RENUVA™ SOY-BASED POLYOL RIM FOR AUTOMOTIVE EXTERIOR APPLICATIONS

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Abstract

There are many formative trends in today's OEM composite marketplace which are driving the investigation and development of alternative feedstocks from natural or renewable resources in the plastics industry, such as environmental sustainability, reduced dependence on crude oil, and the high cost of petroleum-based derivatives.

This paper will describe the development of a novel soy oil based polyol (under the RENUVA™ tradename) which has technological advantages in terms of odour, physical properties, compatibility and processability in polyurethane application over existing soy-based polyol. The paper will further describe the development partnership undertaken by The Dow Chemical Company and Polycon Industries (a division of Magna International) to utilize this "green" polyol to develop a Reaction Injection Moulded (RIM) polyurethane formulation suitable for painted exterior applications. The paper will outline the developmental iterations done to accomplish this goal and to maximize the soy-based polyol content in the RIM composite for physical property and processability optimization. The paper's conclusion will demonstrate the viability of a 50% soy-based polyol solution to meet the processability, paintability, and physical property specification of a current Original Equipment Manufacturer (OEM) RIM program through direct comparison of extensive trial work done on series production fascia tooling at Polycon.

The paper will extend this development work into potential opportunities for the RIM polymer involving exterior composite applications for heavy equipment or agricultural machinery, where natural resource feedstocks would have clear market desirability.

Background

There currently exists an industry focus on renewable resources and "green" technology, and a distinct informed consumer bias toward solutions which reduce their dependence upon petroleum and minimize their carbon footprint. Dow and Decoma along with their customers are looking to evaluate bio-based solutions in the automotive market place. The development of such solutions for their OEM customers could serve to further technological innovation in this arena and provide a flexibility of feedstock options. One area that shows some promise in polyurethane chemistry is the incorporation of seed-oil based polyols in thermoset applications.

Dow Polyurethanes has engineered and developed a Renuva™ soy-based (or, potentially, other seed-oil based) polyol solution which has low-odor and higher performance characteristics than existing soy polyol solutions. This unique process for making highly engineered polyols from bio-based feedstock can make the polyols suitable for the rigorous demands of automotive applications. The primary bio-sourced feedstock being utilized for Dow's natural oil polyols is soy oil, although other seed oils could be used as well. Dow is at the stage of scaling up this technology and looking for appropriate markets in which to place these polyols in order to augment their existing position as a preeminent supplier of polyurethane chemistry. The primary objective in this customer validation study was to evaluate the effectiveness, processability and viability of Dow's Natural Oil-based Polyol (NOP) system when coupled with Polycon Industries' RIM process expertise in a commercial automotive exterior application. This work builds upon the successful polymer and process development work done in the laboratory which established that the polyurethane/polyurea composite formulation was viable. The key desired outcomes for the trials were threefold:

- An evaluation of the processability of the material and projected ease of implementation into Polycon Industries process,
- An evaluation of the physical properties of the NOP containing parts,
- Manufacture of parts for paint testing, functional testing and dimensional consistency at Polycon Industries.

This data will all be presented and compared against the well-established baseline generated by current production parts and process outputs at the production moulding and paint site.

The scope of this report encompasses several iterations of the NOP formulation run at Polycon Industries. Over time, as the formulation was optimized, attempts were made to determine the maximum amount of NOP that could be used in the end polymer and still meet the processing and functional property requirements of the polymer system. The project goals were designed around the VOC (Voice Of Customer) parameters of meeting the following conditions:

- Polymer properties to meet production OEM specification
- Maximization of the soy polyol substitution in the RIM formulation
- equivalent surface aesthetics and polymer processability using current production operations.
- Minimization of the loss of any mean value key mechanical property (e.g. flexural modulus, elongation) versus the control production fascia formulation.

The Dow Manufacturing Process for Renuva™ Soy Polyol

The Dow Chemical Company has developed a unique process for making highly engineered polyols from bio-based feedstock suitable to meet the rigorous demands of automotive applications. The primary bio-sourced feedstock being utilized for Dow's natural oil polyols currently is soy oil, though other seed oils could be used as well. Soy oil as a renewable feedstock has many strengths, particularly because it is globally available and it is cost competitive compared to other oils. It has available unsaturation (C=C) where transformation chemistry can be performed to append the hydroxyl groups necessary for the manufacture of polyurethane thermoset polymers.

