Title: Choosing the best alternatives to MOCA cured TDI polyurethanes

Abstract: MOCA has been included in the Annex XIV list of regulated chemicals under REACh in Europe. On November 22, 2017, MOCA will reach its “sunset date”, and users of MOCA in Europe must now plan for this. Many MOCA users in other regions of the world are wondering what the regulatory future for MOCA is in their regions, and what the alternatives are. There are no “drop-in” replacement systems that meet the cost-benefit profile of MOCA across the board. Choosing the right replacement is a matter of the needs of the application and the ability of the various alternatives to best meet these needs. No one alternative will satisfy all requirements. Chuck Demarest was first to lead this discussion, presenting a recent PMA paper “Life Beyond MOCA”, in which he discussed some of these alternatives and their chemistry. This paper proposes to continue this effort, adding physical testing data, dynamic testing (DMA) for the alternatives, and discussing issues such as thermoplasticity, fatigue resistance, resistance to degradation, and suitability for softer and harder formulation needs. Additional alternative systems will also be studied.
MOCA, or methylene-bis-o-chloroanaline has been industry standard curative for hot cast polyurethanes for decades. Recently, ECHA, the European Chemicals Agency, has put MOCA on a list of regulated chemicals under the regulatory framework of REACh, the Registration, Evaluation, Authorization, and Restriction of Chemicals. MOCA has been given a “Sunset Date” – a date by which its manufacture or use in the European Economic Area must cease, unless a prior authorization has been granted. The Sunset Date for MOCA is November 22, 2017.

While the REACh regulations do not directly apply outside of Europe (unless involving export to Europe), this regulation has created concern that further regulation may be coming to North America and elsewhere as well. Processors are looking to understand the risks, and what their options might be. Unfortunately, there is no one alternative diamine or polyurethane system that is the best replacement under all circumstances, and the advantages and disadvantages of the various alternatives needs to be considered in light of the needs of the application.

Chuck Demarest recently presented a paper to the PMA entitled “Life Beyond MOCA” where he started to address this question, and today we will update that presentation with additional data and candidates. As a scope, we will stick to MDI and TDI based systems with alternative curatives. Other specialty isocyanate based systems have a place, but are less likely to become general purpose TDI-MOCA replacements because of the inherent cost disadvantage of any specialty isocyanate monomer. We will also limit our data to PTMG ether systems, with only a few comments on esters. Full study of esters and other soft segments such as polycaprolactone polyols could be the subject of future work.
MOCA cured TDIs have a lot going for them. They are among the most user friendly hot cast systems, with generally reasonable pot lives, green strength during cure, very good physical properties, and a wide range of hardness available. They are less sensitive to moisture than other systems like MDIs, and are somewhat forgiving to slight deviations in ratio. MOCA cured systems can also have very good dynamic properties (low hysteresis, good modulus retention, and high critical temperature). And to add to all of this, MOCA is reasonably economical.

So where should one go if MOCA is not a possibility anymore? The first thing that comes to mind is other diamines that can be used with the same prepolymer. But these are generally more expensive, and the lowest cost common curatives are not diamines, but diols such as butanediol. As a result, MDIs cured with butanediol have an inherent cost advantage, making them a natural first consideration.

The properties of butanediol cured materials can also be very good and competitive with TDI-MOCA systems. However, processing can be more of a challenge for a number of reasons. First, the MDIs are much more moisture sensitive than TDIs, and high humidity can easily cause problems such as bubbles and skinning. The butanediol is also hygroscopic, and becomes wet easily simply from exposure to humid air, even for short durations of time. Ratio of butanediol systems is more challenging, and the green strength during cure can also be more problematic, leading to greater incidence of cracking or bonding problems.

MDI systems are also more limited on hardness range than their TDI-MOCA counterparts. While the TDIs readily reach high hardness like 75D, this is more difficult with MDI. MDIs have higher NCO for the same hardness than TDIs, and as a result have higher exotherms, more shrinkage during cure, and much more difficulty in processing.
Dynamic properties of MDI-BD cures are good, but not quite up to their TDI-MOCA counterparts. Modulus declines as the material temperature rises, and the “critical temperature” is lower. MDI esters can show even more softening than the ethers shown here. MDIs can be said to be more thermoplastic than their TDI counterparts.

