Isosorbide Methacrylate as a key building block in thermally and UV cured Bio-Based polymer systems

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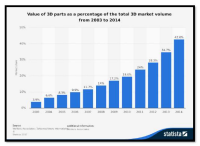
Background - Additive Manufacturing

In recent years, additive manufacturing has been the rising innovation within industrial production and prototyping.

This production technique hastens the manufacturing, sampling and application of certain chemical formulations for specific fields such as aerospace, automotive and supply chain.



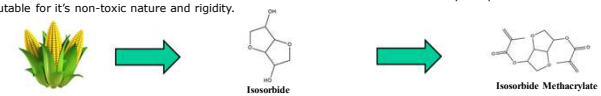
Advantages:

- Cheaper
- Quick prototyping & testing
- On-Site application
- Manufacturing of small, intricate machine parts
- Flexibility of production scale

Motivation

In recent years, bio-based polymer systems have been investigated as a substituent to petroleum based polymer systems due to carcinogenic compounds and endocrine disruptors used during production. Bio-based polymer systems allow for new, interesting structures with improved thermomechanical properties to be researched.

Isosorbide is derived from d-sorbitol which is sourced from corn hemicellulose. This cycloaliphatic molecule is reputable for it's non-toxic nature and rigidity.

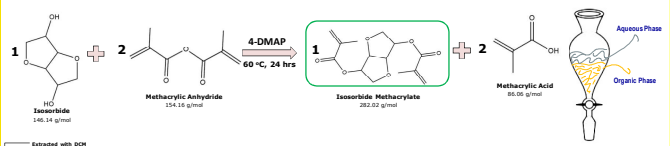


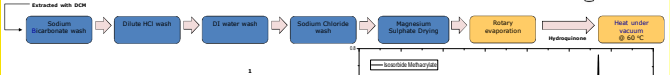
Isosorbide Methacrylate (starting monomer) is a low viscosity resin which presents high-performance thermomechanical properties within cross-linked polymer networks. However, IM is brittle and cannot be used solely in systems that require sturdy mechanical resilience.

This project focuses on:

- Building blended polymer systems using IM by leveraging its low viscosity to improve its toughness while building on its thermomechanical advantages.
- Incorporating UV cure mechanism into blend formulations to increase part intricacy/resolution and mitigate thermal residual stresses for on-site industrial applications within additive manufacturing.

Synthesis - Isosorbide Methacrylate





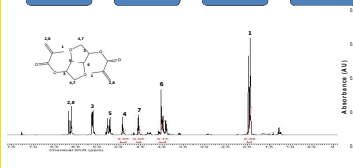


Figure 1: ^{1}H NMR of Isosorbide Methacrylate

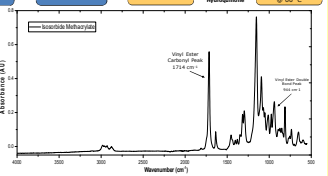


Figure 2: FTIR spectrum of Isosorbide Methacrylate

Preliminary Results

- Thermally cured blends between isosorbide methacrylate (IM) and the methacrylate of a long-chain fatty acid (MFA) were investigated to mitigate brittleness induced by excessive crosslinking of IM by increasing aliphatic content of the polymer network with MFA. This monofunctional methacrylate also helps reduce the concentration of double bonds within the formulation.

Table 1: Characterization of thermally cured IM MFA blends

Blends by wt% (IM:MFA)	Viscosity (Pa.s)	Extent of Cure	Cure Shrinkage (V/m)	Tg - tan delta (°C)
20:80	0.05052	95%	6%	52
40:60	0.04542	95.4%	9.2%	100
60:40	0.03622	92.8%	10.4%	120
80:20	0.03637	89.9%	10.6%	140
IM	0.04073	91%	-	>180
MFA	0.05441	-	-	-35

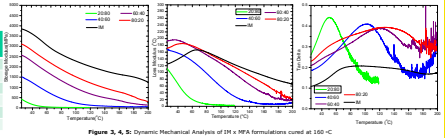


Figure 3, 4, 5: Dynamic Mechanical Analysis of IM x MFA formulations cured at 160 °C

UV curing - Digital Light Processing (DLP)

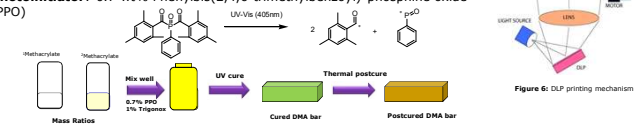
Printer: AnyCubic UV Photon 3D printer

Light: 405 nm Ultraviolet Light

Print Time per layer: 100s

Layer Thickness: 100 mi

Photoinitiator: 0.7 wt% Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (PPO)



