Practical Method of Determining Stoichiometry of an MDI-Based Elastomer System

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ABSTRACT

Stoichiometry (NH/OH:NCO) is critical in obtaining the optimum properties of MDI-based elastomers. Stoichiometry of elastomers cured with MBOCA can be easily determined using X-ray fluorescence (XRF); however, no direct analytical method exists for diol-cured elastomers. This paper will show the stoichiometry effect on a wide variety of properties of an MDI-based elastomer system, and then show how to use the elastomer properties that are significantly impacted by stoichiometry to set up a method to determine the stoichiometry.

In the process of quantifying this relationship between stoichiometry and physical properties and examining how these properties change with time, another hypothesis was formed: Would it be possible to also predict and accelerate the time in which a part is fully conditioned and is able to be put into service? This is especially important in dynamic applications such as high load wheels where the typical time before the wheel is put into service is 30 days.

INTRODUCTION

Knowing the stoichiometry of a cast elastomer can have many benefits. From a quality perspective, the accuracy of the parts being made can be determined along with the consistency of the machine or person performing the casting. In the case of using an MM&D machine, the ability to check the stoichiometry would be a great tool for measuring or determining the processing machine variability. In a 1993 technical paper presented to the PMA [1], the author even states that “only frequent calibrations of all equipment can avoid stoichiometric problems. Also, knowing the stoichiometry helps when analyzing failed parts in the field. For example, if it is known that the part failed due to poor tear strength the stoichiometry could be checked to see if it was too low.

In the world of hot-cast, heat-cure polyurethane elastomers, the two primary isocyanates that are used are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Typically, a TDI-based system will be cured with an aromatic diamine. Some of the more common diamine curatives have an element in their chemical structure such as chlorine or sulfur. With these elements present in the final elastomer, the weight percentage of that diamine can be easily determined by way of X-ray fluorescence (XRF), and then the stoichiometry of the part can be calculated, if the %NCO is known. On the contrary, an MDI-based system is almost always cured with a diol or triol. The most common curative is 1,4 butanediol (BDO). Of course, BDO doesn't contain any elements that would be useful for XRF analysis, making it very difficult to determine stoichiometry.

Complicating this issue further is the fact that MDI-based, diol-cured elastomers are usually more sensitive to ratio change in that their optimal properties exist in a small stoichiometric window. Conversely, TDI-based, amine-cured elastomers are very
robust systems with a much wider stoichiometric window to achieve optimum processing and performance.

While no direct analytical method exists to check the stoichiometry of a cured, MDI-based elastomer, a physical test method may be the best option, since most physical properties will vary as stoichiometry varies. The key will be to find a physical property that satisfies most or all the following criteria:

- Large dependence on stoichiometry
- Low cost
- Easy to perform
- Fast results

Analyzing TDI/amine systems by XRF satisfies most of the criteria, with the exception of being a low cost test method. As a result XRF is a convenient means of calculating stoichiometry. An XRF can cost about $30,000, which for a typical processor, might not be a viable option.

To find the most sensitive property to stoichiometry, a thorough stoichiometry versus property relationship was developed using a standard MDI-based polyester prepolymer cured with 1,4-butanediol. Compression set was chosen as the best for determining stoichiometry. This choice was validated by predicting the stoichiometry for multiple blind (“known”) samples. From the literature, Smith [1] states that “compression set may be used…to evaluate stoichiometry”, so there is precedence for this study.

We found that there was a strong effect of conditioning time on the compression set. It takes about 30 days of conditioning time for the compression set to reach a constant value. In phase two of this study, we tried to determine which factors most affect compression set over time. Catalyst type and humidity level were two of these factors. We discovered that exposure to high humidity caused the compression set to achieve a constant value in only one week.

It is known that MDI-based elastomers cured with 1,4-butanediol take about 30 days to achieve optimum dynamic properties, which also happens to coincide with the normal compression set conditioning time. Therefore, in phase three of the study, we correlated compression set to the dynamic performance of a high load wheel and evaluated how humidity level affects the length of time to achieve optimum dynamic properties.

