DYNAMIC MIXING OF ADIPRENE® L-100

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Abstract: This project used a dynamic mixing system purchased from BDTronics to investigate automatic mixing and dispensing of polyurethane formulations to replace archaic hand mixing techniques at Pantex Plant that resulted in poor quality parts and inability to have good repeatability between results on lots of material. Over the course of approximately 18 months several curing agents and secondary extenders were evaluated but Ethacure® 300 and 1,4 butandiol were found to be the most similar to the previous curatives. Room temperature and heat cured formulations were identified to meet the needs of Pantex Plant Plastics Shop. By varying the formulation using the plasticizer benzylbutylphthalate (BBP), Ethacure® 300, and 1,4 butanediol, and adjusting the curing time and temperature, to the final physical properties were adjusted to include compression, tear, hardness, and tensile strength. A modeling study evaluated molds using a software package called Moldflow®. Moldflow® software helped determine the best points to place injection holes, vent holes and identified if damming issues or void formations would occur. This study determined that the new formulations as well as new colorants identified would be a good replacement for the production tools used at Pantex Plant.

Keywords: Dynamic Mixing; Plastics; Moldflow

Introduction

This paper summarizes a joint endeavor between West Texas A & M University (WTAMU) Engineering and Computer Sciences Department and Pantex. The project establishes a process for dynamic mixing system purchased from BDTronics to include investigating formulations and automatic mixing of polyurethane formulations replacing archaic hand mixing techniques to increase quality, safety, and efficiency.

The focus of the project includes the development of formulations using liquid curing agents to replace the solid curing agents Cyanacure™ and trimethylolpropane (TMP). Cyanacure™ is an amine curing agent used with the pre-polymer Adiprene® L-100 in various hand mixed polyurethane formulations at Pantex Plant. TMP is a solid hydroxyl terminated curing agent that when coupled at various levels acts synergistically with Cyanacure™ to soften final products. To convert from hand mixing to dynamic mixing, two alternate liquid curing agents were evaluated. Ethacure® 300 (E300) and 1, 4 butandiol (BD) are both liquids at room temperature and have similar properties to TMP and Cyanacure™. The materials developed in the Pantex plastics shop is used for coatings, seals, cushions, tool covers, table covers, sealing rings, and many other applications.

As part of the conversion, Pantex requested formulations and curing parameters that meet the following expectations:

- Targeted hardness reached and stable within 24 hours
- Less voids, warping, shrinking and rework
- Repeatable and reproducible results between batches
- Ability to have Adiprene® formulations cured at room temperature for coating applications
- More flexibility in curing temperatures and times
- Better color differentiation between mixes
- Help with mold designs to minimize warping, void volumes and under filling

After a laboratory evaluation at the manufacturer's site, principle investigators determined that the Cyanacure™ and TMP would not work in a dynamic mixer due to the elevated temperatures needed to melt TMP and Cyanacure™.

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Further investigation revealed that consideration of Ethacure® 300 as a possible replacement for the MBCA occurred before Cyanacure™ was adopted at Pantex Plant. Based on this information, investigators conducted a second laboratory trial where Ethacure® 300 worked as an alternative to Cyanacure™. The plasticizer BBP did not have synergy with E300 at the previous loading levels used with Cyanacure™ for creating soft polyurethane segments. Reformulation using the new mixer needed to encompass the entire range of hardnesses. Several plasticizers with similar functionality were evaluated to attempt to find L-100 based polymers with the same functionality and physical properties as the current mixes with increased tear. The Manufacturing Division agreed to purchase a dynamic mixer and requested development assistance to identify appropriate formulations, curing parameters, and develop the new colorant system.

The experimental design refined the composition of each formulation to achieve the hardness ranges. The second aspect of the experiment determined the proper curing parameters that result in a cured and post annealed sample where the hardness did not change over time. In some formulations, the change in cure parameter results in variations of the hardness by several points. Identifying formulations that meet each hardness range is accomplished by development of stoichiometric ratios to produce materials within a few points of the targeted hardness. Cure parameters are adjusted and if that does not result in a final hardness that meets the requirements, the mixture ratios are adjusted and then the material reformulated. A study at Pantex Plant in 2007 resulted in four formulations with colors identifying the ranges. This process entailed a hand mixing procedure and while the formulations worked well, the hand mixing process led to problems with batch to batch variations as well as issues with parts shrinking due to high temperature cures which occurs in in most unfilled polyurethanes cured at anything above room temperature. The higher the temperature the more shrinkage occurs (Szycher, 1999), voids form due to the introduction of air into the molds during filling, lengthy fill times are necessary, and locations of vents and injection are based on trial and error.

The experiments conducted during this research project with the new L-100 formulations examined the effects of curing with different ratios E300 and BD, as well as the effects of cure temperature and time on hardness. The use of the plasticizer BBP with Ethacure® 300 was used in formulation for the grey material. The project scope included:
Screening experiments

- Determining best temperature and time for curing in order to stop creep from occurring
- Physical and chemical reactivity testing of the new L-100 formulations with the best results
- Analysis of molds using Moldflow® software.

Methods, Assumptions and Procedures

Current Mixing Process

The Plastics Shop currently uses a blend of Adiprene® L-100 and the curatives Cyanacure and trimethylylpropanol (TMP), with BBP, a phthalate plasticizer, used to adjust hardness as needed. The current process works well if only the formulation contained two constituents. Currently all mixing is done using an antiquated process by hand in paper buckets that is lengthy and takes 2-3 hours to prepare materials and the mold. The first step includes reconstitution of the prepolymer to a pourable liquid. Paper buckets are weighed and the large bucket is marked for an approximate amount to add. Kits with the dyes, extenders, and curing agents are weighed based on the amount of L-100 required. The curing agents are heated in an oven. L-100 is placed in a steam kettle and degassed. L- 100 is removed, reweighed and the curatives are adjusted based on the amount of L-100 lost in transfer. The technician verifies the amounts in use before mixing. After hand mixing the final mixture is degassed again then injected into the mold and multiple injections may be needed depending on the mold size. The mold is then placed into a walk-in oven to cure.