But with good physicals and cost competitiveness, the processing hurdles may be worth trying to get past. This may be especially true at the lower end of the hardness scale, and also especially with esters. Note that MDI-BD systems have improved hydrolysis resistance vs TDI-MOCA, and with esters, this can be especially important. TDI-esters are the most defensive in hydrolysis resistance among the common types of hot cast elastomers, and this is often enough to disqualify them from consideration in an application, even at ambient conditions, if the part life is expected to be long. MDI-esters have more reasonable hydrolysis resistance at ambient conditions and are suitable for a larger number of applications.

Also available on the market are “quasi MDI” products, which are mostly esters. These systems have high NCO and are cured with butanediol and a polyol curative to reach a variety of hardness values. Proponents of quasi systems tout the flexibility to produce a range of hardness, and the low viscosity of these systems. However the same negatives mentioned for MDIs still apply, and because of the higher NCO, these systems have even more exotherm, more shrinkage, and more cosmetic issues. Additionally, these materials have dynamics that are defensive vs MDI prepolymers.

So MDIs cured with BD have a place, but they aren’t as good as TDIs cured with MOCA across the board. So what should one do if one wants higher hardness, or 90-95A without thermoplasticity and good high temperature performance? Or the lowest heat buildup from hysteresis? Let’s take a look at the TDIs cured with other amines to see what some of the options provide us. As a benchmark TDI prepolymer for comparison, we chose a high performance LFTDI (low free TDI) PTMG prepolymer with 5.1% NCO.
The best known alternatives for curing TDI's are the diamines DMTDA (dimethylthio toluenediamine) and MCDEA (methylene-bis chloro diethylanaline). Let’s take the DMTDA first. This curative has the nice advantage of being liquid at room temperature and lower in EW (107), resulting in less curative required. And the physicals properties are good. Dynamic properties, however, are defensive to MOCA. The tangent delta is considerably higher, indicating higher hysteresis.

One of the things that have been learned over time is that some curatives benefit from higher temperature cure. For comparison, we have cured at a much higher temperature; 140 C. Tensile, elongation, and tear have improved. To go outside the box, we have also experimented with a high stoichiometry cure. This provides some very interesting physicals, however the cured parts had significant sulfur odor, and we do not recommend going to this extent. Interestingly, the dynamic performance improves with both of these high temperature cures, including with high stoichiometry.
MCDEA is also a well-known diamine alternative. MCDEA usually provides cast elastomers with higher hardness than MOCA, when using the same prepolymer, so for the sake of this comparison we switched to a 3.8% NCO LFTDI-ether prepolymer. (All other LFTDI cures in this paper use a 5.1% NCO prepolymer). The desired hardness was achieved. Properties look generally good; however tear was defensive to MOCA. And despite its reputation, our dynamic testing indicated the tangent delta to be not quite as good as MOCA either.

Using a higher temperature cure, we were once again able to see an improvement. Tensile and elongation are high, tear has reached 60, and compression set is down to 23. Dynamic testing also demonstrates significant improvement, with tan deltas now reaching MOCA levels at critical temperature. Some may recall past papers on MCDEA that suggested dynamic performance exceeding that of MOCA. However, that was not seen with this prepolymer system at this relatively low hardness.
A somewhat lesser known curative is PDPAB (propanediol bis p-aminobenzoate), perhaps best known for its ability to be used in FDA grade applications. Properties of this curative also look good, except that 40% compression set is beginning to get a little high. Compression sets this high sometimes can be an indication of other problems such as creep and properties at higher temperatures. Dynamics are somewhat defensive, particularly as temperatures rise.

