Effective Additives for Improving Abrasion Resistance in Polyurethane Elastomers

ROBERT CZEISZPERGER

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

JORDAN DUCKETT

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

ALANA PASTULA

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

TREVOR KALINOWSKI

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

ABSTRACT

ELIZABETH DUCKETT

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

STEVE SENEKER

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

DUSTIN MATTISON

Anderson Development Company 1415 E. Michigan St. Adrian, MI 49221 USA

Polyurethanes have been long known for excellent abrasion resistance, especially when compared with other materials such as rubber, plastic, and metal. However, the abrasion resistance can be further improved by the addition of additives. In this paper, the effect of various additives on the abrasion resistance (ASTM D5963-Rotary Drum Abrasion) of various polyurethane systems will be presented. Multiple isocyanates, polyol backbones, curatives, stoichiometric ratios, and multiple additives will be evaluated in an effort to identify the most effective routes to improving abrasion resistance without compromising the physical/mechanical properties. The methods of incorporating various additives will be discussed as well.

Material

INTRODUCTION

Polyurethane elastomers are used for many reasons. Toughness, high tensile and tear strength, and good dynamic properties are a few of these reasons that separate polyurethanes from rubber, plastics, and metal. One of the primary reasons urethane elastomers excel is their excellent abrasion resistance. They are used in many applications where wear resistance is the key property. Table 1 contains a list of various polymers and the abrasion each resistance of as reported in literature (gatesmectrol.com, 2019). It shows that urethane compares very well with other types of polymers.

thermoplastic urethane	0.4-3.2
ionomer	12
nylon 6/10	16
nylon 11	24
HDPE	29
polytetrafluorethylene	42
nitrile rubber	44
nylon 6,6	58
LDPE	70
rigid PVC	122
natural rubber (tread formulation)	146
SBR (premium tread formulation)	177
SBR (tread formulation)	181
plasticized PVC	187
butyl rubber	205
ABS	275
neoprene (polychloroprene)	280
polystyrene	324
Tables about a 0047 where 1 4000 we wight	5000 L 1

Weight Loss (mg)

Table 1. Abrasion Resistance of Various Polymers

Taber abrasion, CS17 wheel, 1000 gm weight, 5000 revolutions Ref: Handbook of Thermoplastic Elastomers, Litton Educational Publishing, 1979 From a formulation perspective, there are many ways to enhance the abrasion resistance of polyurethane elastomers. The choice of polymer backbone (soft segment), isocyanate type (hard segment), chain extender (hard segment), and stoichiometric ratio of the isocyanate-terminated prepolymer and chain extender can all influence the final properties (hardness, tensile-tear properties, elongation, abrasion resistance, etc.) of the elastomer and each to a different degree. Additives can also play a major role in the improvement of abrasion resistance and numerous are available in the marketplace.

Many studies have been conducted on the abrasion resistance of polymers and specifically polyurethanes. In Russell, data is shown for several types of polyester polyurethane elastomers, known for their toughness, versus many types of rubber compounds (1997). For the urethane compounds, it is shown that higher stoichiometry (OH or NH₂:NCO) improves abrasion resistance as measured by any method. In the same way, properties such a split tear also improve. Another study shows quasi-MDI-based elastomers slightly outperform TDI-based material (Xie, 2009). In yet other studies, additives such as ultra-high molecular weight polyethylene, silicon carbide, organic surfactant, and a siloxane are evaluated for their ability to improve abrasion resistance (Moore, 2008; Staas, 2004). Most of these additives accomplish this by making the surface of the urethane more slippery (i.e. lowering the coefficient of friction) and thus when a material is rubbed across the surface there is less tendency to abrade material away. In U.S. Patent 6,723,771 a siloxane was shown to improve wear performance in specific applications such as wheels, tires, and track pads (2004). These additives also have the effect of lowering physical properties such as tensile strength and rebound, or of modifying hardness (Staas, 2004).

