Effects of Polyether Polyol Hydroxyl Equivalent Weight on Controlled Release Polyurethane Coatings of Urea (46-0-0)

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Supporting Information

Rotating Drum Coater

Figure S1. The rotating coater is of steel construction with a drum diameter of 16 1/8” with five (5) evenly spaced 1” baffles, an electric motor, and an angle of repose of approximately 60° from the hood surface.

Qualitative Selection of Coating Process Conditions.

Table S1. The coating process conditions were selected through qualitative observations, using the standard formulation reported based on castor oil. The following table summarizes those qualitative observations.

Process Change	Observation	Outcome
Smaller Urea Prills	Urea (46-0-0) prills of SGN 250 are readily commercially available; smaller prill sizes were seen to aggregate more readily	Urea of SGN 250 from American Plant Food Corp. Used
Coater temp < 70 °C	C30 wax additive prills don't melt properly in rotating granules	Coating temp = 80 °C
Angle of Repose	Lower angle of repose (< 60°) led to insufficient granular turnover, higher (> 60°) led to clumping at bottom of coater	Angle of repose maintained at 60° from hood surface
Rotational Speed	Coater rpm too low led to less granular turnover. Too high led to prills bouncing out of the coater	40 rpm coater speed was maintained for all experiments
Iso index < 1.4	Iso index of 1.2 led to insufficient delayed release of coating	Iso index standardized to 1.4 Index = Mol NCO/Mol OH
All iso added at once	Granules became sticky and displayed aggregation	Iso added in two portions
Fewer than 3 layers	Addition of PU coating components in too few applications led to stickier granules and observed aggregation	PU application maintained in 3 separate layers
Time of addition increased	Free flowing granules were achievable with 30 s between component additions. Increased time led to no discernible benefit in layer-by-layer addition.	30 seconds between each component addition
Hot material removed from coater directly	Stopping the coater above 55 °C promoted less free-flowing behavior as the wax continued to solidify.	Granules were allowed to cool to < 50 °C before stopping coater and removing to promote free-flowing granule behaviors
Control release tested immediately	Optimal controlled release behaviors were only reproducibly achieved after >48h of room temperature post-application cure	Coated granules were allowed to sit for 1 week prior to release testing in triplicate.
Change in PU wt%	Lower coating weight < 2.5 wt% PU led to faster release. Coating above 2.7 wt% led to much slower release.	2.7 wt% PU coating was chosen as the standard coating weight to provide better comparisons of coating compositional performance within the tested release timeframes (≥28 days).
Wax Additive wt%	Changes in the wt% of wax additive amount had similar performance shifts to the PU coating wt%.	0.5 wt% total wax additive chosen for standardized performance and application ease.

Crush Strength Comparison of Uncoated Urea and Castor Oil-Based PU Coated Urea.

To validate the presumption that the application of a general polyurethane coating at 2.7 wt% and the wax additive at 0.5 wt% would improve the crush strength of a urea (46-0-0) prill, the Single Particle Crush Strength measurement was performed based on the ASTM standard D4179.1557 (2017edition) "*Standard Test Method for Single Pellet Crush Strength of Formed Catalysts and Catalyst Carriers*". The test was performed on the castor oil-based coating formulation as it was used to determine baseline performance against which release was compared for the *poly*(propylene oxide) triols-based coating formulations. Indeed, a significant increase in crush strength was observed for the coated urea.

Table S2. Crush strength of uncoated and castor oil-based PU coated urea performed using ASTM D4179.

Polyol Used	**Uncoated**	**Castor**
Crush Strength (mPa) (g)	4396	5495
Crust Strength (std)	1087	1264

Full Coating Procedure. Urea prills (0.5-2.0 kg) of 2-4 mm (SGN 250) were optionally kept in an oven set to 80 ^{o}C for up to 24 h prior to coating experiments. Using gloves for hot material handling, the prills were transferred from the oven to the coater and rotation was subsequently initiated at 40 rpm. A heat gun was used to heat and maintain the temperature of the rotating prills at 80 ^{o}C, and an IR temperature probe was utilized to ensure temperature stability. Once the temperature was stabilized at 80 ^{o}C, addition of the coating material was initiated. Generally, for each formulation unless otherwise noted, the following order of addition and timing was observed as recorded in **Table S3**:

Table S3. Order and timing of additions

Component	Time of Addition
Isocyanate (0.4)	0 s
Polyol	30 s
Isocyanate (0.6)	60 s
Wax (50% of total)	90 s
Repeat Above 1x	**30 s between additions**
Isocyanate (0.4)	240 s
Polyol	270 s
Isocyanate (0.6)	300 s

All components were pre-weighed and triethanolamine (10 wt% in polyol portion) reactive catalyst and crosslinker was added to the polyol portion prior to addition. Following application of the final layer, the coated prills were allowed to cool to 50 ^{o}C before they were removed from the coater and set aside at room temperature for a minimum of 1 week, to allow for a full cure, after which release profile measurements could be collected.

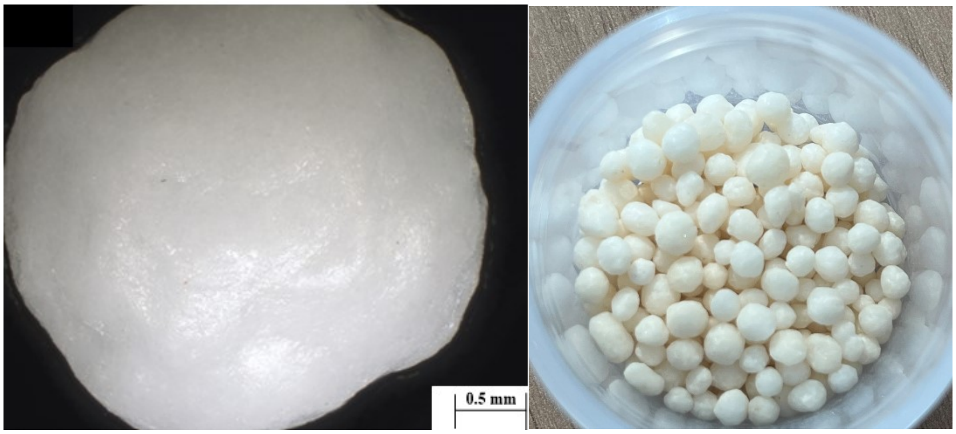

Figure S2. (*Left*) Magnified microscope picture of urea (46-0-0) coated with 2.7 wt% PU and 0.5 wt% wax additive. (*Right*) Picture of coated urea (46-0-0) batch.

Table S4. Component amounts for the formulated coatings for 1kg batch of urea (46-0-0).

	Plaque Formulation Code					
Component	**A**	**B**	**C**	**D**	**E**	**F**
Castor	13.12 g					
P1000		12.88 g				
P700			11.66 g			
P450				9.72 g		
P260					7.29 g	
Glycerol						3.65 g
Triethanolamine	1.46 g	1.43 g	1.30 g	1.08 g	0.81 g	0.41 g
PAPI™ 27 pMDI	12.42 g	12.69 g	14.04 g	16.20 g	18.90 g	22.94 g
C_{30+HA} Wax	5.0 g	5.0 g	5.0 g	5.0 g	5.0 g	5.0 g
PU wt%	2.7%	2.7%	2.7%	2.7%	2.7%	2.7%
Wax wt%	0.5%	0.5%	0.5%	0.5%	0.5%	0.5%
Total Coating (PU+wax) wt%	3.2%	3.2%	3.2%	3.2%	3.2%	3.2%

Refractive Index Calibration Curve.

Where: X = wt% Release Urea; Y = Refractive Index (R.I.)

