

Albemarle Europe SPRL
Parc scientifique Einstein
Rue du Bosquet 9
1348 Louvain-la-Neuve
BELGIUM

Phone: +32 (0) 10 48 17 11
Fax : +32 (0) 10 48 17 17

European Chemicals Agency ECHA
Annankatu 18
00121 Helsinki
Finland

January 7, 2017

Public consultation on 2,2'-dichloro-4,4'-methylenedianiline (MOCA), CAS: 101-14-4, EC No. 202-918-9, Consultation Number: 0096-01. Suitability of alternatives.

Dear Sir or Madam,

On behalf of Albemarle Europe SPRL, we would like to comment on the Analysis of Alternatives as published on the ECHA website. Albemarle corporation is a manufacturer of Dimethylthiotoluene diamine (Ethacure 300®) (DMTDA), CAS No. 106264-79-3, EC Number 403-240-8. Albemarle Europe SPRL is importing the substance into EU and has notified it as a New Substance under EU Directive 92/32/EEC (NONS substance under REACH).

Albemarle has recently developed the product further and is now able to produce a low odour quality of Ethacure 300®. Therefore the claim on page 38 of the analysis of alternatives that the use of Ethacure 300® leads to an unpleasant odour of the final products is not applicable to this quality of the product.

In contrast to MOCA, Ethacure 300® did not show any increased tumour incidence in a 2-year feeding study in rats up to the maximum tolerated dose.

Furthermore as already stated in the Analysis of Alternatives of the applicant, Ethacure 300® is a low viscosity liquid at room temperature which facilitates technical exposure controls and less worker exposure.

The analysis of alternatives claims that DMTDA or Ethacure 300® has less favourable technical properties compared to MOCA for the majority of the applications. Albemarle has recently conducted and published a comparative analysis using standardized test methods for many of the technical properties in polyurethane cast elastomer production. We include a Poster presented at a recent conference and the full publication of the work for your kind consideration in this submission.

In summary this work has demonstrated that Ethacure 300® offers a wide processing latitude and control over reactivity and produces tough parts with desired heat aging and mechanical properties which closely match or are even better than MOCA. Albemarle continues to develop approaches to optimize the performance of PU parts cured with Ethacure 300®. Therefore we are of the opinion that our recent work has demonstrated that the claim of infeasibility of DMTDA or Ethacure 300® as a replacement of MOCA in this area is incorrect.

Best Regards



Dr. Sylvia Jacobi

Corporate Toxicology Director

Enclosures:

Y. Yang, S. Taylor, P. Wiggins, Ethacure 300 versatile curative for polyurethane, PU Magazine, 13 (5), 2016

S. Taylor, Y. Tang, P. Wiggins, Formulating Ethacure 300 in MDI systems with prolonged pot life and desired properties, Poster presented at Center for the Polyurethanes Industry (CPI) Technical Conference, Baltimore MD, September 26-28 2016

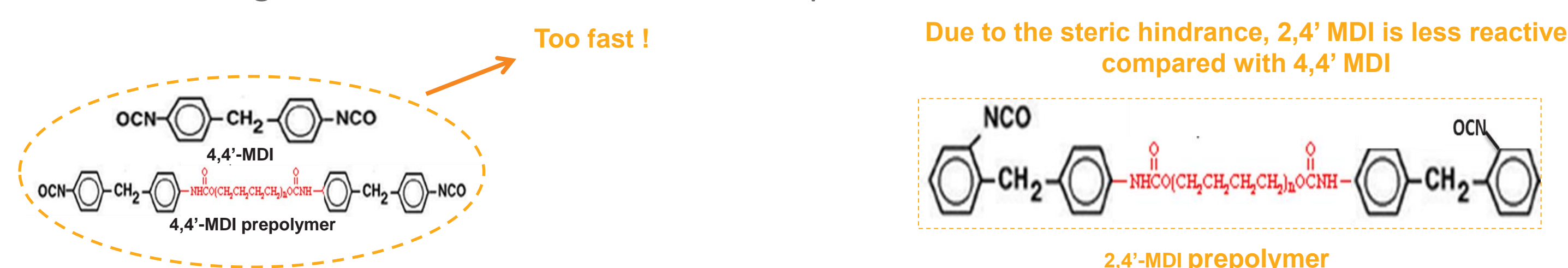
Formulating ETHACURE® 300 in MDI Systems with Prolonged Pot Life and Desired Properties

Shannon Taylor, Yong Tang, Paul Wiggins | Albemarle Corporation, Baton Rouge, LA 70805