Dynamic Mixer Overview

Dynamic mixing is used for dispensing multi-component formulation directly into molds and commonly referred to as a one shot method. Vacuum for degassing as well as mixing formulation is done by equipment. Mixing in the mix head does not introduce air. Dispensing is very accurate with variability measured in the hundredths of a gram. With the right curatives, extenders, and prepolymers a polyurethane elastomer is produced in a single step and dispensed directly into the mold. While many polyurethanes use a static mixing setup, a dynamic mixer allows for an unlimited pot life. This allows fast curing agents to be explored if desired. These dynamic mixing systems are common to the polyurethane industry but typically are two part mixers. When building a system like this, the formulation is already determined and the process is defined. Based on the chemistry of the components and the final mixture, the system is designed to create a repeatable, controlled and automated dispensing process. The machine design is based on expected stoichiometry in

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the future mixes. In the dynamic mixer introduction of moisture or air is limited to transferring from the five gallon container into the Adiprene® tank. Employing an automatic pump system further minimizes moisture and air contamination. The material is then degassed under vacuum and placed under an inert nitrogen blanket. The material is pushed through the system using cavitation pumps and nitrogen gas for pressure. Design aspects include:

- vacuum degassing
- temperature control
- agitation
- controlled temperature conditions
- adjustable and precise dispensing

Figure 1: Forward View of the Dynamic Mixer

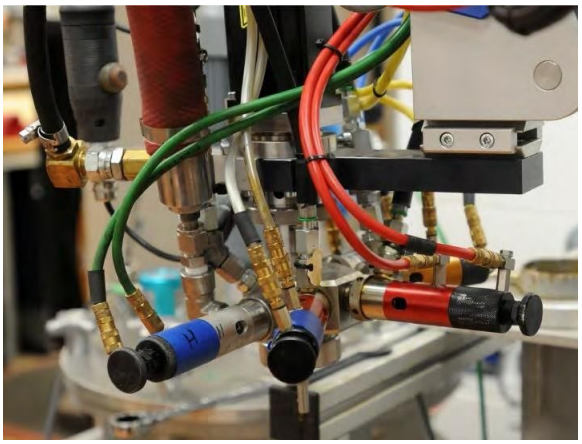

Figure 2: Dynamic mix head with valves

Positive displacement volumetric gear pumps achieve the desired dispensing mix ratios. The pumps and valves are readily changed if a change in formulation is desired. The dynamic mixing occurs at the dispensing head (Figure 2) to homogeneously mix components in the product it dispenses after a preset "wait" time. This results in an unlimited pot life during mixing. With the dispensing rate of 12 grams per second the largest mold at Pantex Plant fills in less than 5 minutes versus the previous 15-20 minutes.

System identification and system performance is based on the following: 3 shifts per day 7.5 hours per shift, 250 days per year. Original custom formulation was based on these starting criteria. Dispensing rate was at 15 grams per second capable of filling the largest mold in 6 minutes (5.44kg). The large Adiprene® tank is double jacketed with two discharge ports. It has an agitator and vacuum system and is heated. The equipment is controlled using a Beckhoff-CX PLU logic controller to regulate dispensing, heating, degassing. The controller contains digital I/Os, USB, Ethernet connection for internet, and flash memory. The software uses programmable logic control with Windows XP embedded security. The dynamic mix head is made of stainless steel which has five exchangeable dispensing valves for the Adiprene®, Ethacure®, plasticizers and cleaning solvent. The mix head is removable for cleaning as well as replacing with other size mixing heads. The dynamic mix head has an adjustable servomotor with the ability to run between 100-5000 rpms. The pumps are DC motor driven and each independently controls the dispensing flow rates for the curing agent and plasticizer. These are volumetric gear pumps. The original design used a progressive cavity metering pump for the Adiprene® L-100 that was changed to a gear pump after several pump failures due to the crimp and the stator covered in FKM. These failures will be discussed later. Six pressure transducers (from 0-40 bar) monitor the working pressure between the dispensing pump and valve. This provides online monitoring of the process and ensures the process is under control. Each of the extender tanks included a full set of tank, hoses, pressure sensor, pump motor and valve. This is an advantage because there is no waste material from changing hoses when a color change or hardness change is made since the components are directly dispensed into the mix head. Temperature regulation for the L-100 includes a fluid cooling unit with water circulation control pump and a distribution manifold to maintain constant temperature (tolerance of ±2 in range of 0 to 30°C) for the hoses and vessel for L-100 as well as the dynamic mix head.

The machine frame is made of tubular aluminum and is on casters and has a self-supported cantilever articulating arm. It is manually operated for free movement in the X, Y, and Z planes. It has a footprint of four foot wide by eight foot long and weighs 2800 pounds. The tubing on the valves and pumps is color coded to match the dispensed formulations to minimize possible mistakes. The large tank contains the Adiprene® the smaller tank to the left is for E300 and the

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four tanks along the back are for the extenders BBP, BD which also contain the colorants.

As part of the project a comprehensive operating aid was created that includes startup, operation, shut down, troubleshooting, cleaning, and preventative maintenance processes to facilitate startup process at the plant. With the new dynamic mixer the PU flowing into the mold (assisted by pressure injection of the polymer) displaces the air inside the mold. Proper air vents placed in proper areas must be part of the mold design or voids will form within the molded part. Using complex geometric shapes with varying wall thickness exacerbates air entrapment. To overcome this obstacle, tall shapes or complex shapes containing thin and thick portions should be filled from the bottom, not from the top to ensure proper filling and air displacement. For these molds a delivery tube system reaching the bottom of the mold should be employed instead of using a small injection port at the top of the mold. As the mold is filled the tube is removed before the PU begins to set. (Clemitson, Castable Polyurethanes, 2008)

Equipment Difficulties

When evaluating equipment in an R & D process, challenges occur. For example, within the first week of operation the main pump delivering Adiprene® to the mixing chamber seized and ceased functioning. The pump was disassembled and failure of a crimp was determined to be the culprit. A new stator with FKM (a fluoroelastomer usually considered chemically inert) was installed. At the beginning of the experiment the manufacturer of L-100 said the typical mixing temperature for L-100 is 165°F. The material was stored at 145°F between mixes. During the next two months of the experiment no issues were experienced. After this time interval, pump failure occurred again with the failure caused by the pump type. Replacement of the pump did not solve the problem. Further consultation with a technical person at Chemtura determined prolonged heating of Adiprene® at the low temperature of 130°F affects the prepolymer causing crosslinking and gel formation that raise the viscosity of the material.

Inconsistencies in Adiprene® flow prompted viscosity testing. Based on the results this issue resulted from two possible scenarios. Either the material reacted with the air used to pressurize the tanks or dimerization occurred. The tank was emptied, cleaned and refilled with fresh material. A nitrogen blanketing system pressurized the tanks. Attempts to dispense the new Adiprene® failed when a clog between the pump and valve occurred. After the hose was cleaned and reassembled, L-100 dispensed with poor consistency resulting in high variations in the test weights. During viscosity tests, the L-100 flow slowed to a few grams per second versus the set point of 11 grams per second. The cause was found to be a clog in the L-100 hose between the storage tank and the pump. While attempting to clear the clog, a leak formed between the Adiprene® hose and the coolant sleeve. Since water acts as a blowing agent in polyurethanes, cured material formed in the hose. To address the ongoing issues, a less precise gear pump was ordered that still gave better precision than hand mixing processes.