Dow's process methodology utilizes transformation technology originally developed at Union Carbide Company (UCC) and couples it with current polyol production technology from the Dow Chemical Company, resulting in a specialized process that produces polyols designed for specific applications such as RIM (Reaction Injection Moulded) polyurethane exteriors. In the four step process[1,2], shown in Figure 1, the triglycerides taken from seed oil feedstock are broken down into fatty acid methyl esters (FAMEs) and glycerine via methanolysis – essentially the same process used to create bio-diesel fuel. The FAMEs subsequently become the building blocks for creating monols via hydroformylation and hydrogenation. Control of the process at each of the steps results in an odor free, consistent, hydroxyl-containing monomer that can be tied together with selected initiators to create different engineered polyols depending on the actual end product performance requirement. Note that this process also allows for the formation of primary hydroxyl groups, necessary for fast reacting polymers – such as RIM or other fast curing polyurethane systems. One can also see from the diagram below that the process itself uses two raw materials - methanol, and glycerine - that can be sourced from renewable feedstocks, as well as being internal recycle streams, further reducing the overall carbon footprint of the polyol's manufacture.

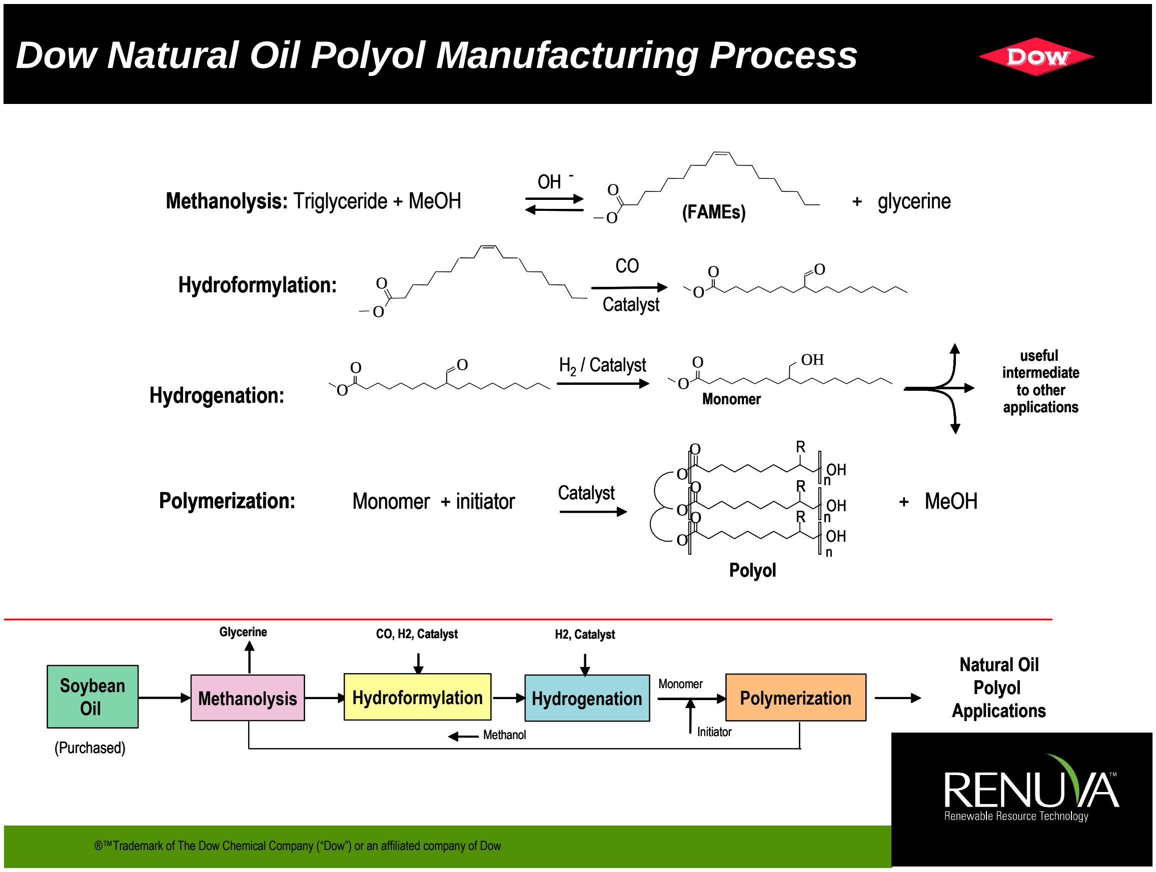


***Figure 1**: Dow Manufacturing Process for Natural Oil Polyols*[3]

Through this manufacturing process a renewable resource-based polyol can be made with a variety of seed oil feedstocks having low odour and is capable of being engineered to have the specific molecular weight distribution and functionality required to meet the rigorous requirements of an automotive application.

Soy-Based Polymer Customer Validation Trial Plan

The plan developed for the trial and evaluation was comprehensive, yet simple and remained consistent throughout the NOP formulation iterations, representing an efficient and effective standardized protocol.

The NOP polyol blends were made up at the Dow development lab and effectively had between 25% and 80% replacement of the petroleum-based polyol with the soy polyol in the liquid blend (Trial Series 1 was 25% replacement, Trial Series 2 was at 80%, and Trial Series 3 was at 50%). A production-sized batch of material with the requisite wollastonite inorganic filler was made in the “Polycon Lite” production blend tank as the polyol formulation. The blended material was then loaded into a well-drained day tank and the process allowed nucleating and equilibrating to the injection master set-up profile parameters at the RIM injection machine.