The study presented here attempts to look at the most effective way to improve abrasion properties while also taking into account processing and retention of other physical properties. As for the choice of abrasion test, there is speculation of the effectiveness of abrasion tests to mimic specific applications (including tests such as Taber, DIN, and NBS) due to the lack of comparability between tests, but relative ranking of materials has been proven fairly reliable (Russell, 2). The aforementioned tests use abrasive paper to abrade the test specimens. Other tests such as ASTM D968 use falling media such as quartz sand for an abrasive. ASTM G65 utilizes a complex apparatus of falling sand and a spinning wheel (Pejaković, et al., 2015). These types of tests can also affect the abrasion results in that if loose media is used, the media

can become embedded into the test sample (Pejaković, et al., 2015). This adds weight to the sample creating an artificially low volume loss over time and can create a slipperier surface. Although, if in the application this phenomenon can happen, then the test still serves its purpose in giving an accurate result. In this study, rotary drum abrasion (ASTM 5963) was the method chosen. It is one of the most well-known methods for measuring the abrasion resistance of polyurethanes. See Figure 1 for a picture of the testing instrument used. The method uses a large cylinder (drum) covered



Figure 1. ASTM 5963 Testing Apparatus

with an abrasive paper. As it is rotated, a sample with a specific amount of force on it (10N in this case) is pressed against the drum and moved across the face of it. The specimen can be rotated or stationary during the test. In this case, we chose rotating, which is Method B in ASTM D5963. The mass before and after the test is recorded and the density of the material measured so that a volume loss can be calculated. Volume loss is more relevant than weight loss since

on a cast part, the dimensional change is what is important as the part wears. If only looking at mass loss, a polyester material (density of ~ 1.2 g/cm³) could appear to wear more compared to a polyether (density of ~ 1.05 g/cm³).

Table 2 outlines the scope of this study and the effects to be investigated and measured. In many cases, the trends of the results from specific effects were already known as mentioned previously. For example, it is known that increasing $(NH_2 \text{ or } OH)$:NCO ratio of a material or using a polyester material preferably to a polyether material can increase abrasion resistance. This study's purpose was to quantify those trends for the purpose of decision making on the type of material to use and the use of additives. In some cases, the more abrasion resistant system may not be the best choice as there are other factors that can come into play in the application such as chemical or water exposure, temperature, cost, or dynamic performance to name a few. When these are factored into the situation, the best system for the application can then be selected.

The additives were selected based on what was found in literature to perform well. A range of addition levels for each additive was studied to find the optimal level. Also, the ease of addition, efficiency and success of incorporation, and effect on elastomer properties and appearance was measured. These variables are important to the processor. In general it is easier to incorporate a liquid additive for a polyurethane processor than a solid. It is for this reason that Additive C (powder) was dispersed in a commonly used plasticizer for urethane materials resulting in Additive B (paste dispersion). The active ingredient levels of Additive B match the levels of Additive C. This was studied, to test the theory if better dispersion into the substrate gives more effective abrasion resistance.

Effect of:	Candidates Studied		
Hardness	85A, 95A, 60D, 80D (LFTDI-PTMEG-MBOCA system)		
Soft segment	PTMEG, PPG, Polyester (adipate-based), Polycaprolactone (LFTDI/MBOCA system)		
Chain extender	MBOCA, MCDEA, DMTDA*, TMGDAB** (Convention TDI and LFTDI systems)		
Hard segment	LFTDI/MBOCA, MDI/1,4 BDO, TODI/1,4 BDO, trans 1,4-H ₆ XDI/1,4 BDO		
Stoichiometry	0.95, 0.98, 1.02, 1.05		
Additives	Additive ID: Name (% added)	Physical Form	
	A: PTFE/PE dispersed in mineral spirits, 32% solids (2%, 4%)	Liquid dispersion	
	B: PTFE/PE/Ceramic in plasticizer, 40% solids (1.25%, 2.5%, 5%)	Paste dispersion	
	C: PTFE/PE/Ceramic (0.5%, 1%, 2%)	Solid Powder	
	D: PDMS silicone fluid-100cSt (1%, 2%, 5%),	Liquid	
	E: Corn oil (1%, 2%, 5%)	Liquid	