Because of the elevated temperature for storage, two hoses clogged resulting in extended downtime waiting on new hoses to arrive. To overcome this setback a local manufacturer of high pressure hoses used the fittings from the clogged hose and fabricated a high pressure hose that worked with the current system. Another stator was ordered with polytetrafluoroethylene (PTFE) and installed, operations proceeded, and then maximum pressure errors occurred during dispensing. Due to schedule conflicts, the material sat in the mixer and aged at higher than expected temperatures. L-100 has active sites that react with other materials or with itself causing the formation of dimers and trimers. In both cases, an increased viscosity (doubled when measured at WTAMU) results. The specification for the high precision stator pump identified in the original design was not for higher viscosity material which caused one failure. The pump was disassembled where it was found that the crimp on the rotor (that had failed during the first week of operations) had failed again. A new rotor was purchased and installed with the pump operating as normal.

While cleaning the dynamic mix head, an attempt to remove the agitator resulted in a sheared shaft. Once the problems were corrected and the machine was operational, small black pieces of the stator sloughed off during dispensing into the molds. This was most likely a reaction between the TDI ends of the prepolymer and the stator. Liquid urethane prepolymers react with themselves through the isocynate and form allophanate branching. This occurs from excessive heat history. Even though the initial contact with Chemtura suggested storing at temperatures at or near 120°F, mixing at 160°F was thought to present any special obstacles; multiple problems with hoses suggested that even at 140°F within 40 days, the allophane reaction occurs. Testing with GPC verified a dimerization reaction occurred and a doubling to tripling of the molecular weight of the prepolymer while resident in the hose. Heat history is one of most common causes of substandard physical properties in polyurethane part production and explains why there was lot to lot variation in the hand mixing. This over heating or reheating results in the TDI levels decreasing, gelled material in the tank and is a cumulative process. Reheating the same tank of material causes irreversible damage. Containers of

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the L-100 should be protected from excessive heat and kept tightly closed under dry nitrogen or dry air. At a temperature of 122°F about 2000 hours produce a loss of 5% NCO content. If raised to 175°F the prepolymer degrades after 82 hours; At 212°F, it fully degrades after 14 hours. Heat history shows itself in the dynamic mixer as increased pressure in the L-100 line and issues with consistent dispensing. The L-100 requires slow heat to get it into liquid form before adding to the dynamic mixer with dispensing at the lowest temperature possible. To dispense the correct amount of material requires the adjustment of pump speeds and the weight of the amount dispensed. To facilitate an easy way to identify correct pump speeds, an Excel pump speed calculation spreadsheet was created.

Dye Experiment

Dyes are added to the polyurethane formulations at Pantex Plant as a visual tool to differentiate between hardness ranges. The machine design includes four tanks dedicated to different plasticizers or an alternate curing agent where each tank uses a specific dye color. The following dye assignments define each hardness range:

80-90 black 65-80 grey 50-65 red 35-50 green

To determine the amount of dye, each were tested in their respective mixes via hand mixes. When evaluating the dyes, the resin was added last in appropriate amounts. To evaluate the effect of curing process on dye and color, two molds are filled with one curing at room temperature and the other at an elevated temperature. Initial tests indicate that the dye mixed much better with the curing agent or plasticizer rather than the prepolymer.

Table 1: Grams of Color in Extender

Color	g	Curative (1000g)
red	118.58	in BD
green	38.61	in BD
black	24.365	in E300
grey	0.327	in BBP

Initial testing indicated when using 2 and 4 parts of colorant, colors were so opaque they were difficult to distinguish between the green, grey, and black. Several other types of powder dyes proved ineffective in improving material results. Further tests conducted on the liquid dyes found that reducing the added amounts by a factor of ten resulted in the sample colors becoming translucent and distinguishable. The new level of colorant is in the range of 0.4 parts for every 100 parts of Adiprene®. The color levels result in a slight change in the shade of the color as parts become thicker or when the cure temperature changes. The red and green pigments used at Pantex are immiscible in the BD and formed micelles. Alternate colorants were found from Polytek. This pigment shows to easily dissolve in the BD and result in translucent polymers as well. Manufacturing personnel liked the produced translucent parts which allows for easy identification of voids.

Testing Procedures

Samples were tested using ASTM D-2240 Standard method of Test for Indentation Hardness of Rubber and Plastics by Means of a Durometer. This method uses a specific indentor forced into the material and is based on the penetration of the indentor under ambient conditions. This is an empirical test and was the screening test for the experiments. An Instron Shore Conveloader Shore A durometer tester was used. All samples were tested at room temperature. The samples were dispensed directly into preheated 6061 aluminum plaque molds with molded part dimensions of 2” x 2” x ¼”. The molds were then cured at various temperatures and times to evaluate the hardness of the test plaques at 1 day, 7 day and 30 days. A Thermal Production Solutions Blue M oven Series DC 146 with a temperature range of 15°C to 350°C and accuracy of ±0.1°C was used to cure the parts.

After meeting the hardness criteria, formulation samples were prepared for tensile, tear C and compression testing. Samples were tested in accordance with ASTM D-624 Standard Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers using the Die C geometry using five un-nicked samples punched from a slab of cured 1/8 inch thick PU and tested using a Model Sintech 10/D from MTS Systems Corporation at a crosshead speed of 20 inches per minute.

Four tensile testing samples were prepared and tested in accordance with ASTM D-412-06 Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension using the dumbbell geometry. Five samples were punched

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from the same slab used for tear testing then loaded into the Sintech machine using a crosshead speed of 20 inches per minute measuring the tensile strength (the maximum tensile stress applied in stretching a specimen to rupture) and peak load.

Compression testing is a historical test for Adiprene® at the Pantex Plant. Compression samples were cured and tested in accordance with ASTM D-575 Standard Test Methods for Rubber Properties in Compression using the 40% deflection test method. Five samples were cut from a ½ inch thick slab and tested in the Sintech machine. While this test method is good for polyurethane foams it is not a valid method when evaluating set occurring in the elastomeric material. The applicable test to use is the compression set. Additionally for the softer PU materials (grey, red, green) the samples should be molded instead of cut, with the softer material and high modulus cutting results in parts that do not meet the criteria set forth in the ASTM method.

Viscosity of a fluid is a measurement of the friction of a fluid when it moves in relation to another layer as measured through the shear stress and rate of shear. Viscosity is molecular weight and time dependent. Many of the formulations were tested for viscosity as a quality control tool and to determine physical values for use in the Moldflow® experiments. Viscosity testing was done on material dispensed from the dynamic mix head using a Brookfield viscometer following ASTM D2196 Standard Test Methods for Rheological Properties of Non- Newtonian Materials by Rotational (Brookfield type) Viscometer. The compounded formulation was dispensed into a 600 mL beaker and placed in the viscometer. The torque percentage is maintained between 10 – 100% until the temperature of the material reaches 40°C. The LV2 spindle was used for testing and the temperature was 120°F.