$$X = \frac{Y - 1.3330}{0.0013}$$

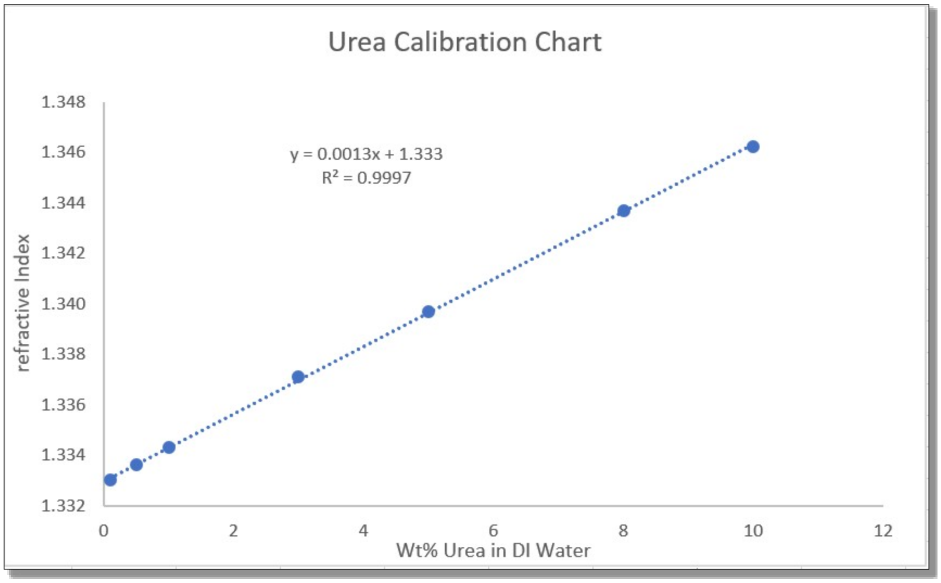

Figure S3. Calibration plot of refractive index to measure amount of release urea in DI water

Crosslink Density Calculations:

Crosslink density was normalized to elastically equivalent tetra-functional crosslinks (ie: 2 trifunctional crosslinks that become linked are elastically equivalent to 1 tetra-functional cross-link).

X = crosslink density (mmol/g); **M$_{>2Fn}$** = Mass of component with greater than 2 functionality

EW$_{>2Fn}$ = Equivalent weight of component with greater than 2 functionality

Fn$_{>2Fn}$ = Average functionality of component with greater than 2 functionality

M$_{tot}$ = Total mass of formulation.

$$\boxed{X = \frac{\sum\left[\frac{M_{>2Fn}}{EW_{>2Fn}} * \left(\frac{Fn_{>2Fn}}{2} - 1\right)\right]}{M_{tot}}}$$

For example, the equivalent weight and presumed functionality of each component is shown in **Table S5**, and the amounts and ratios of materials used in both the coatings and plaques are shown in **Table S6**. The reported assumptions were used to calculate the theoretical crosslink density of each formulation.

Table S5. Functionality and equivalent weight of components used in this study. Equivalent weight is determined as 56100/OH#, where the Hydroxyl number (OH#) is measured by ASTM D4274. The Isocyanate equivalent weight is determined by isocyanate content as measured by D5155. Functionality is assumed to be as reported by the supplier.

Component	Functionality (F_N)	Equivalent Weight (EW)
Castor Oil	2.7	340 g/mol
P1000	3	333 g/mol
P700	3	236 g/mol
P450	3	150 g/mol
P260	3	85 g/mol
Glycerol	3	32 g/mol
Triethanolamine	3	50 g/mol
PAPI™ 27 pMDI	2.7	134 g/mol

Example Calculation: Formulation A

Castor oil: Mass = 14.58 g; Equivalent Weight = 340 g/mol

Triethanolamine: Mass = 1.62 g; Equivalent Weight = 50 g/mol

PAPI™ 27 pMDI: Mass = 13.80 g; Equivalent Weight = 134 g/mol

X= {∑([(14.58g/340 g*mol^{-1})*(1.35 - 1)] + [(1.62g/50g*mol^{-1})*(1.5-1)] + [(13.80g/134 g*mol^{-1})*(1.35-1)]}/ 30 g total mass

X = (0.0150 mol + 0.0162 mol + 0.036 mol)/30g → X = 0.0672 mol/ 30g → X = 0.00224 mol/g

Crosslink Density $_{\text{(Formulation A)}}$ = 2.24 mmol/g

Table S6. Polyurethane plaque formulations, component amounts, and calculated crosslink densities.

	Plaque Formulation Code					
Component	**A**	**B**	**C**	**D**	**E**	**F**
Castor	14.58					
P1000		14.31 g				
P700			12.96 g			
P450				10.80 g		
P260					8.10 g	
Glycerol						4.05 g
Triethanolamine	1.62 g	1.59 g	1.44 g	1.20 g	0.9 g	0.45 g
PAPI™ 27 pMDI	13.80 g	14.10 g	15.60 g	18.0 g	21.0 g	25.5 g
Total Mass (g)	30 g	30 g	30 g	30 g	30 g	30 g
Crosslink Density (mmol/g)	2.52	2.45	2.75	3.17	5.31	4.47

Generation of Polyurethane Plaques and Thermal Testing Procedure.