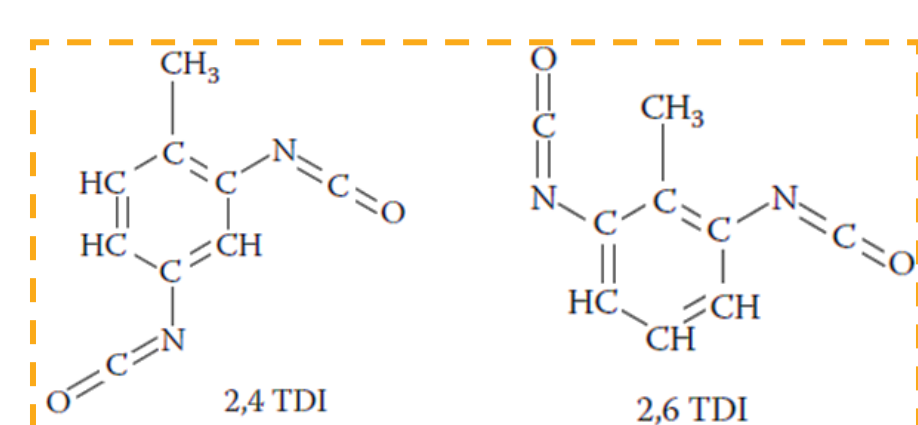
ETHACURE 300 is a low toxicity, easy-to-handle liquid aromatic diamine widely known for its superior properties and extreme versatility in the polyurethane industry. Polyurethane elastomers cured with ETHACURE 300 have demonstrated a broad range of properties such as high strength, high hardness, high modulus, and high elongation at break point. ETHACURE 300 has been solely tided with TDI based isocyanates in cast elastomer. The system delivers moderate reactivity, suitable working time and ideal mechanical properties. The continuously evolving polyurethane industry is constantly pushing for change and innovation. With the November 22, 2017 European sunset date for MOCA, one of the most commonly used curatives in the cast elastomer market, new technology and alternate formulations are needed in this market. In our recent study, curative packages have been developed and applied in MDI-based cast system, as well as TDI-based system. The new ETHACURE 300/MDI system delivers prolonged pot life and desired properties, which represents new opportunities to the polyurethane industry. Our new system discussed herein will offer formulators additional resources as they develop their formulations and applications.

Introduction

- Standard methylene diphenyl diisocyanate (MDI) prepolymers typically have a 99/1 (4,4, 2,4) isomer ratio. The fast reactivity 4,4 position makes it extremely difficult to make elastomer with E300. Increasing the amount of 2,4 isomer which has more steric hindrance causes the reactivity to slow down, thus allowing formulators more time to make parts.



- In this study, MDI prepolymers containing 100 % 2,4 isomer ratio with 4.0% NCO was effectively used to create PU elastomers with excellent mechanical properties with adequate working time.
- Toluene diisocyanate (TDI)-based prepolymers have successfully been used with ETHACURE 300 to prepare elastomers, typically using 80/20 (2,4/2,6) isomer ratio TDI prepolymers. Increasing the amount of symmetric 2,6 TDI allows for better microphase separation within the polymer and can improve dynamic performance of the elastomers.



- In this study, TDI prepolymers with different ratios of 2,4 and 2,6 isomers were used to make elastomers. Evaluations were performed to determine the effect isomer ratio has on the dynamic and mechanical performance of the parts.

What are the benefits of using ETHACURE 300 vs. MOCA?

- In 2010, IARC reclassified MOCA from a Class 2a carcinogen (probably causes cancer) to a Class 1 carcinogen (known to cause cancer). (IARC, vol. 57, vol. 99, in prep.).
- ETHACURE 300 reduces exposure to hazardous chemicals while simplifying processing conditions.
- It eliminates dust exposure.
- ETHACURE 300 exhibits lower eq. wt. (i.e. you need less of it).
- Mechanical properties can be tailored to match MOCA's profile, and in some cases provide better mechanical properties.



Study Objective and Methods

- To develop and evaluate formulations with ETHACURE 300 combined with MDI and TDI-based prepolymers that elongate reaction time while maintaining excellent mechanical properties.

Test	Method	Material	Source
Shore Hardness A	D-676	4.0% NCO MDI Prepolymer	Covestro Desmodur® Max-T40
Tensile Properties	D-412		
Tear Resistance	D-624	4.3% NCO TDI Prepolymer	Covestro Desmodur TT 142L
Compression Set	D-395B		
Resilience %	D-2632	DMTDA (E300)	Albemarle