**EXPERIMENTAL**

The focus of the experiments was on one MDI prepolymer, and this was done to simplify things logistically, but also to be very thorough with our evaluation. We chose a polyester prepolymer (Andur M-22) with an approximate %NCO of 6.50 and a hardness of 85 Shore A when cured with BDO. In all cases, Andur M-22 and BDO were cast with the M-22 at 160-190°F and the BDO at ambient temperature. The reactants were mixed in a State Mix Vortex mixer and cast into 212°F molds. Typical demold times were 30-60 minutes depending on the catalysis. The specimens were then postcured overnight for roughly 16 hours. Numerous physical tests were run on the specimens. They are listed in Table 1.

High load wheels (8"x2") were tested via a dynamometer by Caster Concepts. In these tests, the wheel was initially subjected to an 800 pound load run at 6 miles per hour. The load was then increased by 200 pounds after each hour until the wheel failed. Failure occurred by melting of the polyurethane and/or decomposition of the bond interface between the metal hub and polyurethane. During the tests, a laser thermometer measured the temperature of the wheel where the web and the wheel face meet.

**Table 1. Physical Tests Used**

<table>
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<tr>
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<td>Split (Trouser) Tear</td>
<td>D1938</td>
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<td>Hardness</td>
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<td>Compression Set</td>
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RESULTS AND DISCUSSION

Phase 1: Stoichiometry Prediction

COMPREHENSIVE PHYSICAL PROPERTY STUDY

In the first experiment, M-22 was cast at target stoichiometries of 0.90, 0.95, 1.00, and 1.05. The goal was to find a property that was highly affected by stoichiometry that we could develop a mathematical relationship for and use that relationship to determine the stoichiometry in a production setting. The problem we thought we might run into with this goal was what other variables might influence the data besides stoichiometry. We would need to try to keep the influence of these variables down to a minimum to get the greatest consistency and best prediction capabilities. The factors we thought that might have the largest impact on physical properties are listed below (in no particular order):

- Postcure time/temperature
- Catalyst type and concentration
- Mold temperature
- Conditioning time after postcure

In this experiment we held the first three constant, measuring properties at various time intervals to see the effect of conditioning time on each physical property. The postcure time as stated before, was 16 hours. The mold and postcure temperature was 212°F. The catalyst used was stannous octoate. The catalyst concentration was varied to target a gel time of approximately 4-6 minutes. Tensile and tear data was measured at 1, 4, 7, and 14 days. Compression set was measured at 1, 3, 7, 14, and 35 days. The experiment was also repeated to look at reproducibility of the data. Table 2 in the Appendix has the results of the testing.

From the data, it can be seen that as expected, the array of properties tested all change with stoichiometry and conditioning time. It is important to look at the properties early on in the conditioning period since it is desirable to determine the stoichiometry as soon as possible.

Looking at hardness, the magnitude of difference or lack of difference as stoichiometry and time change is not practical for predicting stoichiometry.

In the figures that follow, the solid lines are data from our first experiment and dashed lines are from the repeat of the experiment. Blue, pink, and green lines denote 1 day, 4 days, and 7 days conditioning, respectively.

In the case of ultimate tensile strength, there is a lot of experimental variation as any aberration in the specimen will lower the value. At a 1.05 stoichiometry (samples D1/D2), we see that the tensile strength is very low, but at 0.90-1.00, the change is not significant or consistent through 1, 4, and 7 days (Figure A).

![Figure A. M-22 / 1,4 BDO](image)

The 100% modulus has a less useful relationship with stoichiometry. There is a peak value at 100% of theory, but the inconsistency at 1 day conditioning time from our two repetitions and the flat slope of the curves doesn’t make it a viable candidate for our study (Figure B).