To a plastic, 50g FlackTek™ mix cup was added the polyol, triethanolamine, and PAPI™ 27 pMDI. The components were then mixed at 2000 rpm for 30s after which the composition was poured into a small aluminum paint can lid treated with urethane mold release. The poured material was allowed to cure at room temperature for 7 days prior to thermal testing.

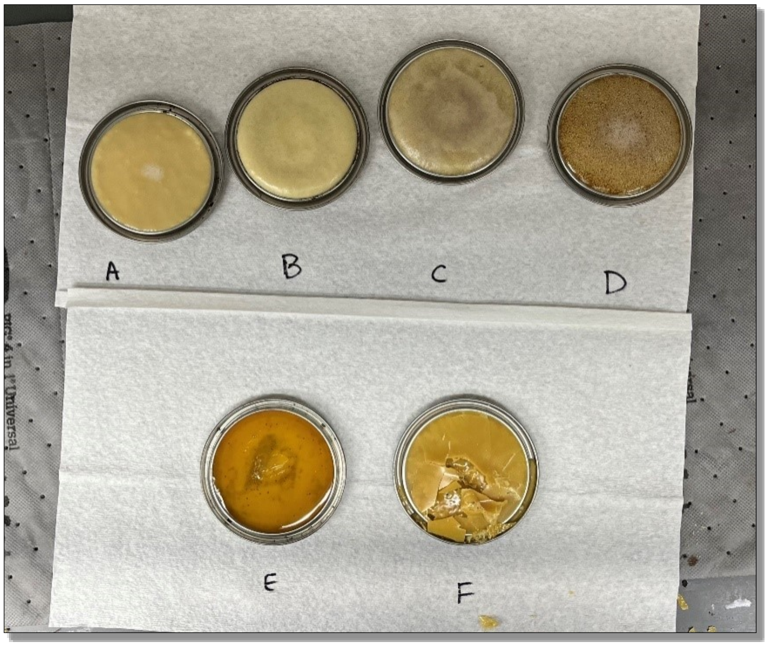

Figure S4. Cured polyurethane plaques of **Coatings Formulations A-F**.

Note: *Given the overindexed nature (NCO:OH >1) of the plaque formulations, at least a minimum of foaming was observed in all cases due to secondary reaction of excess isocyanate with ambient moisture to achieve total cure. Therefore, it was not possible to obtain suitable samples for water uptake or water contact angle which did not physically hold water in the formed cells.*

Glass transition temperature i.e., T_g of the crosslinked materials–

The Q2000 differential scanning calorimetry i.e., DSC was utilized from TA Instruments containing a single cell configuration utilizing 2 thermocouples for heat flow measurement. It was equipped with 2 MFC's to enable switching between gasses during a run. The auto sampler had a 50 sample capacity plus up to 5 reference pans. The sub ambient temperature control was achieved using a refrigerated cooling system (RCS). The temperature of test was varied from -50 °C to 250 °C. The second heat on the sample which is cycle 4 from the method log, was utilized for glass transition temperature i.e., T_g for the crosslinked network upon complete conversion. The T_g analysis was performed using Universal Analysis software from TA Instruments. For each of the coating samples, below is the analysis image from the software.

Method Log:
1: Data storage: On
2: Ramp 10.00°C/min to -50.00°C
3: Isothermal for 3.00 min
4: Mark end of cycle 1

5: Ramp 10.00°C/min to 200.00°C
6: Mark end of cycle 2
7: Ramp 10.00°C/min to -50.00°C
8: Isothermal for 3.00 min
9: Mark end of cycle 3
10: Ramp 10.00°C/min to 200.00°C
11: Mark end of cycle 4
12: Ramp 20.00°C/min to 25.00°C
13: End of method