Table 2. Objectives of the Study

* Dimethyl thio-toluene diamine

**Trimethyleneglycol di (p-aminobenzoate)

EXPERIMENTAL

The casting methods used for this study were typical casting conditions for each of the materials used. The temperatures of the prepolymers, curatives, and molds were in the range of the manufacturer's recommendations. In general, prepolymers were in the temperature range of 160°-200°F (70°-93°C). Mold temperature was 212°-240°F (100°-115°C). The curative temperature varied based on the curative (MBOCA and MCDEA were ~240°F (115°C); DMTDA and 1,4 BDO were ambient; TMGDAB was ~300°F (150°C)). The abrasion samples and plaque samples used for tensile/tear testing were cast by compression molding. Unless noted otherwise, all materials were cast at 95% stoichiometry. Materials were mixed in a centrifugal mixer (State-Mix Vortex VM-200) to ensure a uniform mix. Post cure was overnight at 212°F (100°C) for typically 15-20 hours. The samples were conditioned for a minimum of 30 days at 73°F (23°C) and 50% relative humidity. Before abrasion testing, the samples were gently cleaned with acetone on the surface to remove any surface debris or mold release. Also, per ASTM D5963, a rubber standard sample was ran multiple times during testing to insure consistency of the test and whether the abrasive paper was still performing as it should. Samples were tested in groups to maximize side-by-side ranking and to study the effects laid out in Table 3, thus avoiding day to day variance. There were also measures taken to make sure there was no influence from the previous sample. It was observed that some of the additives could give false low values on subsequent samples even if the abrader was cleaned thoroughly. Repetitive testing confirmed what the true test result was supposed to be. Typically, a sample was run twice unless the first value was significantly different, and in that case a third sample was run. Besides abrasion resistance testing, tensile properties (ASTM D412), tear properties (ASTM D1938), and dynamic coefficient of friction (COF) (ASTM D1894) were also measured on some of the materials.

RESULTS and DISCUSSION

REPEATABILITY of ASTM D5963

Before discussing the results is it good to look at what type of Table 3. Repeatability Study of Abrasion repeatability and reproducibility the abrasion test has. An 85A TDI/PTMEG/MBOCA system was chosen for this. Specimens were cast from one batch of prepolymer at two different times and 4 specimens from each were tested, running each specimen twice. Table 3 has the results of this study. The standard deviation of batch A was close to 3 mm³. Assuming a statistically normal sample, the range of most of the data would be about +/- 6mm³, or about 5%, which if fairly good, but only takes into account one batch of material. Past experience shows that some variability can also exist between batches of the same material, so care should be taken when interpreting differences in samples.

Testing – ASTM D5963

	Batch A	
	Specimen 1	Specimen 2
Run 1 Avg.	140	135
Run 2 Avg.	144	136
Run 3 Avg.	145	141
Run 4 Avg.	146	140
Mean	143.8	138.0
Std. Dev.	2.6	2.9
	Overall Average = 140.9	

The hardness of a material is not a variable that can usually be changed in an application due to load constraints,

functionality of the part, etc. but it is studied here to demonstrate that although harder materials have higher split tear strength, the optimal abrasion resistance of a urethane family is at a lower hardness than the material with the highest split tear strength. For the LFTDI/PTMEG/MBOCA systems shown here (Figure 2), the best abrasion resistance is the 95A material. This could be due to the fact that in that range, the material is tough, but also more resilient and can elongate and flex to avoid abrasion. The 81D material exhibited poor abrasion resistance, whereas the 85A material was better than the 81D even though the split tear was much lower.



EFFECT of SOFT SEGMENT

The effect of soft segment changes can be seen in Figure 3. As expected, the polyester material is more resistant than all other candidates, followed by the polycaprolactone, another type of polyester. The PTMEG is next and then, by far the least resistant, is the PPG. As mentioned above, the split tear strength of the material is somewhat correlated with the abrasion resistance, especially when comparing materials of the same hardness. This makes sense since abrasion can be viewed as the tearing off of very small particles of the material's surface. As



seen here, the soft segment is very influential with abrasion resistance. The reason for this could be that the soft segment is the continuous phase of the elastomer and it makes up the bulk of the volume, so although there is a slight correlation with split tear, it is only a relative indicator and the soft segment type is more important.