Results and Discussion

Formulation, Cure, and Hardness Results

Black

A formulation of 10.97 E300 showed the best hardness results for the black formulation with a range from 80-90 Shore A. At room temperature this formulation cures to the mid-range of the black formulation. A temperature of 93°C for two hours sufficiently cures this material without significant creep. All cure temperatures result in a final Shore A hardness of 84. If a harder material is needed, adjusting the amount of Cyanacure added gives a higher stoichiometric cure ratio resulting a Shore A hardness in the range of 88-92. Preparation of this formulation the A & B tanks on the dynamic mixer results in a clear formulation.

Grey

Grey formulations were varied and multiple formulations were identified for room temperature as well as heated cures. Room temperature cures experience creep in all formulations. With the multiple formulations available, if different physical properties are needed for the same hardness range there is flexibility based on end use. Testing of these formulations' physical properties determine if different grey formulations work better for specific applications. Since a BBP based formulation was picked for the heated cure, the most likely formulation for a room temperature cure is 8.9 parts E300 extended with 40 parts of BBP. This will result in a 75 Shore A hardness. Moisture affects room temperature cures, so humidity plays a role in consistency between batches if cured at room temperature. As expected, inconsistency increases with room temperature cures. When curing at 93°C, the two hour and four hour cure had identical results. When comparing all three curing times, the standard deviation is 0.57 with a 95% confidence range of 68 to 71 suggesting that these three cures are indistinguishable.

Red

Red formulations comprised the range from 50 to 65 Shore A and gave the most flexibility in formulation for both room temperature and heated cures. Many of the formulations targeted green but the results placed the formulations in the red range. While attempting to find a room temperature cure for green and red, several formulations worked with low levels of BD and 100% level of E300. Based on these formulations the 3BD provides the best solution for a room temperature cure. However, if better tear resistance is needed, the higher hardness formulations require evaluation.

Red formulations were evaluated at three different temperatures for a heated cure. These included 71, 80, 93 and 120°C. The BD was kept constant and the E300 was dropped to below 95% stoichiometric cure. The best blend in this situation was the 7 pbw E300 cured for six hours. When E300 was increased to 10.97 pbw and blended with 2.7 BD resulting in higher creep. The six hour cure showed the least amount of creep but also resulted in hardness at the high end of the red scale. When three parts of E300 were blended with 3 parts of BD and the temperature increased to 140°C to force the urethane cure, substantial creep of hardness was observed with a final targeted hardness between 60-62 for all cure

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times. When varying the amount of BD used at 80°C, the result shifted the final hardness towards the upper limits of the red range. None of these were considered a target even though several of them are adequate for red at the upper end of the hardness range. When applying various formulations at 120°C, three of the formulations had very consistent start and finish hardness falling in the middle of the red range. Four parts of BD resulted in a higher amount ofcreep.

Green

Green formulations were the most difficult to obtain consistent results. The best formulations for heat cured green were determined by varying the E300 and keeping BD at 4 parts and curing at 140°C with the five hour and seven hour cures giving consistent with minimal creep experienced. Early in experimentation one of the molds evaluated produced an explosives vacuum lifting fixture. This part has the seal leak rate tested in the Plastics Shop so that vacuum decay does not exceed 2 inches of mercury over a minute period. Based on the new formulation with a hardness of 40 Shore A, it was determined the new formulation sealed better than the old formulation. When introducing irregularities into the surface of the test piece the seal held and formed better to the part with no decay for over two minutes. It is possible to get a green formulation but it is at the upper end of the green range (50 Shore A). One hour at 71°C showed a creep stop at 7 days. However the initial hardness started below the current material requirements at 24 hours.

Mechanical and chemical properties

Table 2: Final Formulation Hardness Results

Final Formulations (L-100/E300/Extender)	Color Code	Cure Temp and Time	1 Day Hardness	7 Day Hardness	30 Day Hardness
100/3.5/3 BD	R1	120°C 5H	59	60	60
100/8.88/50 BBP	Grey 1	93°C 4H	70	71	69
100/10.97/0	Black	93°C 4H	83	84	84
100/4/4 BD	Green 2	140°C 7H	40	40	40

Hardness results are shown in Table 2. The tear strength (resistance to tear) in units of pounds per linear inch is calculated from the maximum load divided by the thickness of the specimen (Table 3). Tear results were higher in all of the formulations except grey. Tensile strength is a measurement of the force required to break the specimen as it is pulled apart. It is expressed in pounds per square inch (psi). The tensile testing is summarized in Table 4 for the specimens tested. For many of the red specimens the elongation stretched beyond the maximum vertical travel of the UTM, so the highest value is reported and explains the 95% confidence for the red formulation. All tensile testing results were higher on the new formulations. Tensile testing is not a good measurement for the red formulation due to the high modulus of the material.

Table 3: Tear Results on Final Formulations

Color	Tear(1b/in)	S.D	95% Conf
Black	430	25	50
Grey	248	5	9
Red	122	2	5
Green	52	2	4

Table 4: Tensile Results on Final Formulations

Color	Tensile (psi)	S.D	95% Conf
Black	4388	249	487
Grey	963	67	131
Red	2320	862	1690
Green	211	5	9

Compression at a load deflection of 40% is a measurement of firmness in pounds per square inch giving the spring force of the rubber. It compares to squeezing a piece of rubber between the thumb and forefinger to determine if the rubber works in the application. It provides a better way of determining what elastomer to use in an application instead of a Shore A hardness since Shore A hardness is more of a surface test whereas compression testing is a measurement of the polymers ability to compress and resist compression. This helps identify materials that will be too rigid or may compress too much in a seal application.

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Table 5: Compression Results of Final Formulations

	Compression	S.D.	95% Confidence
Black	2342	157	308
Grey	1084	27	24
Red	901	10	9
Green	275	6.8	6

The viscosity data are presented in Table 6. Viscosity results provided data into the Moldflow CAD analysis.