All of the trials were run on production fascia tooling in order to appropriately asses the process and performance characteristics of the trial materials in comparison with the production control formulation. The approximate geometry of this fascia is shown in the Figure 2. The wallstock thickness on this part runs from 4mm along the upper shelf down to 2mm out on the lower wings, with the mean wallstock value being about 2.75mm. This is a large part weighing upwards of 5.5 kg. The part is filled through a fan-style gate located on the upper middle part of the fascia between the two middle grille opening reinforcement (GOR) panel locating tabs.

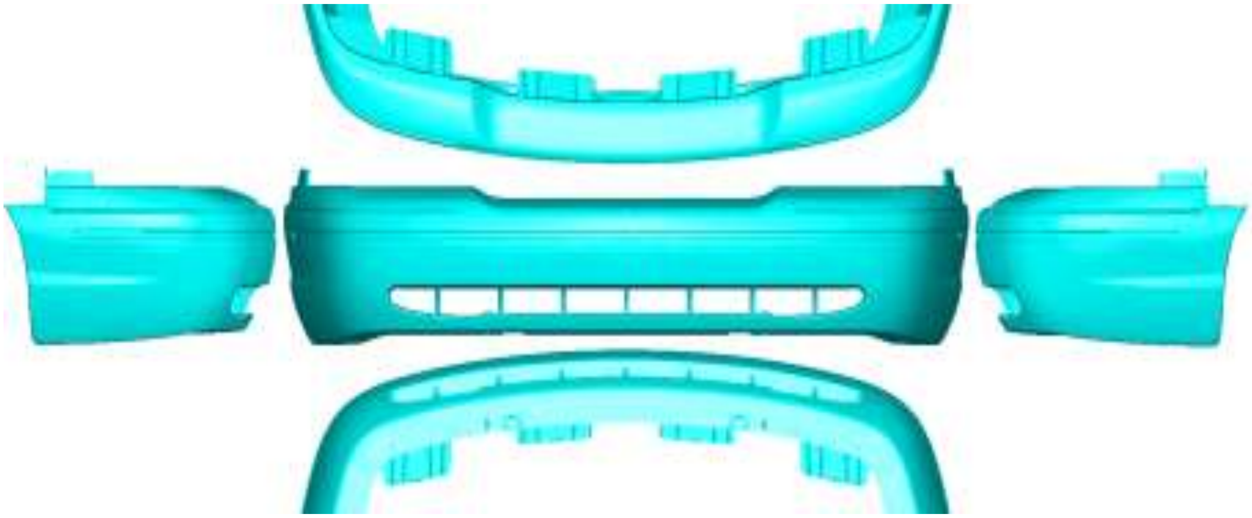


***Figure 2**: Soy Polyol Rim Validation Tooling - Front Fascia Geometry.*

The RIM injection machine process parameters for the soy polyol were set to exactly the same values as the regular production master set-up at Polycon Industries. Mould filling processability metrics such as minimum fill weights, flow progression, etc. were studied through a series of short shots and injection speed variation protocol, then the process parameters were optimized and production-style parts were manufactured for part evaluation.

The assessment of the parts was made on the basis of the following characteristics, with appropriate metrics established for each criteria:

1. Manufacturability (cycle time, releasability, part weight, green strength, etc)
2. Quality (Blisters, flash, porosity, surface quality)
3. Functionality (Paintability, Dimensional Consistency)

During each trial, a significant number of parts were run after the process had been tuned in, and the parts were manufactured at production conditions – with production cycle times, using production handling practices, and post-moulding operations, such as postcure and paint. Polycon Industries retained three parts and tested them according to their standard test sample plan: density, filler content, flexural modulus, tensile, elongation, tears strength and heat sag resistance.

Material Processability -Trials and Results

Trial Series 1 – 25% Soy Polyol Substitution

After reviewing the lab results of data generated on soy polyol RIM materials, the validation team decided that trials should start with a conservative soy polyol substitution goal. A 25% substitution of the existing polyol with soy polyol was selected.

The first evaluation done was a study of the nucleating ability of the polyol with nitrogen – an important step in the RIM process for mould filling. The nucleation bubble size and quality was rated as being consistent with production, and the gas loading reached nominal values in an amount of time approximately equal to that seen in production.

From the start of the moulding trial the parts looked very good: the part surface was excellent, no evidence of sink marks, flow lines, porosity, or improper mix was seen. The release of the polymer from the mould was very good. The part quality was assessed to be very comparable to production. The part appeared slightly stiffer at demould and after cooling, but there were no issues with greenstrength (polymer integrity at demould). Colour, odor, flash condition, and all aesthetic qualities seemed to be equivalent to production.

The part weight was kept at the same established by the normal production mean. The minimum fill study was done, and demonstrated that the part had a 15% pack factor. The usual recommended pack level is 10-15%. The specific gravity of the NOP polyol is less than the petroleum polyol, so theoretically some weight could be saved if the materials process and volumetrically pack similarly, but this was not studied extensively.