MDI Prepolymers with ETHACURE 300 Blends

Figure 1: Dynamic Properties of ETHACURE 300 Blends

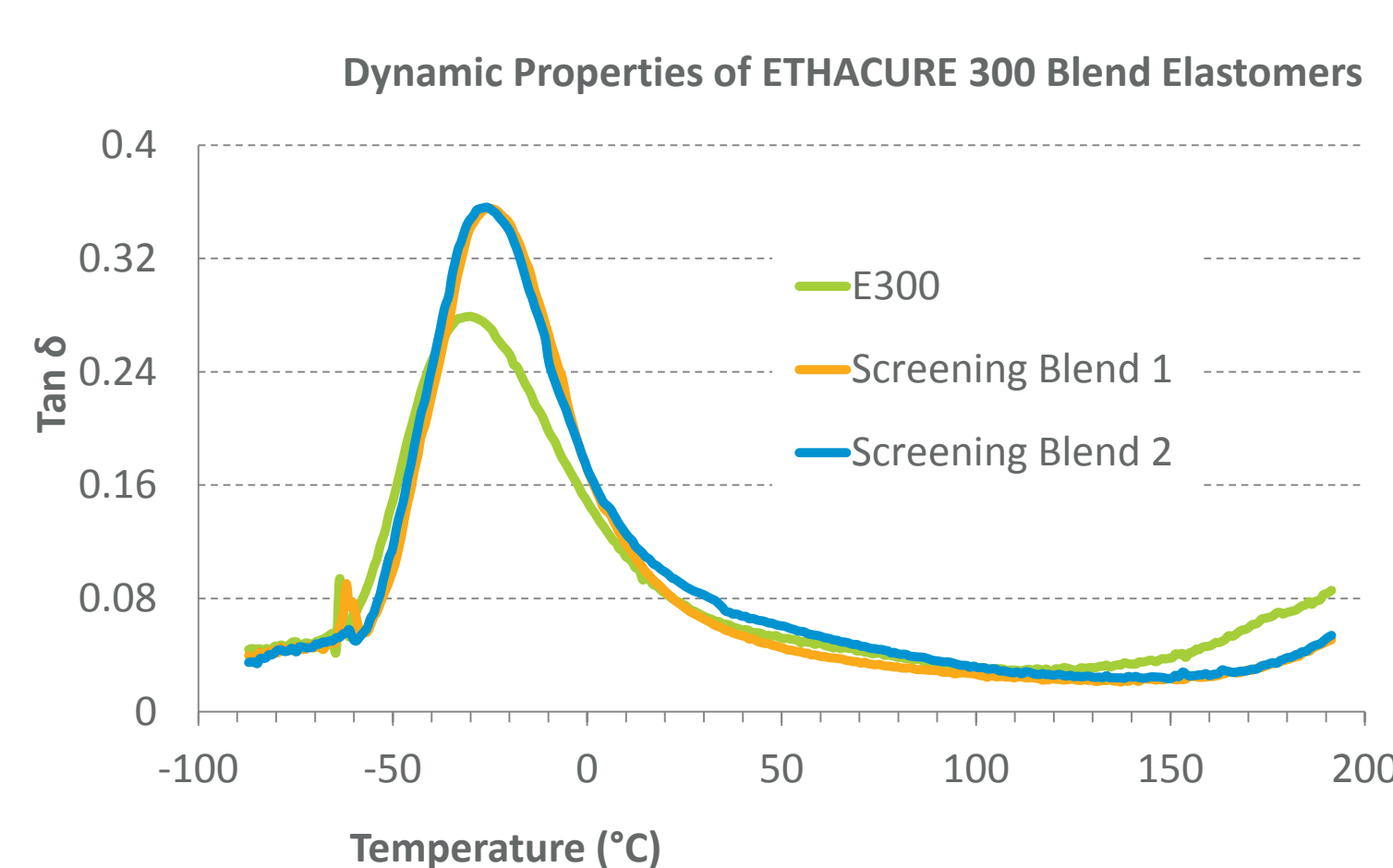


Figure 2: Viscosity Profile of ETHACURE 300 Blends

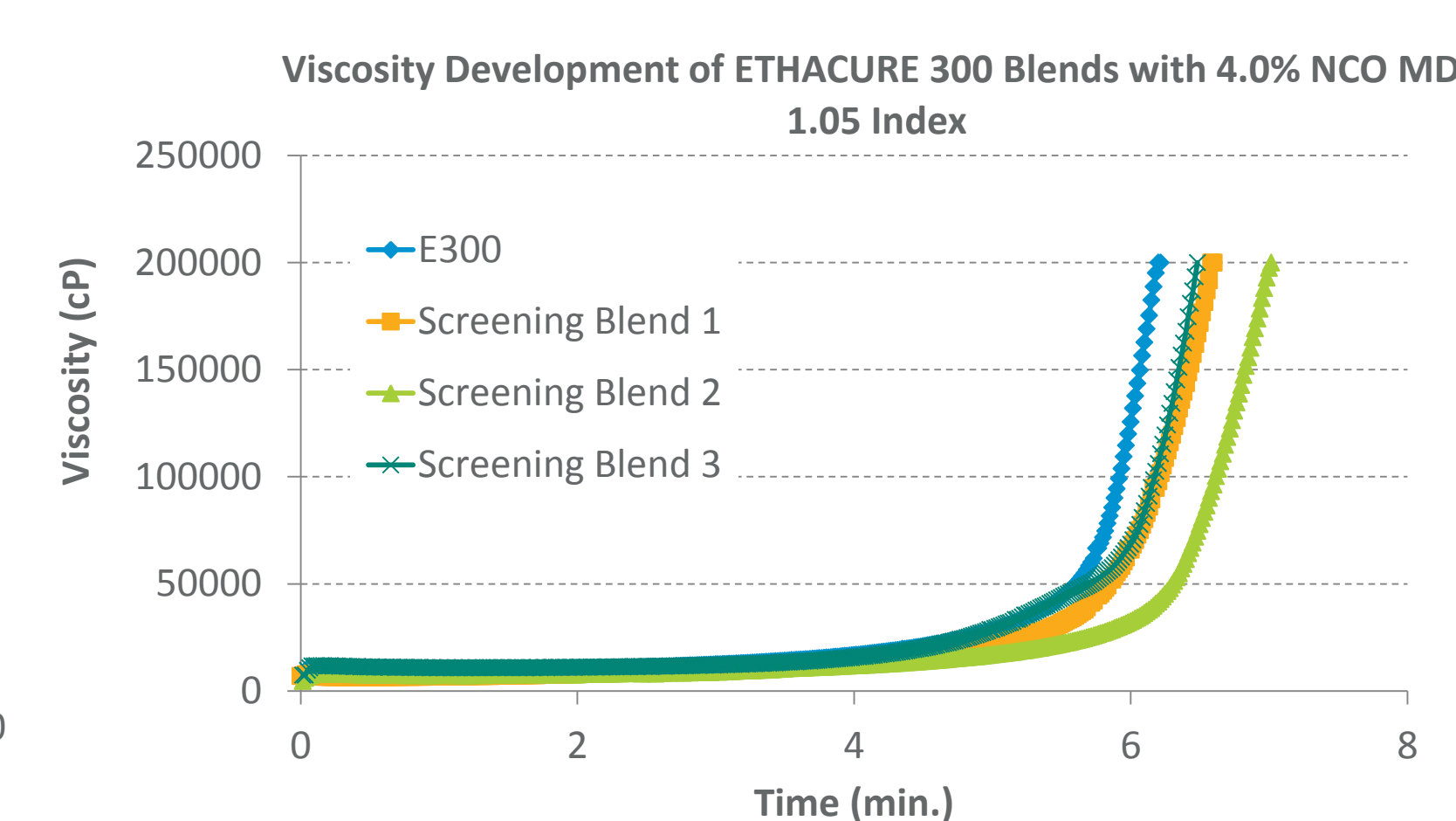


Table 1: Mechanical Properties of ETHACURE 300 Blends with MDI Max T-40

Blend	Screening Blend 1			Screening Blend 2			Screening Blend 3
Index	1.05	1.2	1.3	1.05	1.2	1.3	1.05
Hardness Shore A (10 sec)	84	83	82	82	82	82	85
Tensile Strength (psi)	5376	4264	2512	4341	4788	2534	4756
Young Modulus (psi)	665	2110	1004	664	2535	1057	4251
Stress at 100% (psi)	1133	1048	1046	1130	1092	1067	1150
Stress at 300%	2014	2179	2314	2085	2041	2693	1992
% Elongation	537	415	315	517	468	286	483
Tear resistance (lbf/in)	531	424	391	512	489	402	520
Compression	32	24	26	30	21	29	31
Resilience	42	44	40	46	43	43	45

- Elastomers in Table 1 were prepared using 4.0% NCO MDI Max-T40. The blends evaluated were 90/10 wt. % E300/diol.
- In Figure 1 the E300 blends have lower tangent delta at temperatures above 130 °, indicating these parts are able to dissipate heat quickly.
- Figure 2 illustrates that the blends provide formulators with more time to cast parts by prolonging viscosity development.