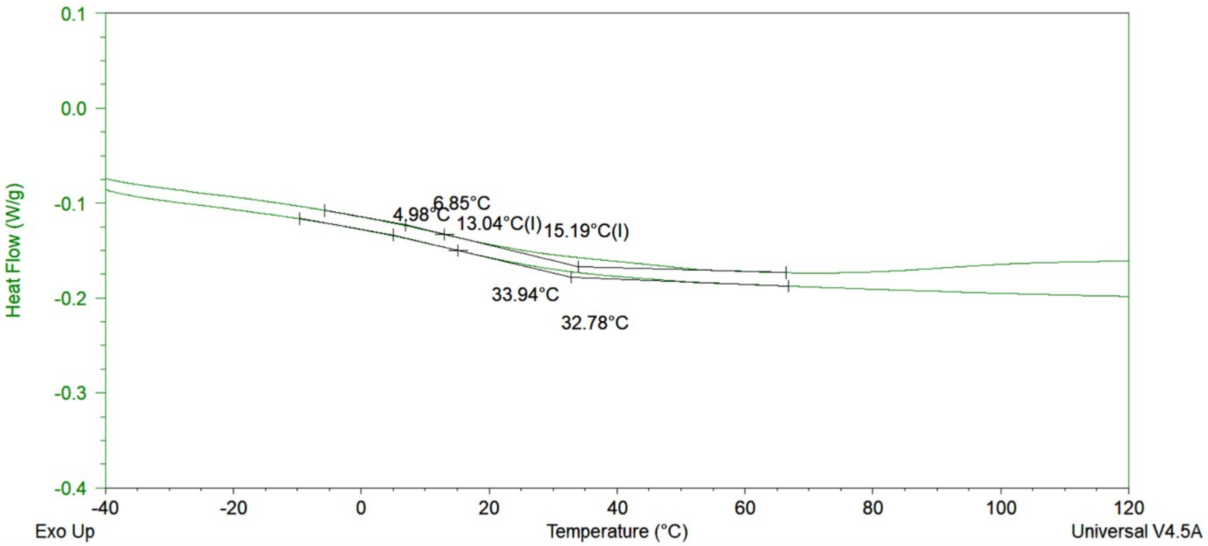

Figure S5. Coating material A synthesized with castor oil as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

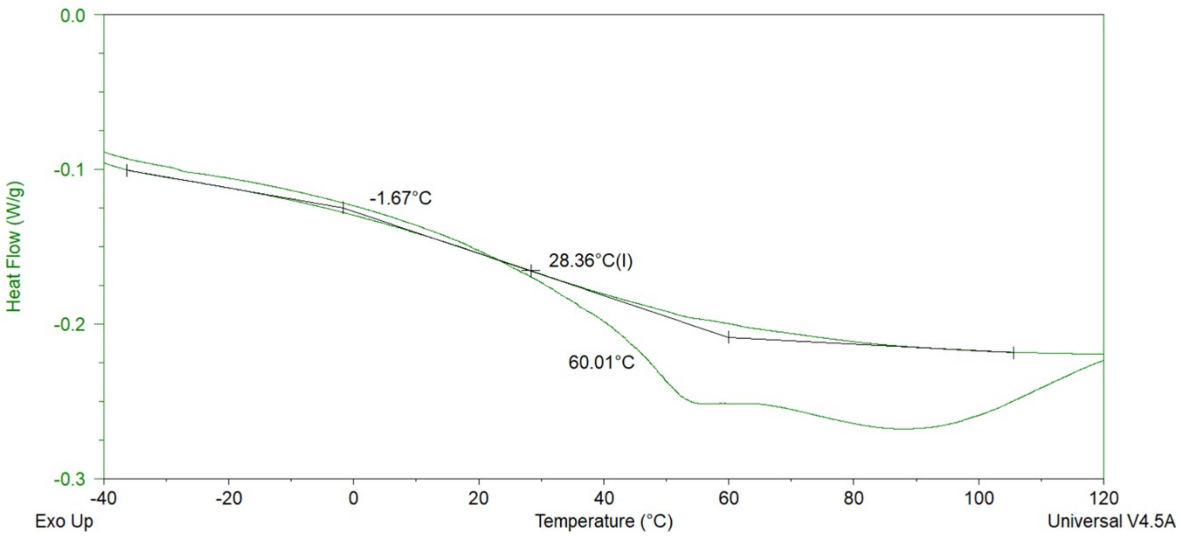

Figure S6. Coating material B synthesized with P1000 as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