The parts themselves looked very similar to production. The molded part came out of the press feeling robust, perhaps slightly stiffer than the production material. The release of the part was very good as well. There were no issues that would be anticipated for productivity. The material dropped in and ran very well.

Trial Series 2 – 80% Substitution

The first trial went so well, and the processability was so similar to normal production material, that the investigation team looked to increase the soy content significantly so that the product could be taken to “failure” – either in terms of processability or functional properties. To that end, the team ventured to trial an 80% soy substitution formula.

The material was blended up at Polycon Industries, and the trial was run using the previously established trial methodology. In most respects the 80% substitution results and processing observations were similar to that seen in the 25% soy trials.

The parts came off very well, and processed in almost exactly the same manner as the production material. Again, colour, odor, flash condition, and all aesthetic qualities seemed to be equivalent to production. The main difference that was seen was that the parts had a noticeably lower stiffness off the mould than the production parts. The parts were slightly easier to tear than the comparable production material, but seemed resilient otherwise. The parts, however, did distort significantly in the grille area when they were put in the Work-In-Process (WIP) racks, or when they were being weighed immediately after moulding. This was raised as an issue that had to be addressed in the next trial. In this formulation design, the end polymer was tailored to match the flexural modulus of the soy poly formulation to the production control in order to match the overall stiffness and “feel” of the part, an important feature of fascias. The parts did feel the same after postcure, but did not feel the same at demould.

The trial went very well from an overall processing and surface quality point of view, and it was very encouraging that parts could be made at such a high level of soy polyol substitution. It was felt that the identified issues from the trial - the low stiffness at demould and sagging - could be improved upon with formulation re-design.

Trial Series 3 – 50% Substitution

After the results of the 80% soy trial, the team established a simple test protocol in the Dow lab to assess the amount of sag of moulded plaques, designed to correlate with the functional failure in distortion seen on the parts themselves. This allowed for a rapid screening of proposed formulation iterations. This was used to differentiate the “stiffness” of the part after demoulding, and allowed some predictability for assessing the amount of sag in the grille opening area of the fascia.

The physical property results from the previous trials were reviewed, and, as is detailed in the next section, some properties had dropped below desired target deviation values, though they were not outside the OEM specification limits. It was decided that these differences could potentially have a significant effect on the functional properties of the part, most notably impact testing, so a goal was set to maximize the soy content, meet the specification requirements and yet not lose any more than 25% of any normal production value. This was set along with the target of improving the stiffness of the part at demould to improve handleability and reduce sag. As a result of lab formula screening and optimization experimentation, a 50% soy formulation was selected.

In the 50% trial the part surface continued to be excellent, no evidence of sinks, porosity, blisters, flow lines or other defects were seen. The parts were generally indistinguishable from production and subjectively rated to be of high quality. The part release from the mould was very good. The part appeared to be slightly less stiff at demould than production but similar after cooling on the trim nest. There were no obvious issues with greenstrength with tearing and part distortion. Colour, odour, flash condition, and all aesthetic qualities seemed to be equivalent to production.

The trials themselves were very much a success from a processability point of view throughout the range of soy polyol substitution seen. The master injection set-up was changed very little throughout the trials. The polymer had performed well through all the trials, and, through iterations, the team had achieved the goal of designing a polymeric material the material which responded as a drop-in replacement for the production control material and was amenable to the current standard work processes at Polycon Industries**.**

Physical Property Evaluation -Trial Results

The physical properties were reviewed from each individual trial throughout the process of the polymer evaluation. The physical property test results from the 25% soy polyol product were very encouraging right from the start. All of the properties met the OEM target specification, although there were obvious statistically significant shifts in the means from the control material.

The flexural modulus, for example, increased slightly, while the elongation and tear strength results decreased (see Table II), but this could be predicted from the polymeric structural differences. This is the obvious effect of the lower equivalent weight and higher cross-link density of the soy polyol material. The table below presents the Impact Property Data versus Production Control -Trial Series 1 (25% Soy Polyol).

Table I*: Impact Property Data versus Production Control -Trial Series 1 (25% Soy Polyol)*

Properties	Control Polycon Lite	Trial Series 1 (25% Soy)
Multi-Axial Impact Peak load RoomTemp.	**643.25**	**630**
Multi-Axial Impact Total energy @ Room Temperatures	**401.5**	**384.8**
Izod Impact @ @ Room Temperatures	**44.2 kj/m2**	**33.6 kj/m2**
Izod Impact @ -40	**15.8 kj/m2**	**13.9 kj/m2**

With these reports in hand and the positive feedback from the processing evaluation metrics, the team moved toward at high substitution level of 80% soy. The results with the high soy level showed that the moulded parts were too “soft” at demould despite the fact that the polymer was designed to match flexural modulus of the control production material. The physical property data revealed 50% loss in some key parameters, which was considered unacceptable, even though they still met the minimum OEM specifications. It was decided that the loss in any one property could not exceed 25% from the control mean value (and, of course, still meet the specification minimum), and that formulation fine tuning work needed to be done on the area of sagging and handling of the parts as they progressed through the production process.