EFFECT OF CHAIN EXTENDER

For TDI-based systems, many common amine curatives exist. The four chosen in this study were for specific reasons. MBOCA is a workhorse in the cast urethane industry. MCDEA is viewed as a high-performance curative. TMGDBA can be used for compliance to 21CFR177.1680 dry food applications. DMTDA is an easy to use liquid alternative to MBOCA. These four aromatic diamines were cast with PPG, PTMEG, polycaprolactone and polyester prepolymers.



Typically, casting with MCDEA results in a higher hardness material, so slightly lower %NCO prepolymers were used with MCDEA to better match hardness. See Figures 4-7 for the results of these comparisons.

With the PPG (Figure 4), as was seen in Figure 3, the abrasion resistance was very poor. In fact, with the sample cured with TMGDAB, the sample was worn down so much, the test had to be stopped before it had

fully completed. This is shown in Figure 4 by a shaded bar. The resistance of the MCDEA-cured material was slightly better, but still not good. In Figure 5, the PTMEG results show that the resistance of the DMTDA was somewhat better than the other curatives, although, in this case there was no specimen cast with MCDEA to compare to. The polycaprolactone (Figure 6) samples with the four diamines did not show any large difference in abrasion resistance between the curatives. The polyester (Figure 7) specimens also had no significant variation, even though there were moderate differences in the split tear of the samples as shown in the graph. Overall, there is no real indication in these examples to say that one of these diamines has superior abrasion resistance over another. The lack of chain extender effect for the polycaprolactone and polyester-based elastomers could be due to the fact that both of these backbones promote excellent tensile and tear strength.



EFFECT of HARD-SEGMENT COMPOSITION

The effect of hard-segment composition displayed dramatic improvements in abrasion resistance (Figure 8), although changing the overall system is sometimes a constraint for the processor. The hard-segment compositions chosen were from a wide range, trying to capture standard materials and ultra-high performance materials. The soft segment for each material was either polyester or polycaprolactone which are close in



128

MBOCA

118

TMGDAB

119

MCDEA

performance and the hardness was in the 93A range, a typical hardness for high performance materials. TDI/MBOCA and MDI/1,4 BDO are standard materials and they are compared with TODI/1,4 BDO and trans 1,4-H₆XDI/1,4 BDO. These two-hard segment compositions are regarded as ultra-high performance and tough materials used in very

aggressive applications. Split tear strength was also tested on these looking for a correlation with the volume loss. In Figure 8, it can be seen that the ultra-high performance isocyanates (trans 1,4-H₆XDI and TODI) resulted in much higher tear strength elastomers with better abrasion resistance than the standard materials.

Another comparison that can be made is between the TDI/MBOCA and MDI/1,4 BDO hard segments. Figure 9 illustrates this with the same two ~93A elastomers and another two ~84A elastomers. They were all based on polyester soft segments. It can be concluded based on this data that an MDI/1,4 BDO system results in a measureable



improvement in abrasion resistance. This could be because of the morphology difference of the hard segments between TDI and MDI systems. Perhaps larger hard segment domains or having all urethane linkages with less hydrogen bonding results in a slipperier surface, which was studied by looking at dynamic COF. However, the results were inconclusive. Another variable besides split tear that may be a contributing factor is the modulus. The 100% modulus values of both



TDI materials were higher than the corresponding MDI systems, as can be seen in Figure 9. A stiffer material could lead to lower abrasion resistance by not allowing as much deformation when initially stressed.

EFFECT of STOICHIOMETRY

Stoichiometry (NH₂ or OH:NCO) has already been shown to affect abrasion resistance (Russell, 1997). Figure 10 is a comparison of PTMEG-based and polyester-based elastomers, both TDI and MDI, and how changing the stoichiometry affects them differently. The relative change in abrasion loss from 0.95 stoichiometry is plotted. It can be observed that PTMEG-based materials can benefit much more from an increase in stoichiometry. In both the LFTDI-PTMEG and MDI-PTMEG, the abrasion volume loss is approximately 20% better (lower) when the stoichiometry is increased from 0.95 to 1.02. With the polyester systems, this same trend does not occur. This could be because polyester materials already have excellent abrasion resistance and that minor changes in stoichiometry don't override that. In the case of the MDI-polyester, the volume loss is fairly flat from 0.95 to 0.98 and then greatly increases to double its initial value as the stoichiometry is increased to 1.05. The TDI-polyester has only slight improvement from 0.95 to 1.02 and then starts to increase in volume loss at 1.05. Based on the data, targeting a stoichiometry of 1.00 to 1.05 would be optimal for a PTMEG, but for a polyester, 0.95 to 1.00 would be ideal.