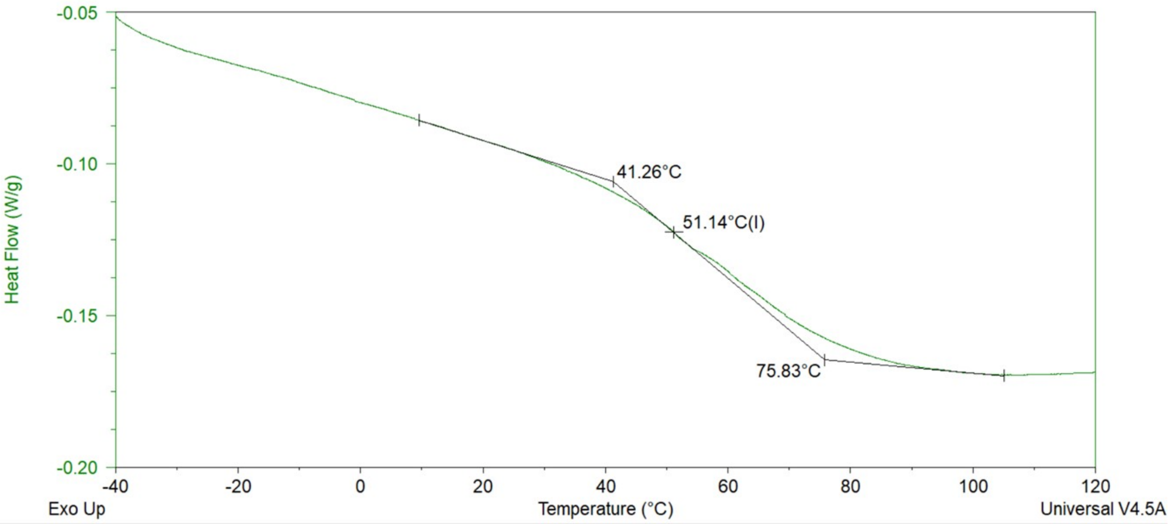

Figure S7. Coating material C synthesized with P700 as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

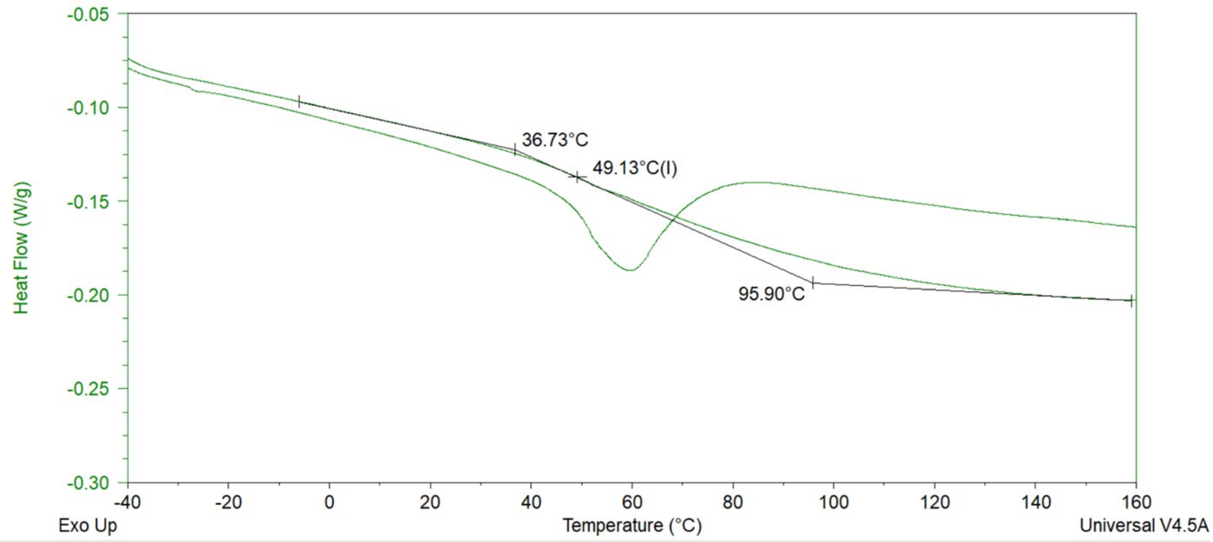

Figure S8. Coating material D synthesized with P450 as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