![Figure B. M-22 / 1,4 BDO](image)

Similarly, the ultimate elongation also shows too little change and too much inconsistency at 1, 4, and 7 days (Figure C).
The split tear increases as stoichiometry increases. At a 1.05 stoichiometry, the split tear is much higher than at 1.00, but at the lower stoichiometries the curve is somewhat too flat to be able to come up with a good mathematical model (Figure D). Also, as time progressed, it should be noted that the split tear actually decreased for samples A1/A2 and B1/B2 and that could be attributed to the material cross-linking further from the excess isocyanate in the material continuing to react. Samples C1 and C2 (1.00 stoichiometry) are pretty flat as might be expected since there is no excess isocyanate to react.

All the properties thus far have shown a relationship with stoichiometry where usually there is a maximum or minimum value in the range we cast parts. However, with this type of relationship, it would be impossible to know which side of the maximum or minimum point of the curve you are on without some additional information.

Compression set gives us this information. It is unlike any of the other properties in that the percentage change is much higher over time. Also, the change in compression set versus stoichiometry is different for short conditioning times than long conditioning times. Initially, the compression set curve is sort of V-shaped (Figure E) and we would have the same issue of not knowing which side of the “V” we’re on if not for the other interesting result we observed. When the specimen was removed from the test apparatus, materials that were <1.00 stoichiometry had a dimpled appearance (see picture) whereby the outer portion had recovered better than the inner portion. Our assumption was that the excess isocyanate hadn’t fully reacted and the material on the outside was picking up moisture from the air and reacting with it to eventually form urea bonds, giving the outside region a higher polymer molecular weight. This led to a lower compression set. This phenomenon wasn’t taken into account for the three day measurements in Table 2 (A1 and B1) and consequently, those values aren’t used later in our prediction models.

It is these observations that pushed us into thinking that maybe we could use compression set as the best predictor for stoichiometry. Even with a “V” type of curve, the presence or absence of the dimple effect could tell us if the sample was on the hydroxyl (stoichiometry>1) or isocyanate (stoichiometry<1) side. From a practical point of view, it is also the easiest and lowest cost test of all the tests we did.
We cast another series of samples, now looking just at compression set. We stayed with the same range of stoichiometry, but with smaller increments. Table 3 has the results of the testing. We looked at 1, 3, and 8 days. Again the same general trend occurred where there was a minimum value at a 1.00 stoichiometry of about 40%. On the excess isocyanate side, again the dimpling effect occurred, denoted by an inner and outer value. The change was minimal from 1 to 3 days as confirmed by our initial study and this one. With how much variation we had from these first two studies, we started to doubt whether a reliable predictive model could be produced. The goal was to at least come up with a semi-quantitative model that utilized the dimple effect and the V-shaped curve from the data.

**PREDICTION MODELS**

Caster Concepts cast four blind samples of M-22 for us to analyze for compression set and determine the stoichiometry. They processed the material in the same manner as we did and catalyzed with stannous octoate. The blind samples were labeled A, B, C, and D and had compression set run on them at 3 days and 1 week. We didn’t run 1 day values since in our previous tests there was no difference between 1 and 3 days.

Figures F and G are scatter plots of all the relevant compression set data collected at 3 days and 7-8 days, also using stannous octoate as the catalyst. Initially, we did some “eyeball” predictions for each sample based on the scatter plots, which are listed in Table 4.

Since the data visually looked to have descent correlation, we decided to do some linear regression analysis to get a more solid and mathematically-based model. Two separate linear relationships can be modeled using a stoichiometry of 1.00 as our changing point, or knot. Figures H and I show the same plots as before only now with regression lines. Above a 1.00 stoichiometry of 1.00.
stoichiometry, the R^2 value is very good; both conditioning times are above 90%. Below a 1.00 stoichiometry, however, the relationship isn't as strong, but it is still good with R^2 values of 0.75 and 0.79. There were more outliers in the data below 1.00 stoichiometry, which if removed would significantly improve the fit of the model. We could possibly attribute some of the outliers and worse fit to the dimple effect that was seen in the samples below a 1.00 stoichiometry. This effect made it harder to measure the interior thickness, thereby almost certainly causing more variation, and in turn, lowering the R^2 value.