Of course, changing stoichiometry can bring other issues, such as increased compression set, decreased rebound, and inferior hysteresis properties. In the case of the MDI-polyester, compression set was ran on the four samples in Figure 10 and the results were 21%, 31%, 49%, and 51%, from low to high stoichiometry. Hence, a significant change in the polymer morphology occurs by increasing the stoichiometry higher than 1.00 and both compression set and abrasion resistance are negatively affected. This supports the general understanding that MDI/1,4 BDO systems have a narrower stoichiometric processing window than TDI/amine-cured systems.

EFFECT of ADDITIVES

The goal of additives in a material is to enhance a particular property without sacrificing any of the other attributes of the material. The goal of the selected additives from Table 2 is to find addition levels of each material that maximizes abrasion improvement while minimizing the effects on physical properties. To that end, the tensile strength and split tear was measured on each material to quantify physical property changes and some coefficient of friction testing was performed. Also, the ability of the additive to mix into the elastomer was observed. In some cases, the solid additive had small clumps of material in the cured casting, which of course could greatly affect the tensile strength. In general, tensile strength can be affected very easily by any type of aberration in the specimen; consequently, results must be evaluated carefully for true differences due to the higher variability of tensile strength measurements. Of course, other effects could be problematic for some cast parts, such as adhesion to metal. If a material has a slipperier surface it is probable that adhesion to metal could be affected, but that is beyond the scope of this study. Also, in many applications requiring good abrasion resistance, such as wheels and rollers, grip can be very important.

Figures 11-13 display the effects of the additives on abrasion and tensile/tear properties on three systems: an 85A LFTDI-PTMEG cured with MBOCA, an 85A LFTDI-Polyester cured with MBOCA, and an 83A MDI-Polyester cured with 1,4 BDO. Figure 11 is the LFTDI-PTMEG, with split tear and abrasion volume loss displayed in orange and blue bars, respectively, and tensile strength plotted in green. The tensile strength of the control was 5000 psi and the split tear was 40 pli. In most cases, the tensile strength with additives was 50-60% lower than the control value, except for Additive A, which had tensile values in the range of the control. Overall the split tear was not affected quite as much. Most values were around 30pli, representing a decrease of 25%; though Additive C was 36 pli (10% decrease) for all 3 levels. The specimens with Additive A had tear values of 46 pli and 60 pli with 2% and 4% addition, respectively, indicating that the tear strength actually improved. As far as abrasion resistance, all the additives had a positive effect except the corn oil (E). During testing, the first volume loss was very low, but upon subsequent testing on the same specimen, the value kept rising until it was close to the control value. Evidently, the PTMEG and the corn oil are not



compatible, leading to the corn oil migrating to the surface, which leads to better abrasion resistance only at the surface of the material. Additive D, the silicone fluid, appears to be the most effective abrasion additive as at only 1% the

volume loss is 37 mm³; however, at higher addition levels there was no improvement. At the 2.5% and 5% addition levels of Additive B, the abrasion loss was also the same as Additive D. Interestingly, at the same active ingredient level, Additive C was slightly higher at values 43mm³ and 40mm³, compared to 36mm³ and 37mm³ of Additive B. This is not a large difference, but does give rise to the possibility that by pre-mixing the solid additive in a plasticizer there is better dispersion of the powder into the polyurethane matrix. Additive A at 4% loading was similar to Additive C, which makes sense since the % solids at 4% is about 1% active ingredient and they are similar types of materials.