The team decided that an “intermediate” soy polyol level would be appropriate and the team set a goal for having a formula with 50% substitution. In the 50% soy polyol run the physical property results were very encouraging. They hit all the points of the design criteria: the matched flexural modulus, tensile strength, density, heat sag and filler, and exhibited a loss of just under 25% of nominal production values as per the standard set by Polycon Industries, and as designed by Dow in the lab. This property degradation was observable, yet still allowed the polymer to meet the OEM specification requirements. This data is presented in the summary section below rather than in the individual test table.

The following graphs indicate the physical property history of the development work to date with the soy polyol formulations. The table summary of the Trials Series Physical Property data versus Production Control data is shown on Table II below, and in the Spider charts shown in Figures 3 and 4.

***Table II**: Trial Series - Physical Property Summary*

Properties	**Specifications**		**Polycon Lite (Control)**	**Trial Series 1 (25% Soy)**	**Trial Series 2 (80% Soy)**	**Trial Series 3 (50% Soy)**	**Validation Trial (50% Soy)**
Density	*ISO 1183*	0.95-1.15 g/cm^3	1.003	1.018	1.023	1.01	1.01
Solid Content	*ISO 3451.1*	7% - 9%	8.35	8.34	7.99	8.35	8.27
Tensile Strength	*ASTM-D638*	16.8 Min.	21.68	23.47	20.061	24.5	24.6
Tear Strength	*ASTM-D624*	38kn/m Min.	64.68	58.107	56.45	63.2	65
Elongation	*ASTM-D638*	100% Min.	426	335.62	193.36	296	243
Flex Mod.	*ISO 3451-1*	202 MPa Min.	243	274.61	224.85	243	299