SEM Imaging PU Elastomer

Figure 3: 1.05 Index Blend 1

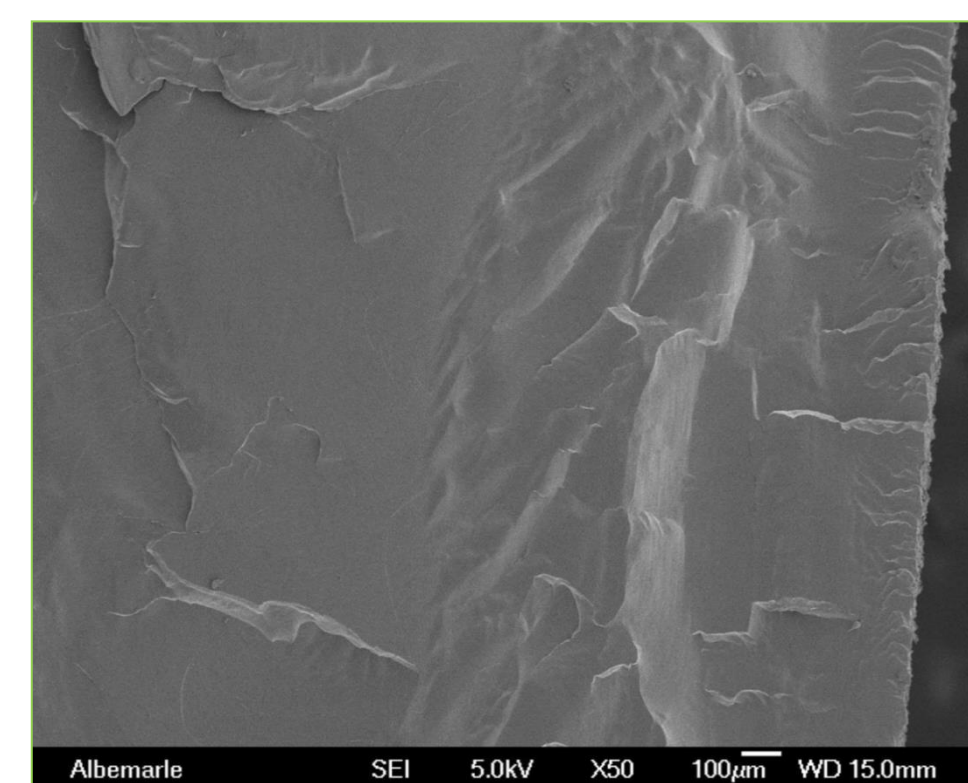


Figure 4: 1.3 Index Blend 1

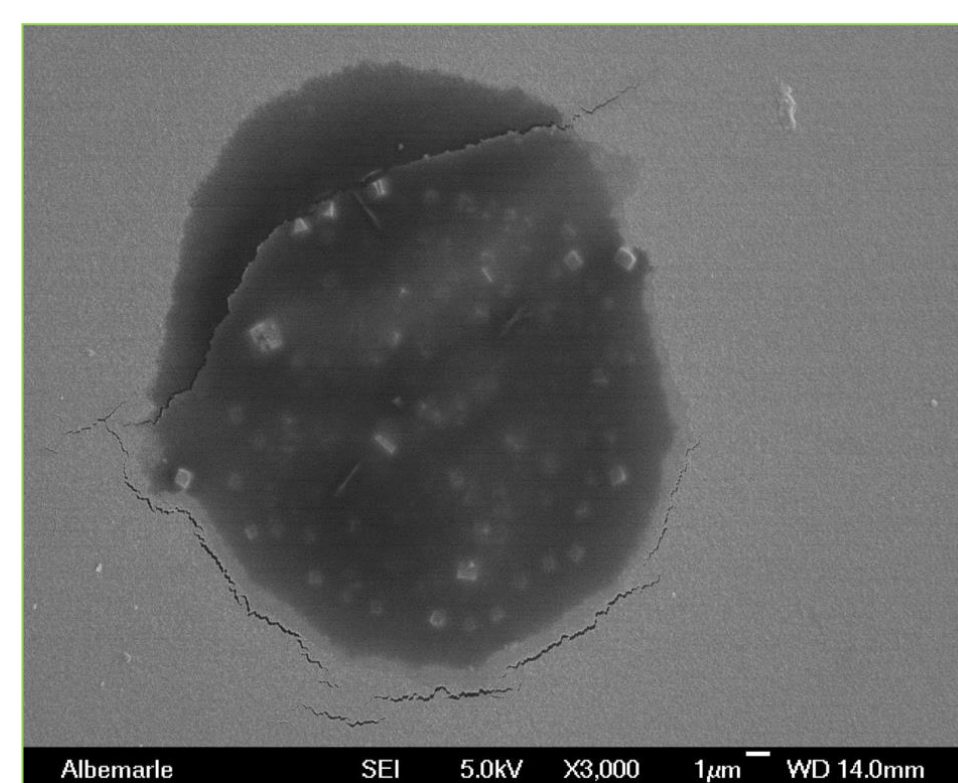
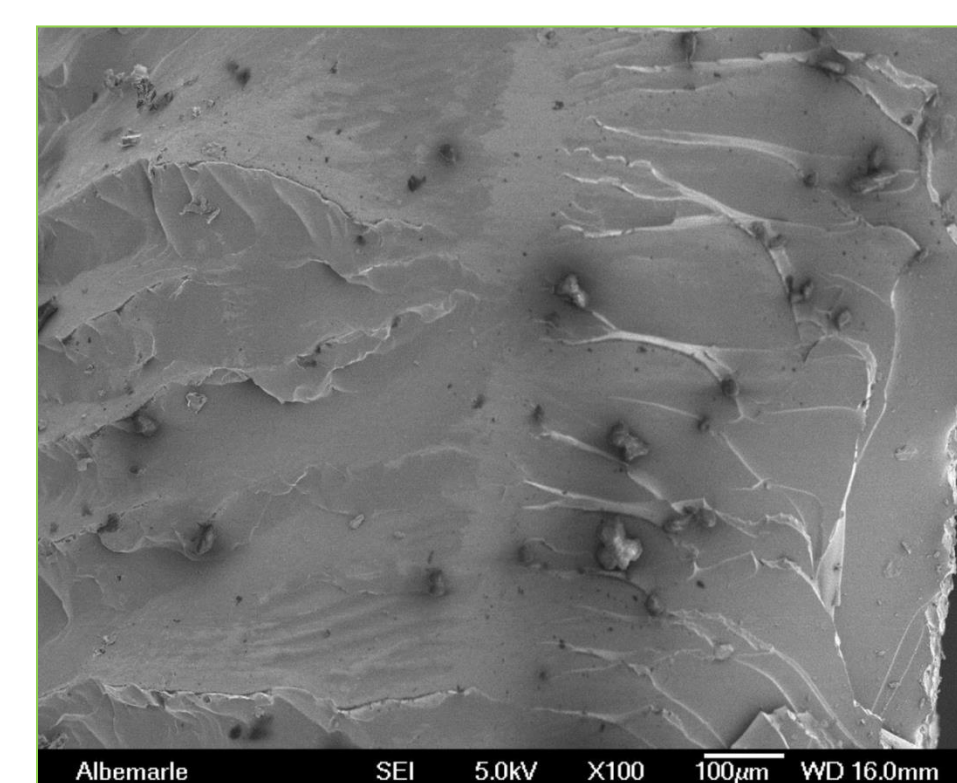