Table 6: Viscosity Testing of Formulated Compounds

Color	Material/Composition	Fluid Temp. (°C)	Viscosity (cP)	% Torque	RPM
Green	100/4/4BD	55.0	2768	92.3	10
Green	100/4/4BD	53.6	2738	91.3	10
Red	100/3/3BD	54.0	2783	92.8	10
Red	100/3/3BD	53.4	2615	87.2	10
Black	100/10.97/0	54.6	2888	96.3	10
Grey	100/8.88/55BBP	45.7	1141	76.1	20
Grey	100/8.88/55BBP	46.0	1089	72.6	20
Black	100/10.97/0	56.3	2840	94.7	10
Green	100/10/5BD	52.4	3371	89.9	8
Green	100/10/5BD	54.0	3086	82.3	8
Green	100/10/5BD	54.0	2954	78.8	8
Green	100/5/4BD	54.0	2872	76.6	8
Green	100/5/4BD	54.0	2962	79.0	8
Red	100/3.5/3BD	54.0	2932	78.2	8
Red	100/3.5/3BD	54.0	2969	79.2	8
Grey	100/8.88/50BBP	44.0	1386	92.4	20
Grey	100/8.88/50BBP	44.0	1342	89.5	20

Moldflow® Study

Autodesk Simulation Moldflow® is a software suite designed to simulate the plastic injection molding process and provides a quick, simple method to prepare, run and post-process analyze an injection mold. It also has fast, easy- to-use wizards for creating multiple cavities, runner systems and cooling circuits. Included with Autodesk Simulation Moldflow® is an extensive material database. Material creation tools exist to import, change/modify and create materials to be used for any analysis and a report generator to create reports to contain any of the results derived from the analysis. The reports can contain images of the part(s) analyzed, including animations. Moldflow® uses finite element analysis (FEA) and the finite element method (FEM) for understanding plastic injection molding. The computer simulation software predicts how material flows during the injection portion of the molding cycle by analyzing a mesh of the 3D part model. The program simulates flow by calculating the flow front growth from the first node to connecting node, starting at the injection node. The cycle continues until the flow front expands to fill the last node. There are several models used in the software, the following were included in this study, and a select few of these are detailed below:

- Nominal wall thickness
- Draft angle
- Under cut
- Molding window analysis
- Flow resistance
- Gate suitability
- Fill time
- Plastic flow

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Autodesk Simulation Moldflow® requires accurate material-property data in order to generate the best predictions. It contains a materials database holding rheological information required to perform analysis for more than 8000 polymers. A personal database is used to store material-property information custom created by the user. The following is a brief sampling of some of the results obtained from Moldflow and utilized to refine mold designs.

The Design Advisor within Moldflow analysis is the initial experiment which provides feedback on the design of the part including: nominal thickness, draft angle and undercuts. The nominal wall thickness result calculates the nominal wall thickness of the part, and then displays the thicknesses in bands relative to the nominal wall (Figure 3). The wall thickness is expressed as a percentage of the nominal wall (colored legend left in Figure 3) or as values. Ideally the part thickness should be as uniform as possible. Lower variance from the nominal wall thickness reduces filling and packing problems to avoid warping or surface defects such as weld lines or voids. Variations in part thickness may cause flow variation such as race-tracking or hesitation and may also result in excessive part warping.

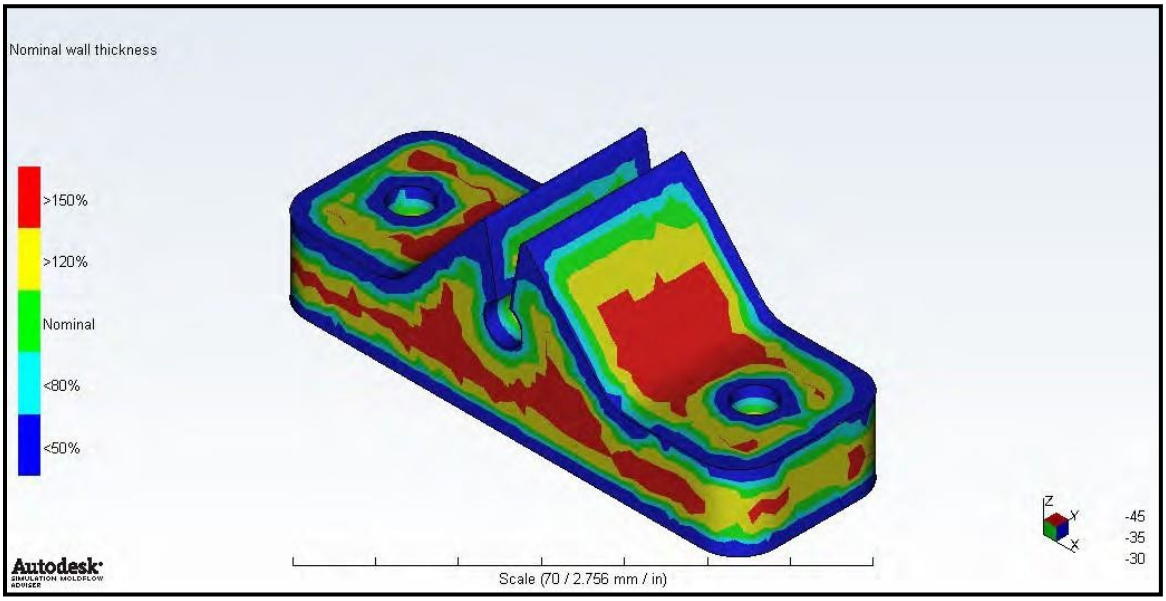

Figure 3: Nominal Wall Thickness

Autodesk Moldflow® Advisor has the capability to determine if a part will fill completely under specific processing conditions. If the plastic does not completely fill the cavity, then the part is short shot. A short shot occurs when the flow of plastic freezes off before all of the flow paths have filled. A part can short shot due to many different or combined factors such as flow restrictions due to long or complex flow paths, low melt and/or mold temperature, slow injection speed, or hesitation in thin sections, or fast curing.

Moldflow® Advisor helps determine what materials work best for the part with regards to mold filling such as pressure, shear stress, or temperature distribution. By using Moldflow® as an early evaluation tool in the design cycle of molds, the finalization of the mold design are accomplished quickly instead of by trial and error. Advisor helps narrow down processing conditions to mold a part. Suitable molding conditions are determined from a Molding Window analysis, and used, perhaps with slight modification, in subsequent filling analyses. In addition to optimizing the molding conditions, a Molding Window analysis is used as a quick initial analysis to compare materials or gate locations. Significant analysis time is saved by determining good processing conditions before running filling analyses.

Advisor has algorithms to determine where the gate (injection location) is located or if multiple gates are required. The Gating Suitability result is produced by the Gate Location analysis when the Advanced Gate Locator algorithm is used. The Advanced Gate Locator algorithm minimizes the flow resistance when determining the best gate position for the first and only injection location. The user can specify prohibited gate regions to block the solver from placing an injection location in the prohibited areas such as critical mating surfaces or surfaces requiring visual aesthetics. The Gate Location analysis produces a Flow resistance indicator plot and a Gating suitability plot. The Flow resistance indicator result (Figure 4) shows the resistance to the flow front from the gate(s). If the flow resistance is not evenly distributed from the injection location(s) to the end of the flow paths, defects or filling problems may arise.