Figure 12 is a similar graph, but the material is a LFTDI-Polyester. In this case, the tensile values of all materials with additives are in the 5500-7000psi range with a control value of 7800psi, representing an average drop of only 20%, which was much better than the PTMEG. Neglecting Additive A, the split tear values were all in the range of about 115pli, a 43% loss of tear. Additive A exhibited an average of only 17% loss in split tear. The abrasion loss of all



samples dropped to about one-third of the original value. The silicone fluid was the most effective additive at the lowest level just as in Figure 11, although really only by 2-3 mm³. The biggest surprise was the corn oil, which had a much improved compatibility with the polyester, since it had very good abrasion resistance not only at the surface, but throughout the entire specimen. However, the split tear had the largest drop of all samples. Overall, these results are consistent with polyesters having better abrasion resistance then PTMEG.

The MDI-polyester cured with 1,4 BDO is displayed in Figure 13 with the effects of the additives. The control had a tensile strength of 6700 psi, a tear strength of 220 pli, and an abrasion volume loss of 70 mm³. The tensile strengths of almost all the specimens were in the range of the control, with the exception of one sample, which was the sample with 4% of Additive A. For the split tear, all samples other than Additive A exhibited an average loss of 24% from the control. Unexpectedly, the tear strength with 2% and 4% of Additive A greatly increased the tear from 200 pli to 308



pli and 343 pli, respectively. With the two LFTDI systems, a similar trend was observed in that the tear strength had the best retention with Additive A, but in this case, the test results seem to be much above what might have been expected. For the abrasion resistance, since the material was an MDI-Polyester, the volume loss values were really low for the control as expected. Again, 1% silicone fluid (D) had superior abrasion resistance with the lowest addition level of the additives, though Additives B and C were close or equal to the silicone fluid (D). Additive E was fairly effective, but again not as much as Additives A, B, C, and D. This is the point where the price of the additives and physical property retention would need to be considered to select the best additive.

Table 4 is a summary of the dynamic COF results ran on the two polyester-based systems above with Additives A and B. From the results it can be seen that the additives definitely lower the dynamic COF; however, there is no consistent pattern. The MDI-Polyester had much lower COF with Additive B, while the TDI-Polyester exhibited lower COF with Additive A. COF testing depends a lot on the surface of the material being tested and can have a lot of variability. More data would need to be collected before any trends can be verified.

Additive	85A TDI/Polyester/ MBOCA	85A MDI/Polyester/1,4 BDO
None	0.87	0.79
Α	0.42	0.66
В	0.49	0.27

Table 4. Dynamic COF - Polyurethane on Steel

COMBINED EFFECTS OF ADDITIVES AND STOICHIOMETRY

Additionally, after initially testing was completed, another study looking at the combined effects of stoichiometry and the addition of some of the additives was completed. The results are below in Table 5. The 85A LFTDI-PTMEG-MBOCA system was tested with Additives A, B, and D since there was the most room for improvement in abrasion and as previously shown, stoichiometry affects PTMEG-based materials much more than polyester-based materials. The data for the combined effects showed mixed results from increasing the stoichiometry and using additives. With Additives A and B, there was no benefit to increasing the stoichiometry, as the abrasion resistance was essentially unchanged. With Additive D, there was decrease in volume loss resulting a 30% improvement in abrasion resistance. More testing would need to be completed to understand if these trends hold for other urethane systems, as well as whether the additives used behave in the same manner. With an increase in stoichiometry, the amount of free MBOCA would be higher and perhaps that factors into the interaction with the silicone and/or the PTFE/PE polymers.

Stoichiometry	Additive	Volume Loss (mm ³)
0.95	4% Additive A	40
1.05	4% Additive A	43
0.95	2.5% Additive B	33
1.05	2.5% Additive B	35
0.95	2% Additive D	33
1.05	2% Additive D	23

Table 5. Combined Effect of Stoichiometry and Additives onAbrasion Resistance of an 85A TDI/PTMEG/MBOCA System