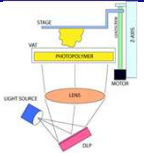


Figure 6: DLP printing mechanism

IM x MFA - UV Cure

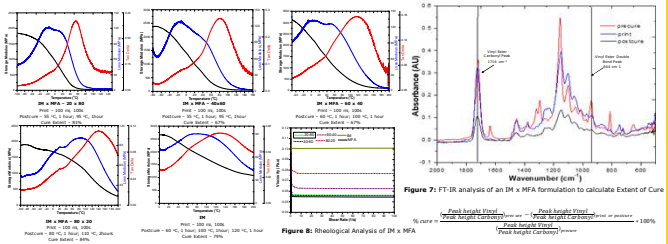


Figure 7: FT-IR analysis of an IM x MFA formulation to calculate Extent of Cure

Figure 8: Rheological Analysis of IM x MFA

Single Batch Reaction Method

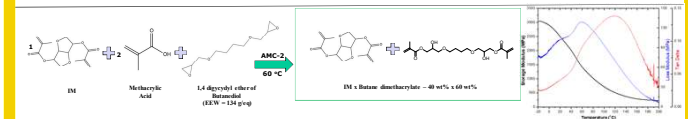


Figure 9: DMA of IM x Butane-dimethacrylate (40:60)
Postcure – 60 °C, 1 hour; 100 °C, 1 hour; 120 °C, 1 hour Cure Extent – 90%

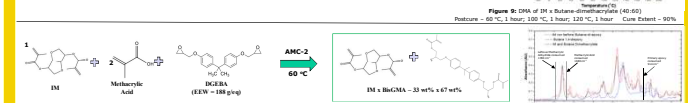


Figure 10: FT-IR confirmation of single batch reaction method

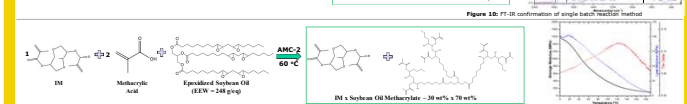


Figure 11: DMA of IM x Soybean Oil Methacrylate (30:70)
Postcure – 80 °C, 1 hour; 140 °C, 1 hour Cure Extent – 75%

Comparative Analysis

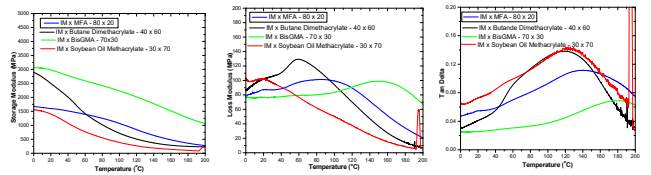


Figure 12, 13, 14: Comparative DMA analysis of select IM blend formulations for UV printing

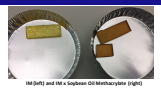
Table 2: Master Table of UV cured IM blend formulations

UV cured Blends by wt%	Viscosity (Pa.s)	Density (g/cm^3)	Extent of Cure (Print)	Extent of Cure (Postcure)	Cure Shrinkage (Print) (V/m)	Cure Shrinkage (Postcure) (V/m)	K_c Avg	K_c Std Dev	G_c (kJ/m^2) Avg	G_c (kJ/m^2) Std Dev	Tg – tan delta (°C)
IM:MFA											
20:80	0.0565	1.0551	76%	81%	8.7%	8.8%	0.1412	0.013	0.009	0.002	58
40:60	0.0591	1.0844	24%	67%	9.0%	9.8%	0.2157	0.019	0.024	0.004	82
60:40	0.0626	1.1147	58%	67%	9.4%	9.5%	0.2202	0.035	0.024	0.008	112
80:20	0.0767	1.1476	27%	84%	8.2%	8.7%	0.2367	0.056	0.029	0.013	140
IM	0.1008	1.1825	44%	79%	6.0%	8.5%	-	-	-	-	‡130
MFA	0.0544	-	-	-	-	-	-		-		-35
IM:BisGMA (70:30)	0.3853	1.1696	53%	95%	8.4%	8.6%	-		-		180
IM : Butane-dimethacrylate (40:60)	0.5747	1.1652	69%	90%	6.8%	8.6%	-		-		120
IM : BisGMA (33:67)	220	-	-	-	-	-	-		-		-
IM : Soybean Methacrylate (30:70)	0.7713	1.0760	71%	75%	7.1%	7.2%	-		-		124

Conclusions

→ In conclusion, we were able to tackle the following research problems:

- Optimizing a synthetic route for Isosorbide Methacrylate
- Discover UV printable blend formulations with IM that mitigate brittleness
- Develop synthetic route for making blend formulations for UV printing that require little to no work up

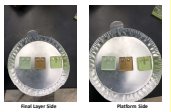


IM (left) and IM x Soybean Oil Methacrylate (right)
Postcured @ 80 °C, 1 hour and 140 °C, 1 hour

Future Work

→ In the future, we would like to tackle the following research problems:

- Develop a method to determine optimal post-curing procedures for UV printing
- Develop formulation-specific working curves for printing with the AnyCubic Printer
- Synthesize more methacrylate formulations using the single batch synthesis method



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2. Isosorbide-methacrylate as a bio-based low viscosity resin for high performance thermosetting applications – JM Sadler, 2013

Acknowledgements

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