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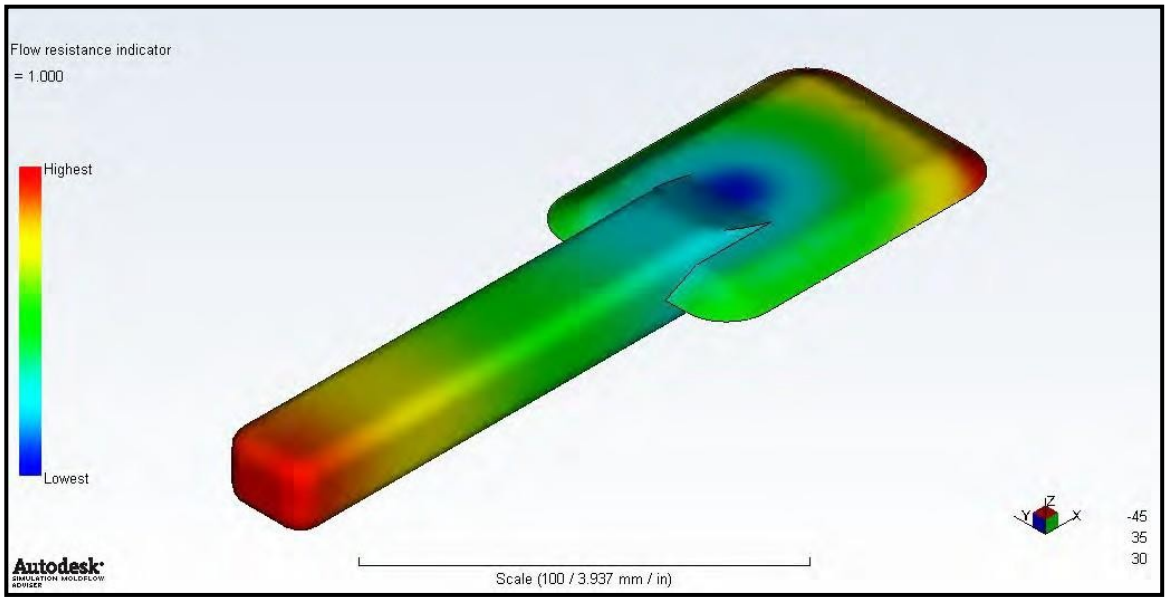

Figure 4: Flow Resistance Indicator

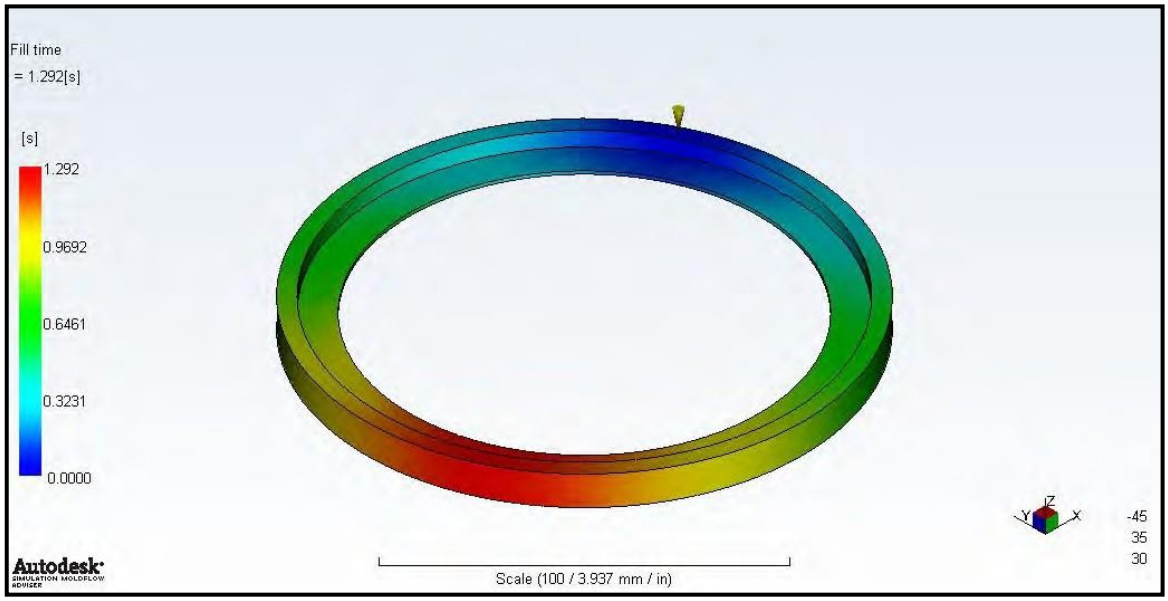

Figure 5: Fill time result.

The Gating Suitability analysis quantifies each place on the model for its suitability for an injection location. The suitable areas shown in this result are worth pursuing as potential injection locations. The best areas shown on the result do not necessarily represent a good solution for a high quality part or high confidence of fill, but rather the best one for the specific case at hand using the selected material.

Some of the most important and most used results are generated from a Fill analysis. The Fill analysis predicts the plastic polymer flow inside the mold in the filling phase. This analysis is often run as the first part of a Fill+Pack analysis sequence. A Fill analysis calculates the flow front growing through the part incrementally from the injection location, and continues until the velocity/pressure switch-over point has been reached. Results generated from a Fill analysis include the Confidence of Fill and Quality Prediction results, as well as Fill Time, Injection Pressure, Pressure Drop and Flow Front Temperature results. The Fill time result (Figure 5) shows the position of the flow front at regular intervals as the cavity fills. It also shows how the material will flow around part features which are the cause of weld lines and possible gas traps. By ensuring all extremities of the mold fill at the same time this minimizes issues with the end product.

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The Fill analysis also generates a Plastic flow result plot. The plastic flow result is a different representation of the fill time result. The fill time and plastic flow results can be animated to visually show how the plastic flows from the injection location to the end of fill. The Confidence of Fill result displays the probability of plastic filling a region within the mold cavity under the conditions set for the analysis. This result derives from the pressure and temperature results. The Confidence of Fill result uses four colors (green, yellow, red and translucent) to indicate whether the part will definitely fill, may/will be difficult to fill or may have quality problems, or will not fill and results in a short shot. If the part is all green, the part is easily filled and part quality should be acceptable. If yellow is displayed, the part may be difficult to mold or quality may not be acceptable. As the percentage of yellow increases, the difficulty in molding the part increases and the part quality decreases. If yellow and red is displayed, the part is extremely difficult to fill or quality is more likely unacceptable. If the part displays any translucent, the part cannot be molded because a short shot will occur. The confidence of fill result is determined by both material melt temperature and injection pressure. A medium quality prediction may be caused by low or high flow front temperatures, cooling times, shear rates, or shear stresses. Autodesk Simulation Moldflow® Advisor contains features to help determine the cause of quality problems as well as suggestions and procedures on how to correct these problems.

