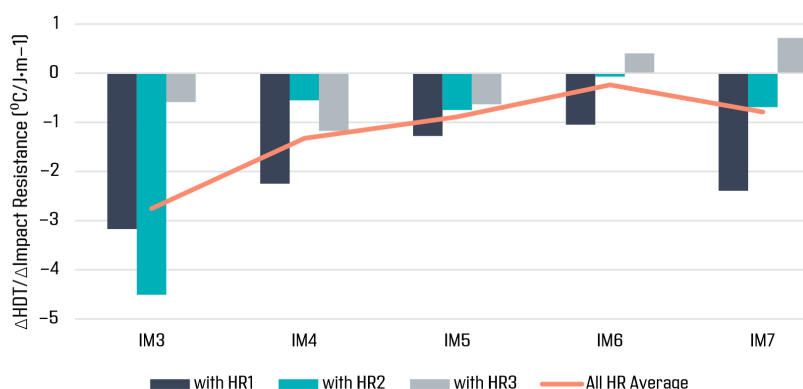

Figure 10. Triangular Area for each HR–IM Combination

Tensile Properties of Select Formulations

The tensile properties for select formulations can be found in Table 4. Formulations based on IM4–IM6 were chosen based on the balance of their impact resistance and HDT properties. IM1 was also selected as it showed a better balance of properties than IM2. The No IM control formulas are reported for comparative purposes.

As anticipated by their functionalities and molecular weights, HR1 and HR2 have higher tensile strengths and somewhat reduced elongations relative to HR3. However, HR1 appears to be much more toughenable through the addition of the IM. In each HR1 case, elongation increased and tensile strength either stayed constant or increased as well. IM6 continues to perform the best of the difunctional IM showing the best overall properties of those materials. Remarkably, there does not appear to be much degradation in tensile properties when using IM1 with any HR. This material, then, might find use as a viscosity reducer in certain higher viscosity formulations that will not drastically affect the physical properties.

Table 4. Tensile Properties of Select Formulations. Standard Deviation is 10–15% of reported values.

Hard Resin	Modifier	Tensile Strength (MPa)	% Elongation	Young's Modulus (GPa)
HR1	No IM	53	4.9	1.9
	IM1	55	5.3	2.1
	IM4	53	8.1	1.3
	IM5	56	6.9	1.4
	IM6	61	7.7	1.5
HR2	No IM	53	4.2	1.8
	IM1	54	3.8	1.8
	IM4	27	6.5	1.1
	IM5	38	4.5	1.3
	IM6	40	4.5	1.3
HR3	No IM	42	5.0	1.7
	IM1	39	6.1	1.5
	IM4	27	6.3	1.3
	IM5	28	7.8	1.3
	IM6	27	7.8	1.1

Conclusion

This work has evaluated the performance of several urethane (meth)acrylate resins in a model 3D printing formulation targeting high impact resistance and HDT. Although the ideal formulation viscosity will vary based on the specific 3D printing process being used, all formulations had a viscosity lower than some 3D printing materials currently on the market. The results of this study con-firm that in general there is a trade-off between impact resistance and HDT where an increase in one is coupled with a decrease in the other. However, the severity of the trade-off is not consistent across all materials making it possible to achieve a good balance in resistance properties through material selection. In this study, several material combinations exceeded 75°C, and even 100°C, in HDT while providing up to 50 J/m in impact resistance. Material molecular weight appears to influence viscosity, impact resistance, and, to a lesser extent, HDT more so than functionality. A deeper analysis into the various materials' substructures would likely provide further insights for future material improvement.

References

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