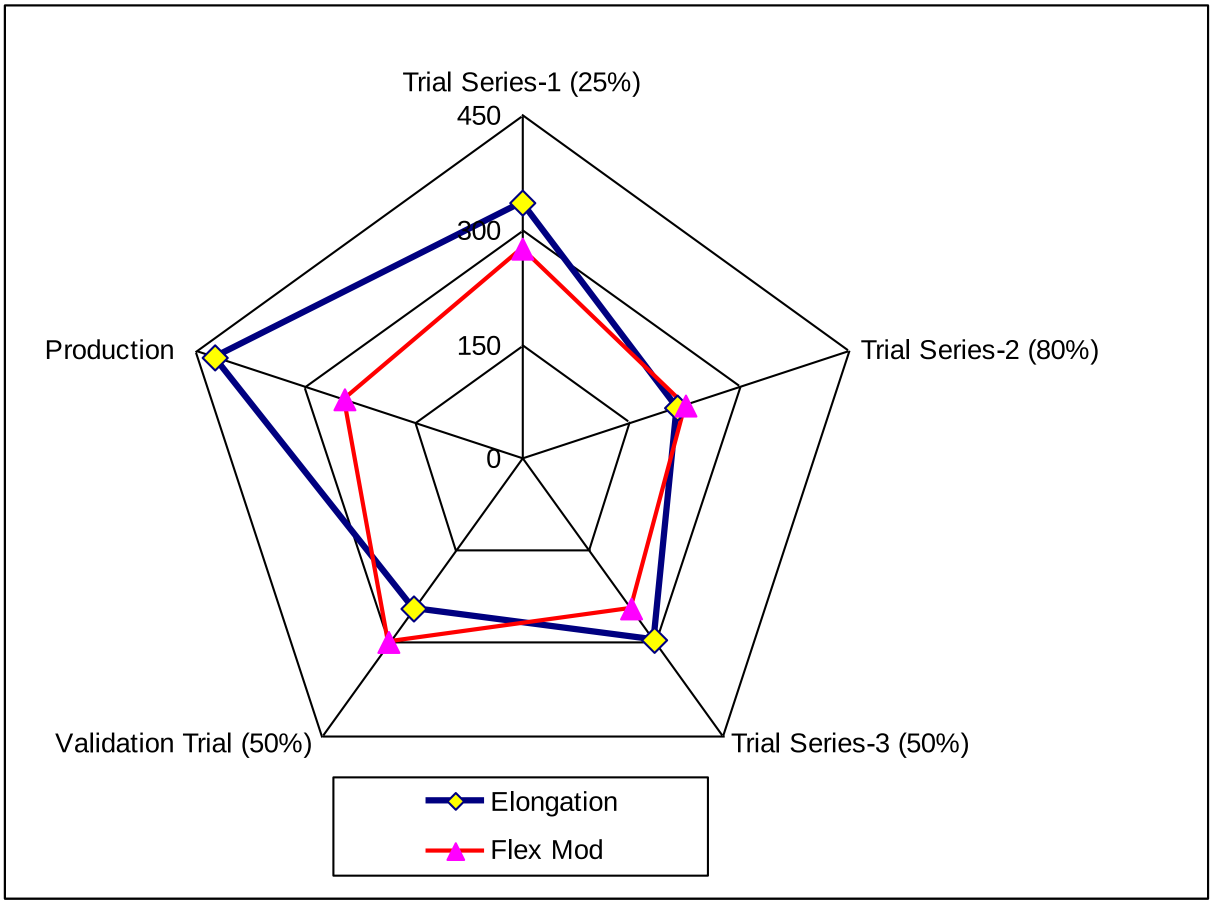


***Figure 3**: NOP Trial Run Summary - Elongation and Flexural Modulus Flexural Modulus*[3]

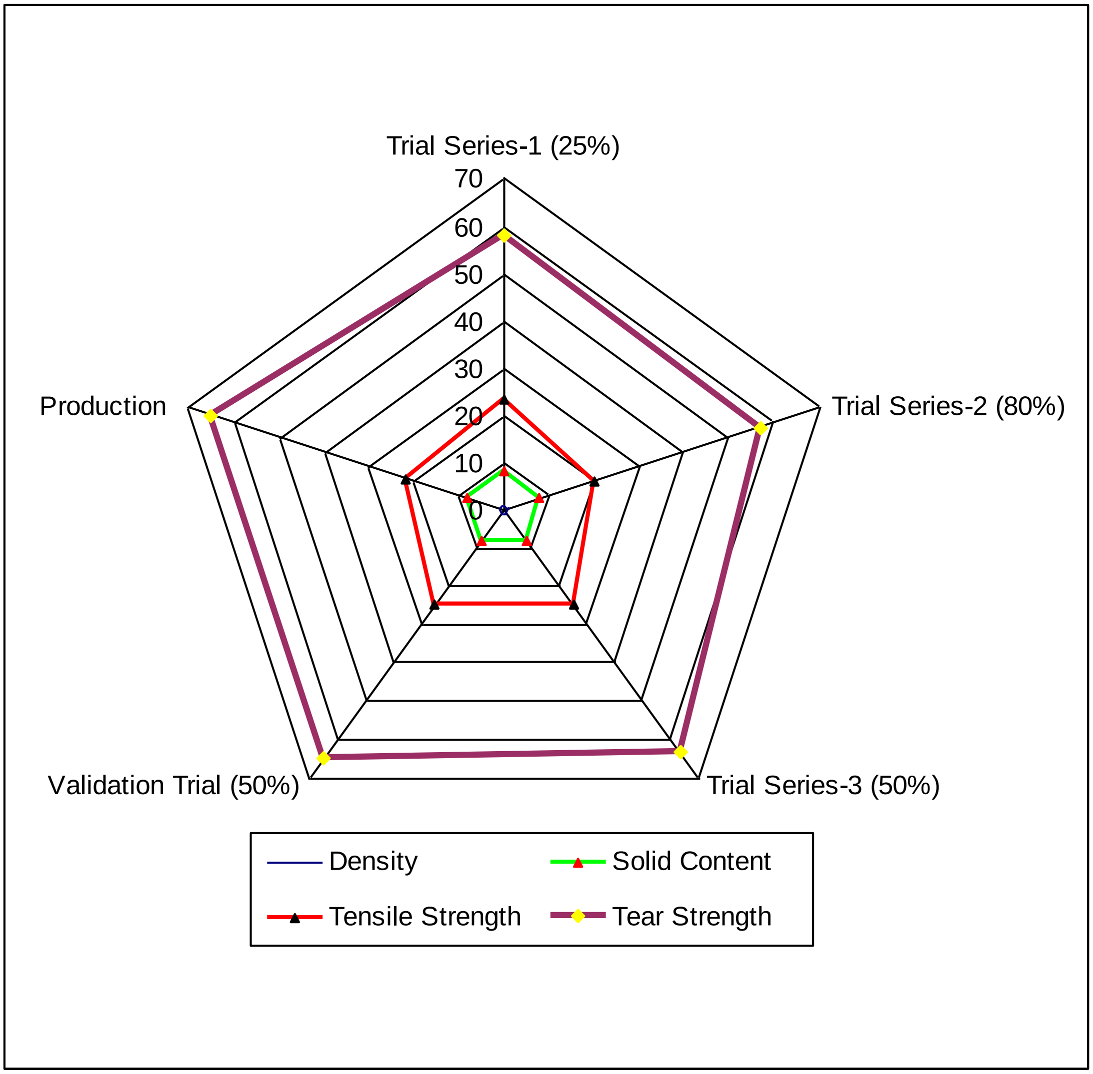


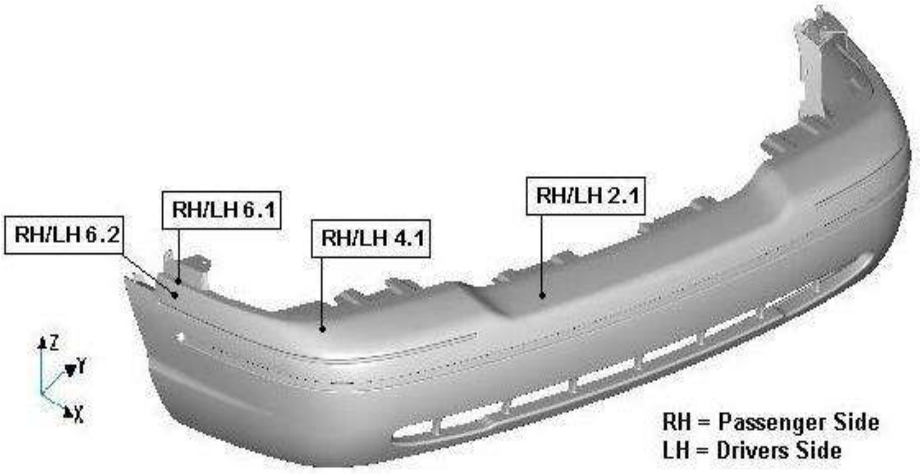
Figure 4: *NOP Trial Run Summary – Physical Properties*[3]

Dimensional Stability Evaluation -Trial Results

Thirty (30) piece dimensional capability studies were undertaken by Polycon Industries using Coordinate Measuring Machine (CMM) data on the test fascia to evaluate tolerance deviation and material shrinkage after bake. 4 data points were measured for each side of the part (Driver "RH" & Passenger"LH") as shown on Figure 5.and Table III. The results were promising and the parts fell right in line dimensionally with where the production material ran. No observable issues were encountered.

Table III: *Dimension Stability*

Location	LH 2.1	LH 4.1	LH 6.1	LH 6.2	RH 2.1	RH 4.1	RH 6.1	RH 6.2	
Tolerance	± 1.90	± 1.90	± 1.90	± 1.90	± 1.90	± 1.90	± 1.90	± 1.90	**SRINK**
Production Control									
Mean	0.34	-0.66	-0.87	-1.32	0.33	-0.4	-1.36	-1.24	990
Series -1 25% SOY POLYOL									
Mean	-0.71	-1	-0.62	0.293	0.331	-0.48	-0.91	-1.18	990
St Dev	0.098	0.111	0.096	0.058	0.108	0.136	0.127	0.087	0
Series -3 50% SOY POLYOL									
Mean	-0.73	-1.17	-0.54	0.176	0.369	-0.45	-1.24	-1.35	990
St Dev	0.131	0.155	0.206	0.136	0.214	0.347	0.3	0.198	0



***Note: All testing performed as per specifications & frequencies outlined in O.I. 10.1.0012**

***Figure 5**: Dimensional Gauge Study -Data point location*

Paint Performance Evaluation-Trial Results

Four sets of fascias were primed with a conductive primer and top coated with a 1K base coat and 1K clear coat in four different colours (White, Black, Light Metallic and Dark Metallic) according to the OEM PPAP requirements using paint systems that are commercially used today in RIM applications.. The Polycon Lite formulation with 50% Soy Polyol substitution passed all of the specifications required for new material/paint approval on all 4 colours tested.