The average temperature result (Figure 6) shows the velocity-weighted temperature average through the thickness of the part at the end of fill. Because of the velocity weighting, areas of low temperature have a very low velocity and areas of high temperature have a high velocity. If the average temperature is too low in a thin area, hesitation or a short shot may occur. If there is also a weld line in this area, the weld line will be more visually obvious. If the average temperature is too high, material degradation or surface defects may occur.

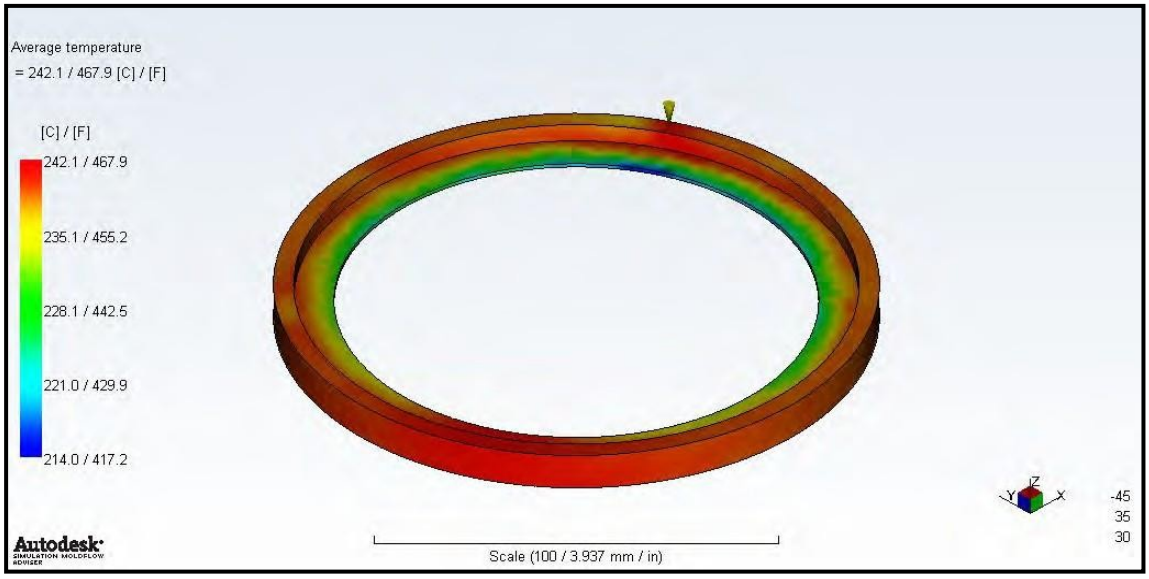

Figure 6: Average Temperature

The Temperature at flow front result shows the temperature of the polymer when the flow front reaches a specified point in the center of the plastic cross-section. The Temperature at flow front result uses a range of colors to indicate the region of lowest temperature (in blue) through to the region of highest temperature (in red). The flow front temperature should not drop more than 2°C to 5°C during the filling phase as a general rule. A large drop in flow front temperature indicates the injection time is too slow, or areas of hesitation exist in the mold design. When the confidence of fill result is poor, the temperature at flow front result determines whether the problems are caused by low melt temperatures.

Similar to the Air trap result, Moldflow® Advisor can predict the formation of weld lines. A weld line (which refers to either a weld or a meld line) is a weakness or visible flaw created when two or more flow paths meet during the filling process. A meld line is typically formed by parallel flows and weld lines are formed by flows meeting at higher angles, often head on. Weld lines can be caused by holes or inserts in the part, multiple injection gates, or variable wall thickness where hesitation or race tracking can occur. The quality of the weld line is dependent on the material type, the type and amount of fillers, and the pressure and temperature at the weld line. Weld lines should be moved to areas

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where strength is of less importance and visual appearance less obvious. The Weld lines result displays the angle of convergence as two flow fronts meet.

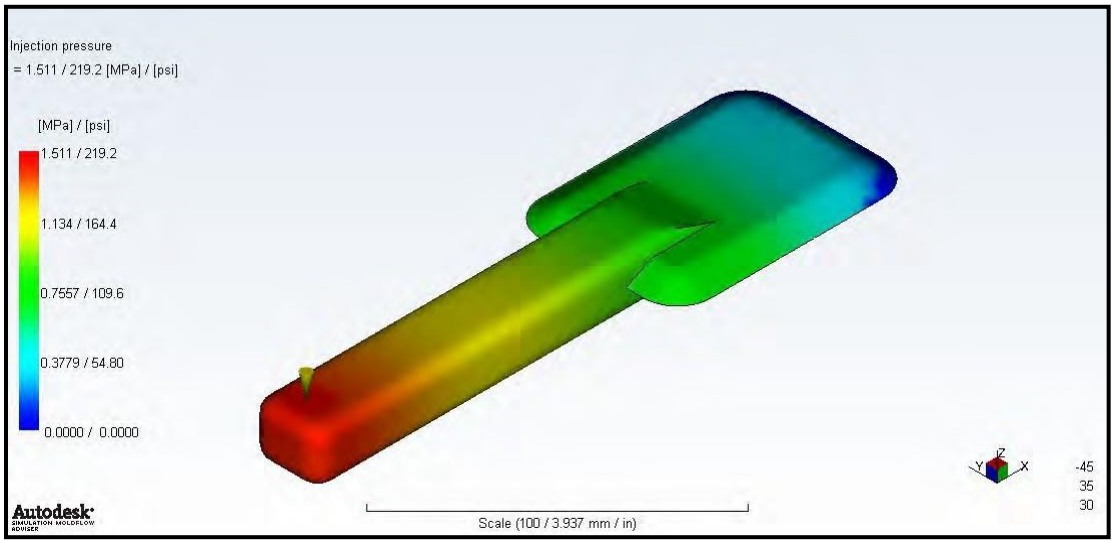

Figure 7: Injection Pressure

The Injection pressure result (Figure 7), is produced by the fill analysis and shows the maximum injection pressure value obtained before the velocity/pressure switch-over occurs during the filling phase. The pressure at a specific location starts to increase after the melt front reaches the location, and continues to increase as the melt front moves past, due to the increasing flow length between this specific location and the melt front. The pressure difference from one location to another is the force pushing the polymer melt to flow during filling. The maximum pressure occurs at the polymer injection locations and the minimum pressure occurs at the melt front during the filling stage. The magnitude of the pressure or pressure gradient depends on the resistance of the polymer in the mold. This is because a polymer with high viscosity requires more pressure to fill the cavity. Restricted areas in the mold, such as thin sections, small runners, and long flow lengths, also require a larger pressure gradient and, therefore, a higher pressure to fill.