ADDITIVE PROCESSING and ELASTOMER APPEARANCE

The ability to incorporate an additive easily and completely is important to the cast urethane processor. Additives A, D, and E were all liquid materials and were easily added to the prepolymer just before mixing in the curative. Also, liquids are easier to incorporate into a meter, mix, and dispense (MM&D) machine operation. One drawback of Additive A is that it is a dispersion that separates slowly over time and becomes two phases. Also, mineral spirits has a distinct odor which might be an issue for the processor or end user. Regarding mixing, Additive A also needs to be mixed and redispersed just before use. Additive B was a very soft paste that incorporated into the mix without any clumping. The paste was syringable, but not pourable, so it would not be viable for an MM&D machine. Additive C was a powder that mixed into the prepolymer fairly well, but in some cases there was some very small clumps in the elastomer. Powders such as this are best mixed in with a centrifugal mixer. Based on the abrasion resistance data, Additive B (paste) was slightly more effective than Additive C (powder), lending to the theory that better dispersion of the same additive can improve the performance of that additive. The percent active ingredient of Additive B was 40% as stated earlier. After the initial testing from Figures 11-13 was completed, a 20% solution was prepared and it resulted in a low viscosity liquid that did not separate over time. Figure 14 displays a test of whether better dispersion of the additive yields better abrasion resistance. All three systems tested above were used. The results were consistent between all materials. As stated above, the 40% dispersion had slightly better abrasion resistance, but the 20% solution, which was liquid,

exhibited similar results to the powder. This could be due to the slight increase in plasticizer from 1.5% to 4.0% by weight in the system which would negatively impact physicalmechanical properties by a slight amount. A nonseparating liquid would be a nice advantage over Additive A (liquid dispersion), and since it is in a universal urethane plasticizer, it has excellent compatibility in both polyester PTMEG-based and cast polyurethanes.



In terms of elastomer appearance, Additive D, the silicone fluid, gave both the polyesters and the PTMEG an opaque white appearance, which could change the color of a cast part. Additives A, B, and C gave the elastomers a translucent appearance, which didn't affect the LFTDI-polyester or the MDI-polyester since they were translucent and opaque, respectively, to start. The LFTDI-PTMEG was clear without additives, and only with Additive E, the corn oil, did it stay clear. Additives A, B, and C made it translucent and Additive D turned it opaque as stated above.

CONCLUSION

From the data collected in this research, several conclusions can be drawn. First, the soft segment has a large effect on abrasion resistance. In fact, polyesters and polycaprolactones are superior to PTMEG by 20-40% and to PPG by a factor of 3 when comparing like materials. When comparing common aromatic diamines for curing TDI materials, no large difference was observed. Again, since the soft segment is the continuous phase and the bulk of the volume of the material (especially at an 85A), it has the most influence. By changing the stoichiometry of various materials, it was seen that MDI-polyesters and TDI-polyesters cannot be improved much by increasing the stoichiometry from 0.95 to 1.02. Regarding the effect of hard segment composition, an MDI-based elastomer is more abrasion resistant than a TDI-based elastomer, on the order of 10-30%, depending on the hardness of the material. Due to their higher toughness and extremely high split tear, ultra-high performance diisocyanates cured with 1,4 BDO such as trans 1,4-H₆XDI and TODI, result in more abrasion resistant materials than standard materials such as TDI/MBOCA and MDI/1,4 BDO. These differences in abrasion for the hard-segment composition are likely due to a combination of polymer morphology, tear strength, and modulus.

Lastly, it was shown that additives are the most effective method of improving abrasion resistance. With additives, a PTMEG-based material can have much better abrasion resistance than a polyester-based material without additives and almost as good as a polyester with additives. Combining the effect with a higher stoichiometry also proved to be helpful, but only when using Additive D. These improvements in abrasion would be useful in high wear applications involving water or moisture, or areas where microbial resistance is required, where a polyester-based material could not be used. However, coefficient of friction, adhesion to metal, and grip should be a consideration before using an additive with any system. A PDMS silicone fluid (Additive D) resulted in the best abrasion resistance with the lowest addition level, although appearance was altered the most. The PTFE/PE blend in mineral spirits (Additive A) provided the best retention of physical properties while still resulting in excellent abrasion resistance and is a low viscosity liquid. However, it was a liquid dispersion that separated slowly over time. The PTFE/PE/Ceramic blend in plasticizer (Additive B) had similar abrasion resistance to the silicone, and could be added without turning the elastomer opaque. Additive E, corn oil, is obviously an environmentally friendly solution, although it was only effective in polyester-based materials. Additives A, D, and E are also advantageous since they are liquids and could be used easily in an MM&D machine. If considering all factors, Additive A has a nice balance of physical property retention, great abrasion resistance, and relative ease of addition.