Table 5 lists a comparison of our "eyeball" predictions, the linear regression model predictions, the actual stoichiometry of each blind sample, the error (based on the regression values), and the SSE (sum of squares for the errors) for 3 days and 7 days. The eyeball guesses and the regression values were almost the same, as one would expect. The regression model did a fairly good job of predicting the stoichiometry of each sample with most of the errors around 0.01, which exceeds the original expectations for just a semi-quantitative model. The 3 day predictions were closer than the 7 day predictions, overall, based on the SSE, however, if you break up the data into the two separate regressions, the 7 day model was closer for the >1.00 stoichiometry sample.

One could go further and develop a relationship between stoichiometry and time (for stoichiometries < 1.00; above 1.00 there is no significant change with time) and combine that with the previous models to lower the error, but that is beyond the scope of this research.

**Phase 2: Elastomer Conditioning Time and the Effect on Compression Set**

**EFFECT OF CATALYST**

The next set of experiments focused on investigating how catalyst type and concentration played a role in the compression set change over time. We chose 3 stoichiometries for this experiment: 0.92, 0.98, 1.02. We chose these to have one set clearly on the isocyanate side, one on the hydroxyl side, and one set close to where most processors typically cast their MDI parts.

Table 6 has the results of using 2 different types of catalyst, stannous octoate, and triethylenediamine (TEDA), a tertiary amine. We also cast some using no catalyst. It is easy to see from the data that there is a difference in using a tin catalyst versus a tertiary amine catalyst. The amine catalyst gives a slightly faster cure, and based on the earlier conjecture of humidity affecting the cure, this makes sense. It’s known that stannous octoate catalyst can lose activity with exposure to water, while the amine catalyst will push the water-isocyanate reaction, thus giving it an advantage. At a 0.90 stoichiometry, the tin catalyzed specimens actually had a lower value after one day, but after more days of exposure to...
the air, the compression set values for the amine catalyzed specimens were lower. Of the 0.98 specimens, only the amine catalyzed specimens had significantly lowered in compression set after one week. The 1.02 specimens matched our data from Table 3 very well in that there was no significant change with time for the compression set when the stoichiometry is greater than one. The uncatalyzed materials show little to no decrease in compression set for the 1 week time period, supporting again our idea of humidity accelerating the cure, since the isocyanate-water reaction is relatively slow when uncatalyzed.

EFFECT OF RELATIVE HUMIDITY

The next phase of experiments looked at the effect of the humidity in the air on compression set. As seen in Tables 3 and 6, there is a difference in compression set when using different catalysts, and that combined with the dimple effect we measured early on, we knew that the moisture in the air must play a significant role in the curing process after an elastomer is taken out of the curing oven.

Table 7 shows the results of our study. We ran the compression sets at 1 week, 2 weeks, and 4 weeks. We cast the samples at three stoichiometries: 0.92, 0.98, and 1.02, and using the same catalyst scheme as in Table 6. We chose a high, low, and ambient relative humidity (RH) for the testing. The low humidity specimens were kept in a dry box purged with nitrogen and argon. The high humidity specimens were kept in an 86°F oven with a water source to supply the moist air. The RH varied from 80-85%. The ambient samples were kept at room temperature (~72°F) and roughly 20-30% RH.

As expected, there was no effect on the samples at a 1.02 stoichiometry. The specimens at 0.98 were very much affected by the RH. The materials in the "wet" atmosphere reached their final value at one week as opposed to the "dry" specimens which still hadn't achieved as low of a value at four weeks. Furthermore, the same trend can be seen with catalyst effect that was seen in Table 6. The uncatalyzed materials dropped in compression set over time in the "dry" atmosphere which means that even though the RH in the dry box was extremely low, it wasn't exactly zero, and some reaction with water was likely taking place. At a 0.92 stoichiometry, the humidity effect is the most pronounced. Figure J is graph of compression set versus time of the 0.92 specimens. The "wet" materials (green

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Table 7. Effect of Relative Humidity - M-22 / BDO

Ambient = 70-75°F/20-30% RH
Dry = 70-75°F/0-13% RH
Wet = 86°F/80-85% RH

Figure J. M-22 Compression Set - 0.92 Stoichiometry
Phase 3: Conditioning time and dynamic performance