BDACB (butyl diaminochlorobenzoate) is another available diamine advertised for use in cast polyurethanes. Properties look good, except the compression set came out even higher. Because of this, it may be wise to conduct additional testing of large strain cycling and creep properties before recommending its use. Interestingly, our first check indicates dynamics are a closer match to MOCA than with PDPAB. In this case,
the manufacturer indicates that higher temperature cures lead to inferior properties, so further improvement is unlikely.

MBMA (methylene bis-methylantranilate) is another diamine that can be used to cure LFTDI prepolymers. In this case, however, the cured material was measured to have both lower tensile and elongation, and both lower tear and higher set. While the dynamic properties were fairly good, especially the tangent delta, the physical properties are not up to the levels of the others.
The newest diamine that I am aware of is CDETDA, (chloro diethyltoluenediamine). This would seem to be a good idea; DMTDA is DETDA with methylthio groups used to withdraw electrons and slow down the reactivity of the amines. However, these groups have been the cause of odor complaints and some UV aging problems with ethers. Use of Cl instead would appear to be a good idea, as Cl has not shown these disadvantages with MOCA and MCDEA.

Yet despite the Cl present, pot life was still on the fast side, about 3 minutes, and clearly faster than MCDEA. Physical properties looked reasonably good, with a little higher compression set, but also a little higher resilience. However, the dynamic properties were defensive. The material has high tangent delta and also softens as temperature rises. It should be noted however, that this was a preliminary R+D sample, and the measured EW was not very closely matched to the theoretical. This testing should be repeated with a sample that has nearer the 106 theoretical EW.

Finally, an attempt was made to cure the LFTDI prepolymer with MBOEA (methylene bis-o-ethylanaline), which has also been mentioned as a potential MOCA replacement. However, with no electronegative substituents, the pot life was unmanageable at significantly less than 30 seconds.

Within the scope of TDIs and MDIs, there is one more approach of interest; Using an LFMDI with HQEE. Physical properties are very good, with improved split tear and rebound relative to MOCA. Dynamic properties are excellent, with tangent delta below that of MOCA within its usable temperature range. The material is somewhat more thermoplastic than MOCA cured LFTDI, but with lower tangent delta, it would not be expected to reach the same temperature under equal loading conditions. A tire model correlation presented by Dick Palinkas to the PMA in 2011 can be used with these DMA data results to demonstrate that load to failure of this material is improved vs MOCA.
Will this system have the same processing disadvantages discussed for conventional MDIs? The answer is no. LFMDI is a considerably different material from conventional MDI. The material shown here was using a 5% NCO prepolymer. It produces a harder elastomer than the conventional MDI shown earlier, which was nearly 9% NCO. This material has less than 1% free MDI. The conventional MDI shown earlier has about 20% free MDI. This is not nearly the same as the more modest difference between conventional TDI and LFTDI.

Because of the lower NCOs used to reach a given hardness, a full range of hardness up to 70 or even 80 Shore D is possible with LFMDI. Pot lives are longer than with TDI-MOCA at high hardness, and the low NCO combined with long pot life results in reduced problems with shrinkage and cosmetics. The only negative of conventional MDIs that remain is moisture sensitivity.

Hazards in the workplace come from not only the curatives, but of course from the isocyanates as well. While amines used to cure LFTDI in general have greater potential for health hazards than diols used for MDI, the MDI prepolymer has more hazard than an LFTDI prepolymer because of the high free MDI. The LFMDI-HQEE system is unique in that it is the only system with both no amine curatives and low levels of isocyanate monomer.

One can also use HQEE with conventional MDIs containing high free MDI levels, but doing so can be problematic. HQEE provides short pour life with conventional MDIs, and can produce cured materials with very low green strength and cosmetic problems. A unique problem associated with these cures is the advent of “starring” on the surface of parts. This occurs when reaction products of HQEE and free MDI form and phase separate from the matrix of the polyurethane very early, while it is still a liquid or semi-solid. These “adducts” of the free monomer often tend to plate out on mold surfaces, which are cooler than the bulk of the polyurethane,
and cause severe cosmetic problems. With low free MDI prepolymer, free MDI levels are so low that the concentration of these adducts formed is not significant, and “starring” is not observed at any mold temperature.