Figure 5: 1.3 Index Blend 2



- Increasing the isocyanate/amine index of a formulation can improve the mechanical properties of an elastomer. In Table 1, the 1.2 index sample for screening blend 2 had better properties than the 1.05 index sample.
- Figures 4 and 5 show that moving beyond the optimal index causes uneven dispersion of hard and soft segment and poor alignment within the elastomer. This leads to accumulation of hard segments throughout the PU elastomer, causing mechanical properties to decrease. In Table 1, for screening blend 2, the 1.3 index sample exhibited poorer properties than the 1.2 index sample.

Prepolymers Formulations with Different Amount

Table 2: TDI Prepolymer Formulations

TDI			
TD-S (2,4-TDI)	204	--	--
TD80 (80/20-TDI)	--	204	--
TD (65/35-TDI)	--	--	204
Polyol			
T-1000	436	436	436
T-2000	161	161	161
%NCO	6.8	6.8	6.6
Gel time (E300, 80°C)	3'15"	1'55"	1'20"
Hardness Shore A (10 sec)	46	47	47

The 65/35 2,4 to 2,6-isomer ratio provided the best dynamic properties, giving 60 min. at 280 lb. load and 12 min. at 320 lb. load.

Figure 6: Time to Failure of Wheel

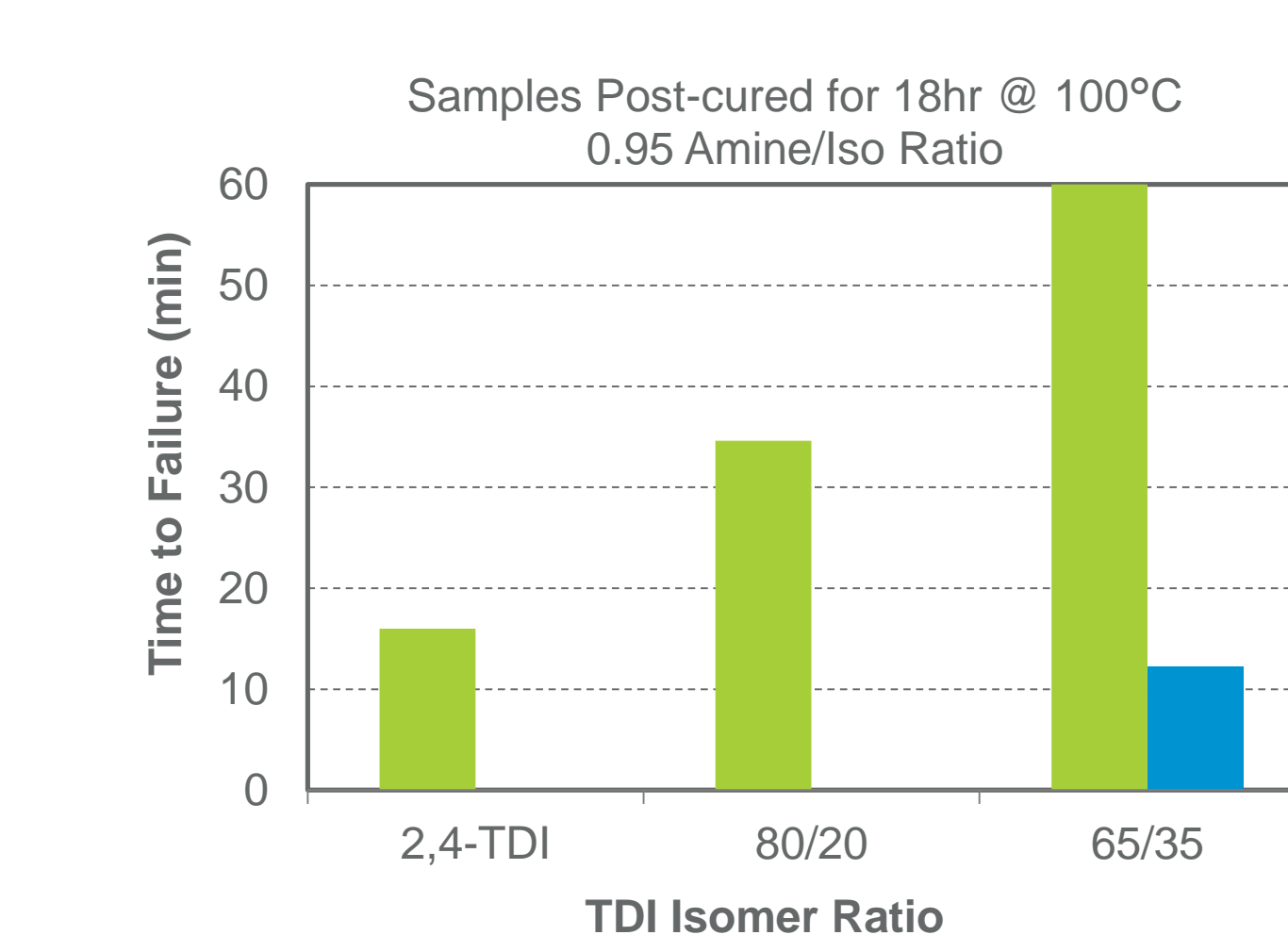
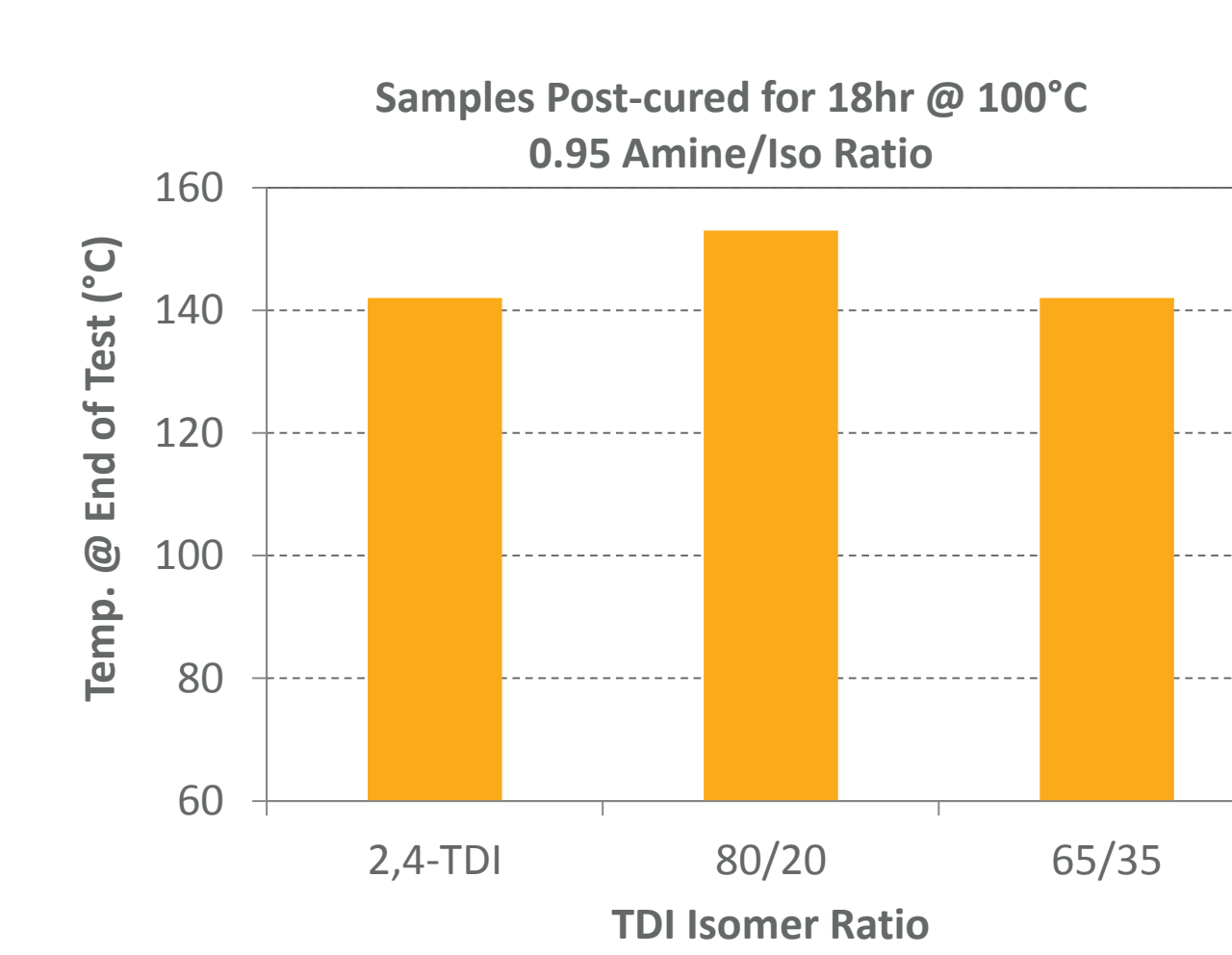