EFFECT OF HUMIDITY ON DYNAMIC PROPERTIES

Our final experiment looked at dynamic properties as related to high load caster wheels. The goal was to show excellent dynamics in a very short period of time, mimicking the trends seen with compression set. Six 8”x2” caster wheels were cast at 95% stoichiometry and catalyzed with stannous octoate. Three were put in a wet environment and three in a dry environment. At various times, the wheels were run on a dynamometer. Table 8 summarizes the test conditions and lists the failure loads and modes of failure. The “wet” wheels ran at loads of ~1000 pounds higher than the “dry” wheels with half the conditioning time. Figure K is a graph of the wheels’ temperature during the run versus time (see Table 8 for the wheel ID). It’s clear that the wheels in high humidity performed at a much higher level. They ran for a longer time and stayed at a lower temperature. At one week, the wheel in the humid environment (Wheel #1) performed as good as the control wheel that had conditioned for 1.5 years (Wheel #6). It reached a load of 2250 pounds while the control only withstood 1800 pounds. While the graph shows the wheels failing at approximately the same time, Wheel #1 had not been expected to perform so well and was actually ran longer the next day after the initial test. However, this data wasn’t plotted. After four weeks, the “wet” wheel (Wheel #5) handled a 71% higher load and ran about three times as long as the “dry” wheel (Wheel #4), which hadn’t improved that much two to four weeks. It had reached a load of 1400 pounds, which was still not as good as the control wheel that reached a load of 1800 pounds. The dry wheel at eight weeks hadn’t been testing by the completion of this paper.

The mode of failure also differed for wet and dry exposure. The “wet” wheels failed mostly due to bond failure while the “dry” wheels experienced material failure, showing that they weren’t fully conditioned yet, and this would be a practical reason to monitor the compression set. A processor could use it to tell them when a part can be put into service, no matter what the conditioning environment.
CONCLUSIONS

Phase 1: Stoichiometry Prediction

Predicting the stoichiometry on cast MDI parts using compression set can be an effective tool. The original four criteria for a good test were:

- Large dependence on stoichiometry
- Low cost
- Easy to perform for the caster
- Fast results

These criteria were pretty well satisfied. Based on the linear regression, a good predictive model was calculated. The model wasn’t perfect but many things could be done to improve the model and lower the standard error of the regression. First, an increase in sample size would help. More data points always help lower variation. Second, it would be good to get the data from many different lots as to get a feel for lot to lot variation. Low lot to lot variation would be ideal, but needs to be proven with data. Third, control of outside variables would help improve the model fit. Variables such as mold temperature, catalyst level, postcure time, and postcure temperature will all have a little influence on the change in compression set over time. Another improvement in the regression could be made by studying the relationship of compression set with time (as mentioned previously) and exploiting that relationship to help make better predictions. It would allow the caster to know when the best time to predict the stoichiometry was, or to pick the earliest time that gives the best predictions. Lastly, using phase two of the paper as a guide, humidity is a very important factor. If two parts were made identically (same stoichiometry), but made in different times of the year, the humidity difference could cause the compression set to be different for one or both of the parts, causing the wrong stoichiometry to be predicted. This would be another reason to use as short of a conditioning time as possible. If one day could be used, that would be ideal, since probably no appreciable amount of cure due to moisture in the air would take place that quick. Otherwise, a consistent humidity would need to be used for the standard data and the unknowns.

Of course, running %NCO on the material and frequent calibration of a processing machine would still be the most effective way of preventing any stoichiometric mishaps. They are easier and can’t be replaced. However, running compression set is a good backup and way to confirm that the target stoichiometry was hit.

In the way of future testing, a lot of possibilities exist. We looked at only one product, an MDI polyester. A complete evaluation of other MDI prepolymers including polyesters (of different types), PTMEGs, and PPGs could be done looking at a full range of elastomer hardnesses. Other isocyanate systems could also be explored such as H12MDI, IPDI, TODI, and NDI.