For a more complete property comparison of these various systems, a study of fatigue resistance was also undertaken. Fatigue resistance can be important in many dynamic applications involving cyclical loading or flexing, including for instance, wheels. The test used by Chemtura is called Texus flex and is briefly summarized in this slide. A small coupon is flexed repeatedly as it passes bearings set to deflect it a controlled amount. The number of cycles needed to grow a crack along the sample to a specified length is recorded as the cycles to failure.

![Fatigue Resistance - Texus Flex](image)

<table>
<thead>
<tr>
<th>Curing Agent</th>
<th>Hardness</th>
<th>Fatigue Life</th>
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<tbody>
<tr>
<td>LFTDI 5.1% NCO</td>
<td>MOCA</td>
<td>94 A</td>
</tr>
<tr>
<td>LFTDI 5.1% NCO</td>
<td>DMTDA</td>
<td>92 A</td>
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<tr>
<td>LFTDI 5.1% NCO</td>
<td>DMTDA 140 C</td>
<td>92 A</td>
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<tr>
<td>LFTDI 3.8% NCO</td>
<td>MOCA</td>
<td>94 A</td>
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<td>DMTDA</td>
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<tr>
<td>LFTDI 5.1% NCO</td>
<td>POPA</td>
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<td>LFTDI 5.1% NCO</td>
<td>BCD</td>
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<td>LFTDI 5.1% NCO</td>
<td>MDOA</td>
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<td>LFTDI</td>
<td>COETDA</td>
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<tr>
<td>LFTDI-HQEE</td>
<td>92 A</td>
<td>1000</td>
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<tr>
<td>Esters</td>
<td>5K-50K</td>
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This paper has focused on ethers, and MOCA cured TDI ethers do not excel at fatigue resistance. At a 35% strain level, it took only 300 cycles to grow an initiated cut half way across the sample coupon. This is one property in which MOCA does not set the bar very high, and all the candidate systems can be viewed as equal or perhaps slightly better than MOCA. By comparison, esters easily have one or two orders of magnitude higher fatigue resistance. Differentiation among these candidate systems on fatigue resistance is therefore best studied in future work on analogous esters.

The highest fatigue resistance material shown in this table is for the 115% theory DMTDA cure. Use of this commercially is not recommended, as the cured material has a sulfur odor, and one might expect that there would also be a small amount of residual unreacted curative in the elastomer. The fatigue resistance is also not all that much improved vs the other candidates. This type of cure was tried because in the past it had shown much greater fatigue resistance with a different prepolymer. This indicates the importance of subtleties of the prepolymer design in obtaining good results. Specialty ether systems are available with orders of magnitude greater fatigue resistance, but they are outside the scope of a discussion on systems that could be considered “TDI-MOCA replacements”.

**Conclusions**

- There are many urethane systems options, and the number continues to grow. There is no one ‘right’ system to replace MOCA.
- Conventional MDIs have inherent cost advantage and a number of tradeoffs/limitations. They are a natural consideration wherever these tradeoffs/limitations are less important.
- This study finds DMTDA, MOCA, and LFTDI-HQEE have attractive characteristics worth considering.
- Carefully consider your application needs, commercial considerations (price/value) and discuss your options with your suppliers.
- Field test to validate and determine value.
In conclusion, there are many urethane options within the realm of MDI and TDI systems that can be considered as TDI-MOCA alternatives, and the number of options continues to grow. Conventional MDIs cured with butanediol have an inherent cost advantage, and a number of processing and performance tradeoffs. They are a natural consideration in cases where these tradeoffs/limitations are less important. For other applications, this paper finds DMTDA, MCDEA, and LFMDI-HQEE to have attractive characteristics worth considering. In discussing these systems with your supplier, taking into consideration the application needs and commercial aspects, the right selection can be made. Finally, field testing is of course always important to validate the performance of the system.

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May 9, 2016