Figure 7: Temperature at End of Test

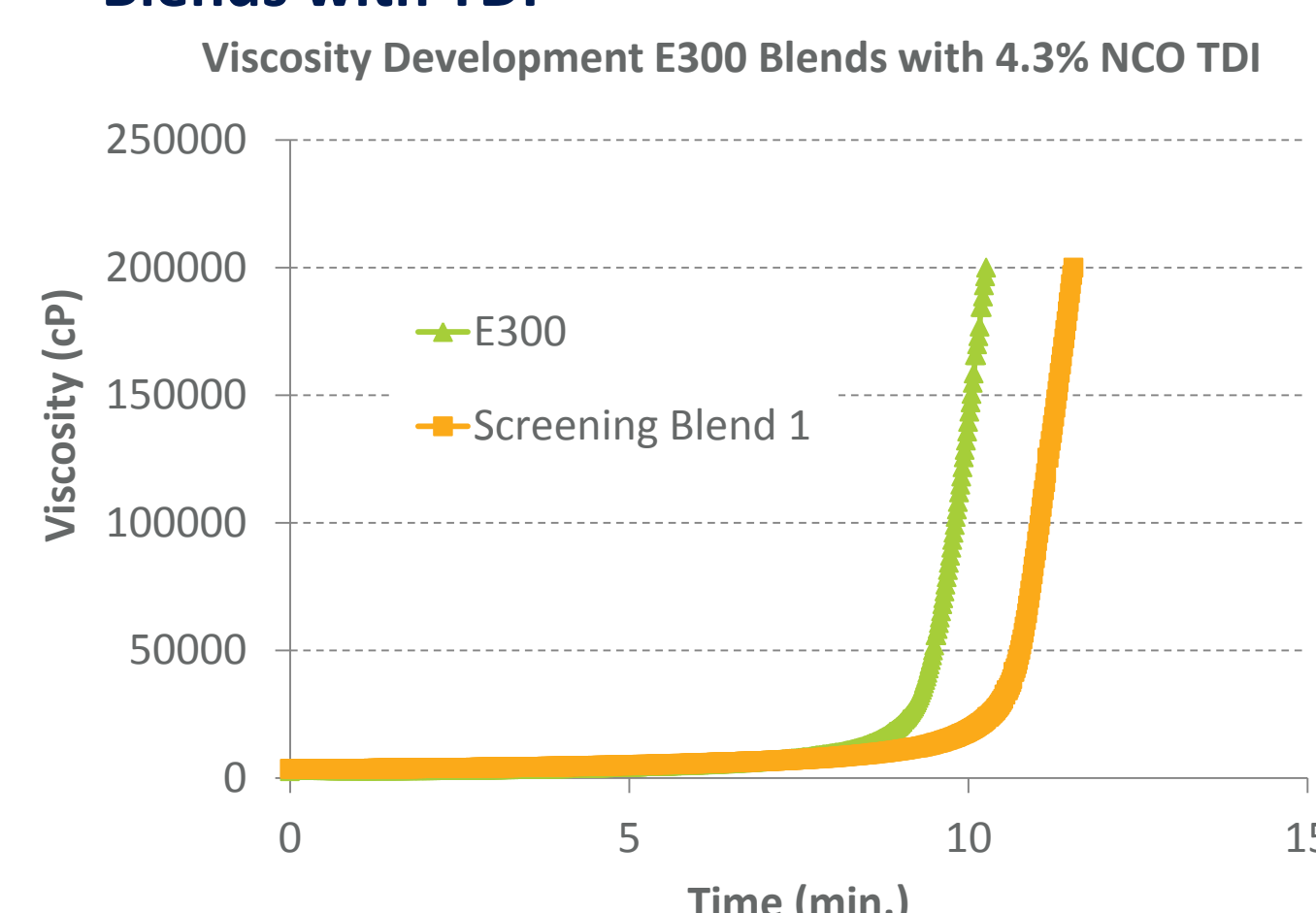


TDI Prepolymer with ETHACURE 300 Amine Blends

Table 3: Mechanical Properties of ETHACURE 300 Blends with TDI

Properties	Screening Blend	E300
Peak Load (lbf)	92	76
Break Stress (psi)	4699	4410
Elongation at Break (%)	13	10
Modulus (psi)	2727	2527
Stress at 100% (psi)	1276	1322
Stress at 300 %	1922	2532
% Elongation	531	388
Tear Peak Load (lbf)	46.1	42.1
Tear resistance (lbf/in)	555	476
Compression	32	
Resilience	46	47

Figure 8 : Viscosity Profile of ETHACURE 300 Blends with TDI



- The elastomers in Table 3 were prepared using Desmodur TT 142L 4.3% NCO TDI. The liquid blend evaluated was 90/10 wt.% ETHACURE 300/amine.
- The screening blend had a significantly higher tear resistance than ETHACURE 300 and higher break stress. The viscosity build up was also prolonged.

Conclusions

- Ethacure 300 is a liquid diamine with extreme versatility. ETHACURE 300 blends in conjunction with a MDI prepolymer with high 2,4 isomer content can elongate pot life and produced parts with superior mechanical properties.
- Elastomers prepared with TDI prepolymers containing higher levels of 2,6 isomer have better mechanical and thermal properties due to the symmetry of the 2,6 isomer and better microphase separation.
- We plan to continue to use this experimental approach to further evaluate ETHACURE 300 blends in different MDI and TDI systems.