Table IV-Paint Performance Testing *(OEM Engineering Material Specification)*

Test	Specification	Requirements	Production "A" Surface	50% Soy "A" Surface	Results Pass / Fail
Film Build	Primer	0.8 Min	0.96	0.96	**Pass**
	Clear Coat	0.8 Min	1.05	1.1	
	Base Coat	1.00 Min	1.2	1.2	
Paint Adhesion	*FLTM BI 106-01*	Less than 5% Removal	0% removal	0% removal	**Pass**
Flexability @ 23°C	*WSS-M2P181-A*	No cracking when bent over mandrel	No cracking	No cracking	**Pass**
Chip Resistance	*SAE J400*	Minimum rating as per Substrate 3mm Max single chip size	8	10	**Pass**
Water Resistance	*FLTM BI 104-01*	No blistering, dulling or softening	No blistering, dulling or softening	No blistering, dulling or softening	**Pass**
Gloss Before	*FLTM BI 110-01*		88.9	91.2	
Gloss After	*FLTM BI 110-01*		87.4	90.5	
Adhesion After	*FLTM BI 106-01 (Method D)*	Less than 5% paint removal	0% removal	0% removal	
Cold Checking Resistance	*FLTM BI 107-02*	No cracks, blistering or change in appearance	No cracks, blistering or change in appearance	No cracks, blistering or change in appearance	**Pass**
Adhesion After	*FLTM BI 106-01 (Method D)*	Less than 5% paint removal	0% removal	0% removal	
Fuel Resistance	*FLTM BO 101-05*	No dulling, surface distortion or softening	No dulling, surface distortion or Softening	No dulling, surface distortion or Softening	**Pass**
	ISO 105-A02	Max. discoloration of 4 - 5 AATCC	5	5	
Adhesion After	*FLTM BI 106-01 (Method D)*	Less than 5% paint removal	0% removal	0% removal	
Thermal shock	*FLTM BI 107-05*	No blistering or loss of adhesion	No loss adhesion was observed	No loss adhesion was observed	**Pass**