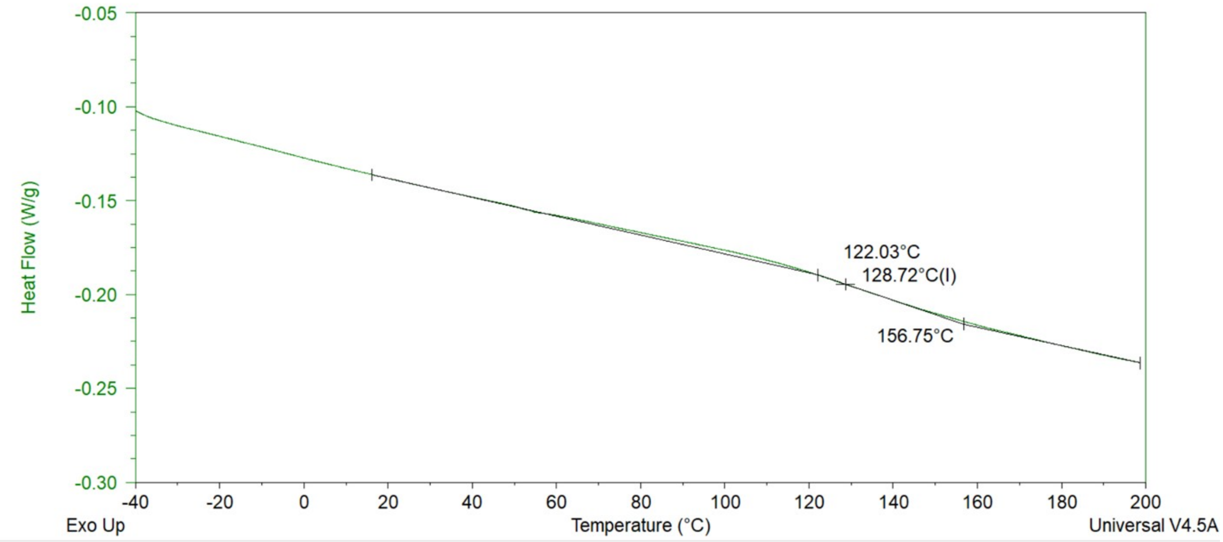

Figure S9. Coating material E synthesized with P260 as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

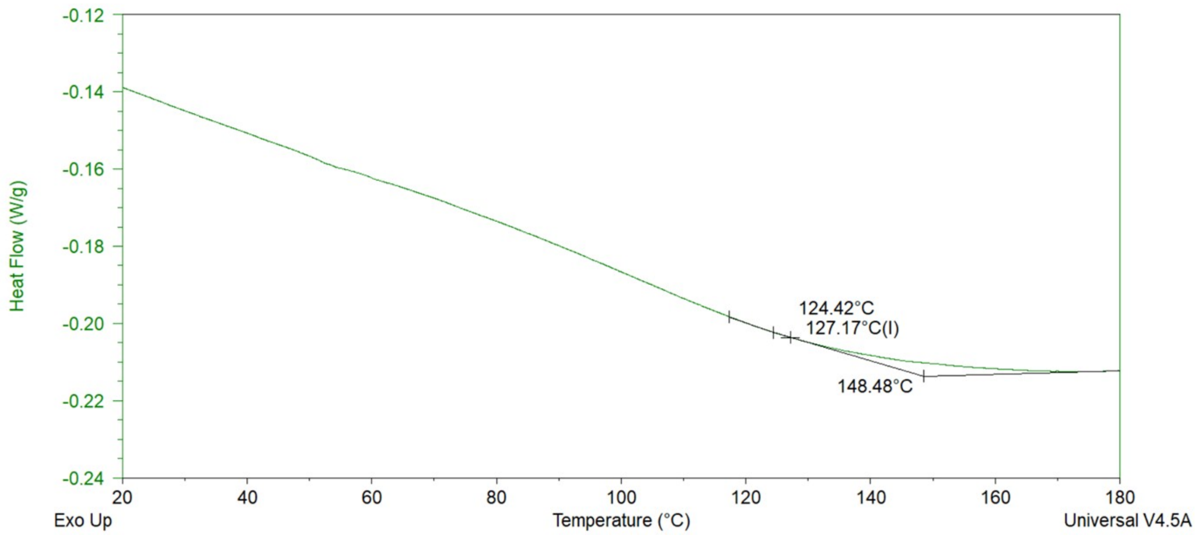

Figure S10. Coating material F synthesized with glycerol as polyol and cured material was analyzed for glass transition temperature using DSC on Universal analysis software.