The final two analyses from Autodesk Simulation Moldflow® Advisor are "fill+pack" analysis and warp analysis. The “fill+pack” analysis generates the fill analysis results and performs a packing analysis. This analysis is run as the second stage of a “fill+pack” analysis sequence. A pack analysis calculates flow front growing from the filled locations in the model when the velocity/pressure switch-over point was reached. This analysis simulates the stage of the injection molding cycle when pressure is applied to the polymer melt to compress the polymer and to force more material into the mold. This compensates for the shrinkage occurring as the polymer cools from the melt temperature to ambient temperature. A pack analysis generates a volumetric shrinkage at ejection result that shows the volumetric shrinkage for each area expressed as a percent of the original modeled volume. A warp analysis is used to diagnose the cause of warping and recommend a solution, such as gate location changes, design parameter changes, or reduction of wall thickness variations. The Warpage indicator, all effects result highlights those areas of the part where the out- of-plane deflections are approaching or exceeding the specific nominal maximum deflection (NMD) value. This result is based on a “best fit” technique where the original geometry and the deformed geometry are overlaid showing the original size and the warped part.

Health and Safety - Vertecbio™ Citrus 120 as a Replacement for Toluene

The Plastics Shop uses toluene for cleanup after polyurethane mixing. Steam vessels are cleaned with heated toluene and the technicians wear a respirator in order to protect themselves from toluene vapors as well as the isocyanates released from heating. The process takes approximately 240 ml of toluene for cleaning. The new system uses VertecBio™ Citrus 120. It removes the cured and uncured polyurethane faster, will require less solvent, and is derived from renewable resources (100% biodegradable and recyclable through distillation). Its flashpoint is 105°F with a boiling point of 226°F. It does not contain hazardous air pollutants (HAP) and is an Environmental Protection Agency approved SNAP solvent (alternate to aerosol type solvents no ozone depleting constituents). VertecBio™ Citrus 120 is a non-SARA (Superfund Amendment and Reauthorization Act) 313 reportable chemical and is approved for plant

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site use. Toluene is considered a hazardous air pollutant (HAP) and is a SARA 313 chemical. The VertecBio™ Citrus solvent is also less expensive than toluene. The Plastics Shop uses toluene as the rate of 15.8 gallons emissions and 5 gallons of liquid toluene waste per year. None of this is recoverable. The new system uses a 5 second cleanout cycle. The system dispenses solvent at the rate of 25-30 ml/second with an average use of 125-140 ml per cleanout cycle. Table 7 compares the chemical and physical properties of the two solvents. The evaporation rate for the new solvent is substantially lower than toluene and will result in minimum emissions.

Table 7: Comparison of VertecBioTM Citrus 120 and Toluene

	VertecBio™ Citrus 120	Toluene
Flash Point (closed cup)	105°F ASTM D93	39.2°F
Vapor Pressure	4 mmHg@68°F	28.5@68°F
Specific Gravity	0.91 @ 77°F	0.867 @ 68°F
Evaporation Rate (compared to Ether)	0.3	4.5
Vapor Density	3	3.1
Boiling Point	226°F	231°F

Based on current practices and the rate at which parts are fabricated this would decrease air emissions 100% and, if the solvent was recycled, decrease liquid waste stream by five gallons. Even if the solvent is not recycled, it is biodegradable since it is based on ethyl lactate and the only waste associated with the system is the solid polymer caught in the solvent filter. The solvent filtrate system allows the same batch of the VertecBio™ Citrus solvent to be used for upwards of a month before a change in solvent is needed. There have not been any toxicological issues with this product.

According to the technical datasheet, Ethacure® 300 (DMTDA) has undergone toxicological testing. No mutagenic or carcinogenic risks are expected. It was found to be slightly toxic orally to rats (LD50 >2000 mg/kg) and nontoxic dermally to rabbits (LD50> 2000 mg/kg. Eye irritation was experienced in observations with rabbits (Albemare Corporation, 2000).

Efficiencies

The new system is more efficient and results in significant cost savings. Tables 8 through 11 document the expected cost and time benefits associated with switching to the new system. In Table 8 the overall cost is unknown due to the need to base estimates on the number of mixes for each color completed in a year.

Table 8: Colorant Change and Cost ($) per 100 grams dispensed

	Black	Grey	Red	Green
Old cost per mix	0.14	0.09	0.08	0.08
New cost per mix	0.03	0.01	0.05	0.05
Cost savings per 100 g	0.11	0.08	0.03	0.03

Table 9 documents the time and costs to currently hand mix the PU in the Plastics Shop based on the man hours used and a conservative estimate of rejected parts overall in the 30% range (it has been estimated on some parts rejection is as high as 80%). There is a possible cost savings of approximately $130k.

Table 9: Mix time and Costs ($)

	Hours	Cost per Mix (Burdened)	Cost per Mix with 30% rejection rate	Cost per year
Manual	2.5	$208.95	$271.6	$141,250
Dynamic	0.25	$20.90	$20.90	$10,868
Annual cost savings				$130,382

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Current plastics mixing requires packaging as five gallon bulk kits. Approximately 22 bulk kits are prepared annually. Each time a kit is created, the Plastics Shop mixes the appropriate material and sends it for testing. Based on past consumption of kits and the new Adiprene® tank holds approximately the same amount of material in 3 Adiprene® kits testing is expected to decrease by approximately 66%. This would result in a cost savings of approximately $41k annually.

Table 10: Annual Packaging and Testing Costs($) All Colors

	Current Hours	Current Cost per Year	Expected Hours	Expected Cost per year
Packaging 22 five gallon kits	120	$10,029	0	0
Testing kits	528*	$44,130	156	$13,039
Total		$54,159		$13,039
Total Savings per year				$41,120

The final area savings area is from switching to a biodegradable solvent. Toluene is 5-½ times more expensive than the VertecBio™Citrus 120. This will result in approximately a $4k saving per year. However, cost savings from establishing a safer solvent alternative are hard to estimate.

Table 11: Solvent Cost ($) Savings

	VertecBio™ Citrus 120	Toluene
Cost per liter	$8.95	$49.25
Amount Used per year (liters)	55(expected)	$95
Annual Cost	$492.25	$4678.75
Cost Savings per year	$4186.5	

Conclusions

The new dynamic mixer was demonstrated successfully when formulation studies were conducted at West Texas A & M University. The project was successful in meeting the following objectives:

- targeted hardness reached and stable within a 24 hour time frame
- less voids, warping, shrinking and rework
- repeatable and reproducible results between batches
- ability to have Adiprene® formulations cured at room temperature for coating applications
- more flexibility in curing temperatures and times
- better color differentiation between mixes
- more efficient mold designs to minimize warping, void volumes and under filling

When compared to current production lot testing, an increase in physical testing values for all four heat cured formulations occurred except in tear resistance for the grey formulation. The experiment identified room temperature cure formulations that would work within each range as well.

The new dynamic mixer reduces cycle time: a 15 minute cycle versus a 2-3 hour cycle per mix. Cleanup is safer, costs less and no longer requires respirator or exposure to toluene. Total cost savings per year is estimated at approximately $176K annually.

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