No practical difference in Film builds, surface aesthetics (distinctness of image, gloss, orange peel) or adhesion issues were noticed with the parts made with Polycon Lite at 25%, 50% and 80% soy polyol compared to Production parts, when initial paint screen testing was done after the trial parts were manufactured All parts tested at the different level of substitutions showed class-A finish surface and comply with OEM Engineering Material Specifications. The table IV showed the paint performance testing results on part made with PolyCon Lite at 50% Soy Polyol substitution painted with 1K (one-component) basecoat and 1K clearcoat (Performance White) when the full paint testing protocol was completed.

Soy Polyol RIM Validation Conclusions

Through the methodical progression of the NOP evaluation trials, the team succeeded in achieving the stated objective of meeting an acceptable property balance using the soy polyol blends in a RIM fascia application, and have achieved an essentially drop-in solution with respect to moulding and processing the part. The trials have demonstrated that a RIM part can be made with adequate surface aesthetics and normal processing techniques at up to 80% substitution of the petroleum-based polyol with the Renuva soy-based polyol. The reality of the target OEM specifications for physical properties, and green strength/sag at demould, however, would seem to limit the appropriate substitution level to about 50% for this particular application. Higher levels of substitution may be possible for RIM applications with different requirements and part design.

The soy polyol material did not caused any blending or processing concerns in handling prior to moulding. As the substitution level increases, however, it is believed that the lower state of cure at demould starts to interfere with the ability to handle the part in the plant – so some minor formulation modifications have to be made to improve this greenstrength property in order to perform comparably to the control production formulation in the current downstream handling and processing of the part.

The material nucleates well, and holds that gas nucleation at least as well as the production material. The processability of the material at the injection machine and the part quality were rated to be equivalent to the standards set by current production. The defect rate that was evaluated during the trial runs was estimated to be similar to the current production, although the sample size of the trial runs was too small to make that conclusion with any statistically definitive authority. The conclusion from operations was that the material did not have any obvious concerns with anything that would affect productivity negatively - other than the slightly “softer” feel at demould at the 50% substitution level. The trimmers actually felt that the material was slightly easier to trim due to this softness. The parts all exhibited a good surface quality through the different substitution levels. The porosity and sink mark evaluations showed the parts to be on par with production. They painted well and have no dimensional concerns.

The impact of the soy polyol on the physical properties is quite evident. The flexural modulus of the polymer increases with increasing soy polyol content, while the impact, elongation and tear properties start to suffer. The lower equivalent weight of the soy polyol leads to a higher cross-link density and a stiffer polymer, which is the main contributor to these polymer attributes. The increase in soy content also leads to progressively lower greenstrength and stiffness at demould, indicative of a slower build of molecular weight. Some formulation modification must be done to counterbalance these physical properties effect. The team decided that a 50% replacement formulation is a very realistic goal for the project when looking at the balance of processability and physical property changes for the fascia application.

Renuva RIM - Summary and Next Steps

In this study, the soy polyol evaluation team has demonstrated the capability of the Renuva-based soy polyol RIM to be used in a demanding commercial automotive application from both a processing and functional property point of view over the range of polyol substitution levels from 25 to 80%. The team optimized the RIM formulation to the point where there is confidence that a 50% substitution level of the soy-based RIM polyol will meet the performance requirements of the particular application OEM screen chosen. A basic understanding of the effects that the soy polyol has on the RIM formulation has been established and thus extensions of this technology to other OEM applications or target specifications can be reasonably modeled and a soy-based polyol solution quickly scaled.

The primary recommendation after this work is that the team proceeds to validate the soy polyol RIM technology solution with OEM's in order to gauge their interest and gain some market "pull", as the RIM polyurethanes market, in general, has been declining due to replacement with thermoplastic solutions.

The marketing strategies associated with soy oil feedstock materials traditionally have been for renewable content, and for cost savings, due to simple, wide-spec quality soy polyols. Dow's approach has been slightly different – to produce a highly engineered, higher value polyols made from renewable raw materials which can compete technically with their petroleum-based brethren, and to implement these products at technology driven polymer moulding specialists like Polycon Industries. The soy-based polyol initiative at Dow is building upon the successes of projects such as this, and continues to evolve next generation Renuva polyols with potentially improved properties. As the technology emerges with new NOP-based polymer architecture, there is the potential to improve the performance of these materials and possibly target higher substitution levels. Such new polymer designs could be focused on higher modulus applications such as body panels, should the marketplace be desirous and accepting these thermoset solutions.

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