Thermal stability of the coating material.

The thermogravimetric analysis, i.e., TGA was utilized for confirming the thermal stability of the coating materials with different polyols in the crosslinked backbone. The data was generated using a TGA Q500 from TA Instruments equipped with a Standard furnace and autosampler. The TGA was configured in standard mode with nitrogen gas purge. An aliquot of the sample was transferred to a standard platinum pan and placed in the autosampler tray. The TGA analysis commenced, and the data was collected using a 10 °C per minute ramp from room temperature to 850 °C under nitrogen. The run was closed with a 5 minute burn in air at the end to clean the pan. The results were analyzed using TA Instrument’s Universal Analysis software.

Method Log:

1: Data storage: On

2: Select Gas: 1

3: Ramp 10.00°C/min to 850.00°C

4: Isothermal for 5.00 min

5: Data storage: Off

6: Select Gas: 2

7: Isothermal for 5.00 min

8: End of method

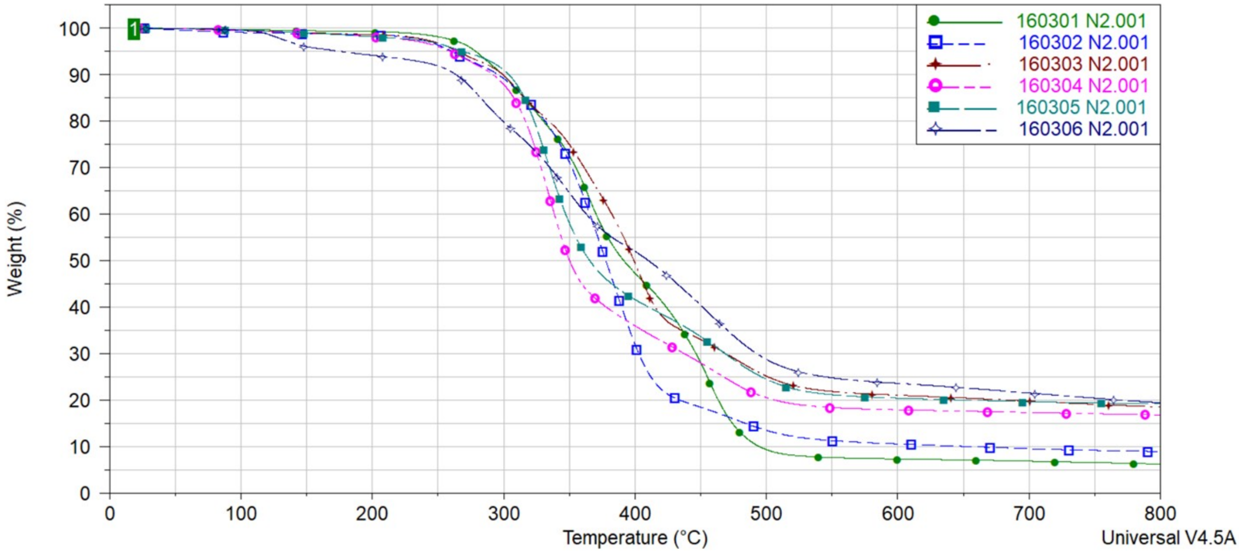

Figure S11. The TGA analysis confirms all coating samples from A to F have mass loss of ~10wt% in a temperature range from 260 to 310 °C. The sample nomenclature is as follows - Coating A (160301), Coating B (160302), Coating C (160303), Coating D (160304), Coating E (160305), Coating F (160306). This confirms the stable nature of coatings during the DSC analysis temperature range for T_g values completed separately on coatings made with similar formulations. The low crosslinked density **Coating A** and **Coating B** showcase low residue at higher temperature of 500 °C and above as compared with the rest of the higher crosslinked **Coating C-F**.