In any application where a cast polyurethane is used, many factors must be weighed to determine the best material. Abrasion resistance is one of those factors that needs to be considered. Other factors could include tensile and tear strength, resilience, compression set, and chemical resistance. The more factors that are considered, the higher the probability of selecting the best material for the application.

REFERENCES

Gates Mectrol. Polymer Abrasion Resistance Table. http://www.gatesmectrol.com/mectrol/brochure.cfm?brochure=5195&location_id=5325 (accessed 3/30/19).

Russell, D., Wible, J. Abrasion Testing of Polyurethane Elastomers. *Polyurethane Manufacturer's Association Conference* 1997.

Xie, R., Tabiner, K., Moss, B., Davies, A. A Performance Comparison of MDI Quasi Systems and TDI Full Prepolymers. *Polyurethane Manufacturer's Association Conference* 2009.

Moore, D. UHMW-PE Micropowder Additives for Cast Polyurethane. *Polyurethane Manufacturer's Association Conference* 2008.

Staas, J. Improving Abrasion Resistance. Polyurethane Manufacturer's Association Conference 2014.

Palinkas, R., Peter, T. US Patent 6,723,771, April 20, 2004

V. Pejakovic et al.: Abrasion Resistance of Selected Commercially Available Polymer Materials. *Finnish Journal of Tribology* **2015** Vol 33, 21-27.

BIOGRAPHIES



Robert Czeiszperger

Robert Czeiszperger is currently a Senior Principal Chemist in the Polyurethane Elastomers R&D 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. He has been working at Anderson Development Company in an R&D role since 1998 developing a variety of polyurethane products and giving technical support, and he has presented several technical papers to PMA, CPI, and CUMA on a wide variety of topics.



Elizabeth Duckett

Elizabeth is a R&D Chemist in the Polyurethane Elastomers Group at Anderson Development Company. She began working at Anderson Development Company as an intern in January 2015. Liz received her B.S. Degree in Biochemistry from Adrian College in the spring of 2015. She accepted a full time position shortly after her graduation.



Jordan Duckett

Jordan Duckett is currently a Urethane Technical Support Chemist in the Polyurethane Elastomers Group at Anderson Development Company. He has a Bachelor's degree in Chemistry from Siena Heights University. He has been working at Anderson Development Company since 2007. He began as an intern while attending Siena Heights University. Upon his graduation, he worked as a Quality Control Technician. In 2011, he accepted his current position as a Urethane Technical Support Chemist in the Polyurethane Elastomers Group at Anderson Development Company.



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 University. 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 Mobay Corporation (currently Covestro). In 1993, he joined ARCO Chemical/Lyondell Chemical. He has been working at Anderson Development Company since 2000.

Alana Pastula

Alana Pastula is currently an intern in the Polyurethane Elastomers R&D Group at Anderson Development Company. She will be graduating with a Bachelor's degree in Biology and Environmental Science from Adrian College in May of 2020. She currently is a member of Beta Beta Biological Honors Society and the Golden Gavel Chapter of Mortar Board. She has also presented research within Biology and Systematics at Adrian College's Ribbon of Excellence Conference in 2018 and 2019.



Dustin Mattison

Dustin Mattison is currently an intern in the Polyurethane Elastomers R&D Group at Anderson Development Company. He has recently graduated in 2019 with his B.S. in Chemistry from Western Michigan University. Dustin has previous experience as an R&D lab technician for Chem Link and two summer internships with Anderson Development.



Trevor Kalinowski

Trevor Kalinowski is currently an intern in the Polyurethane Elastomers R&D Group at Anderson Development Company. He is a member of the Beta Beta Biological Honors Society at Adrian College. Trevor will be graduating from Adrian College in May 2020 with a Bachelor's of Science in Biochemistry.