Phase 2: Elastomer Conditioning Time and the Effect on Compression Set

Catalyst type and humidity level play a large role in how fast an elastomer reaches its final properties. Humidity level is the more effective of these two as shown by the data from Table 7. In a wet environment, catalyst type didn’t make as much of a difference, but at low humidity levels, a tertiary amine catalyst was much more effective in speeding up the cure during the conditioning period of the elastomer than a tin catalyst. This again supports the theory that the amine is pushing the isocyanate-water reaction and possibly other reactions, while the tin has been somewhat deactivated.

It was shown that compression set can be reduced to almost its final value after only one week of exposure to high humidity. In a dry environment, it was discovered that a tertiary amine will lower the compression set to its final value in four weeks, whereas the tin catalyst was far from being at its final compression set value. This makes catalyst choice important in dry environments such as Arizona or even Michigan (in the winter).

Phase 3: Conditioning time and dynamic performance

Wheels that are placed in a humid environment develop greater dynamic properties in a shorter period of time than
wheels in a dry environment. That the “wet” wheels failed mostly due to the bond failing as opposed to the material failing demonstrates that the material could carry more load. The results also show that the MDI polyester material does need some exposure to moisture in order to achieve its full properties. We also saw that dynamic materials conditioned in a dry environment are not ready to be put into service after about one month, which is the typical standard conditioning time, but the compression set could be used as a practical method of monitoring when it is ready to be put into service.

Future testing of this effect would be beneficial. It would be interesting to see if other MDI materials, either of differing hardness or backbones, would see similar improvements in dynamic properties. It would also be worthwhile to expose polyurethanes based on other isocyanates to high humidity to see if they experience improvements in dynamic properties as well. For example, systems based on a TDI-MBOCA (urea) hard segment may not benefit, since they typically are not catalyzed and have a different morphology. In any system, the ability and resistance to absorb moisture after being postcured would likely be an important factor.

REFERENCES


BIOGRAPHIES

Anderson Development Company

Robert Czeiszperger

Robert Czeiszperger is currently an R&D chemist in the Polyurethane Elastomers Group at Anderson Development Company. He has Bachelor’s degrees in Chemistry and Mathematics from Siena Heights University and earned a Master’s degree in Polymer and Coatings Technology from Eastern Michigan University in 2003. In 1998 he joined Anderson Development.

Geoff Dennis

Geoff Dennis has been with Anderson Development Company for 26 years. The first 7 years were spent in the Quality Control Group, and the last 19 in Urethane Technical Support. He received a Bachelor of Science degree in Chemistry from Siena Heights University in 1994. His Urethane Technical Support responsibilities center on product / system development, customer support, and prototype production. Since 2000, a concerted effort has been made in off site customer support and processing assistance.

Steve Seneker

Steve Seneker is a Senior Scientist in the Polyurethane Elastomers Group at Anderson Development Company. He received his B.A. Degree in Chemistry from Point Loma Nazarene College. He received his Ph.D. in Chemistry with an emphasis on Polymers and Coatings from North Dakota State University. After graduation in 1986, he joined Miles Inc. (currently Bayer Corporation). In 1993, he joined ARCO Chemical/Lyondell Chemical. He has been working at Anderson Development Company since 2000.

William Bartels

William Bartels is currently a second year sophomore at Kettering University, pursuing a degree in mechanical engineering. He has been an intern at Caster Concepts for a little over a year and has been the primary operator of their dynamometer.

Denise Kenney

Denise Kenney is currently a Polymer Engineer at Reaction Industries, LLC, a subsidiary of Caster Concepts, Inc. She earned her Bachelor’s degree in Materials Science and Engineering from Michigan State University in 2006. Later that year, she joined Reaction Industries, LLC.
Elmer Lee

Elmer Lee is a senior engineer at Caster Concepts. He heads up the special projects engineering group and is also the product manager for CasterShoX, caster concepts new line of shock absorption casters. Dr. Lee has a B.S., M.S. and Ph.D. in engineering from the Massachusetts Institute of Technology with specializations in product development, testing and manufacturing process development. He began working for Caster Concepts in 2003.