

New modified liquid pure MDI for CASE applications

KATIE L. SKOK and **ROELAND J. TUINMAN**

*Huntsman Polyurethanes
2190 Executive Hills Blvd.
Auburn Hills, MI 48326*

ABSTRACT

Pure 4,4'-methyl diphenyl diisocyanate (4,4'-MDI) has found continued commercial success in urethane applications which require high dynamic elastomeric properties. However, due to its crystalline nature, 4,4'-MDI has a relatively high melting point and is solid at room temperature. Transportation, storage, and handling can be hindered due to melt out requirements and higher temperature storage conditions. Since it is more convenient to handle liquids, the common practice in the industry is to chemically alter the diisocyanate by disrupting the crystalline structure to produce a "liquid pure" variation that is stable at room temperature. In continued efforts to improve the overall stability performance of its "liquid pure" products, Huntsman has developed a new modified MDI, SUPRASEC[®] 9561, which has improved storage stability, temperature stability and extended clarity. This paper will address physical properties, reactivities and prepolymer processing conditions of this new modified liquid pure MDI.

INTRODUCTION

There are many advantages in using a liquid form of 4,4'-MDI. Liquids are easier to pump and less expensive to transport than fused solids or slurries. In general liquids are homogeneous compositions as supplied without the need to homogenize as with slurries or fused solids. In the production of polyurethane articles, a liquid can be added easily by weight or volume and combined with suitable co-reactants at room temperature. This is safer than using the materials at elevated temperature due to the corresponding higher vapor pressure of the heated materials.

A common way to liquify 4,4'-MDI is thru the formation of carbodiimides. At temperatures above 180°C, an isocyanate can react with itself thru a condensation reaction which releases carbon dioxide and forms carbodiimides. However, it is unfavorable to keep an isocyanate at temperatures that high due to the formation of other species like allophanates and biurets. Once the carbodiimide is formed, it can then react with isocyanate in a cyclo-addition reaction across the C=N bonds forming a uretonimine. The end result is a tri-functional, cyclic structure.[1]

A more typical approach in the industry to form carbodiimides includes the use of catalysts, which expedite the reaction and allow it to occur at lower temperatures. Simple trialkyl phosphates will catalyze the reaction, but useful rates are at temperatures in excess of 150°C and in concentrations higher than one percent. Phospholene oxide catalysts are very active and require very small amounts and temperatures as low as 90°C. However the catalyst is active at room temperature and so it needs to be deactivated to stabilize the end product. Generally a strong acid is used, often containing labile chlorine bonds.[2] In both approaches the reaction can be followed by refractive index in order to terminate the reaction when desired NCO% has been reached.

Another way to stabilize pure MDI is thru a prepolymerization process. The pure isocyanate is heated and reacted with low molecular weight polyols. The oligomers formed are sufficient in disrupting the crystalline structure and rendering the material liquid at room temperature. The advantage of this method over a uretonimine route is the ability to keep a difunctional isocyanate. However a disadvantage is that the amount of free pure MDI may be significantly reduced.

EXPERIMENTAL

Materials

Five “liquid pure” type commercially available isocyanates were evaluated side by side. SUPRASEC 9561, RUBINATE[®] 1680, RUBINATE 9433 and RUBINATE 9225 were produced by Huntsman and the final isocyanate was prepared by an unnamed competitor. In order to evaluate prepolymer processing, each isocyanate was reacted down with the correct amount of 2000 molecular weight polypropylene glycol to obtain a 16% NCO prepolymer.

Three different hardness elastomer systems were compared. Jeffol[®] polyols produced by Huntsman were used in the resin systems. Ethylene glycol was obtained from Ashland Chemical. The catalyst package included Jeffcat[®] TD 33 from Huntsman and tin catalyst, Fomrez[®] UL-1 from Momentive Performance Materials. A silicone surfactant BYK A-535 from BYK Chemie was used as an air release agent. Prior to use, polyol blends were degassed in a vacuum oven for 2 hrs. at room temperature. For each system, components were mixed for 30 seconds at 25000 r.p.m. using a DAC 400 centrifugal mixer from Flacktek. Parts were molded into 1/4” thick aluminum mold with a mold temperature of 45°C.

Characterization

Temperature stability was tested by placing test tubes of each isocyanate and prepolymer into a water bath beginning at 10°C and then sequentially reducing the temperature by one degree every two days.

Isocyanates were stored in 8oz glass jars at 25°C and 50°C for a period of two months. Initially and then every two weeks after, NCO %, viscosity, dimer %, and % haze measurements were taken for each sample. NCO % was tested by titration. Viscosity was tested by Brookfield viscometer at 25°C. Dimer % was tested by FTIR. % Haze was tested by HunterLab Colorquest II Spectrophotometer.

The physical properties of elastomers reported were measured using industry standards. Tensile strength and elongation at break were tested according to ASTM D-422. Die C tear was tested according to ASTM D-624. Izod impact test was performed according to ASTM D-256. Heat deflection temperature was tested according to ASTM D-648. Hardness was tested according to ASTM S-2240-95. Shore A, Shore D, and Shore OO measurements were performed according to material hardness range. Reactivities were measured using Gardco Gel Timer from Paul N Gardner Co.

Dynamic mechanical and thermal analysis was obtained using a AR 2000 Rheometer from TA Instruments. Frequency sweep was run at 1 Hz at a temperature range of -100°C to 250°C and at a heating rate of 3°C/min. The glass transition was determined at the maximum tan δ peak.

RESULTS AND DISCUSSION

Product characteristics for the five comparative products are listed in table 1.

Table 1: Product characteristics of isocyanates and prepolymers

	NCO%	4,4' isomer	Fn	Visc. cps, 25°C	Prepol NCO%	Prepol Visc. cps, 25°C
Rubinate 1680	29.6	H	H	40	15.8	1500
Suprasec 9561	29.3	M	M	36	15.9	1300
Competitor	29.2	M	M	33	16.2	1300
Rubinate 9225	31	L	L	30	15.7	1300
Rubinate 9433	31.8	L	L	18	16.1	1000

H-High, M-Medium, L-Low

RUBINATE 1680 is a standard workhorse in the industry for uretonimine modified pure. SUPRASEC 9561 is a new modified pure, designed for lower temperature stability and extended clarity. RUBINATE 9225 is a higher 2,4'-isomer modified product. RUBINATE 9433 is a lower functionality modified product with higher 2,4'-isomer levels. Table 1 will be especially helpful when discussing elastomer performance.

Temperature stability

A critical component of storage stability, is a products ability to remain liquid at lower temperatures. This is especially critical of "liquid pure" variants which have a tendency to form crystals and freeze relatively quickly. Table 2 below provides details of the temperature stability for each product from 10°C down to 0°C at a rate of 1°C every two days. RUBINATE 1680 has the poorest low temperature stability of the five products. This is due to high amounts of 4,4'-isomer which has the greatest tendency to crystallize. Both RUBINATE 9433 and RUBINATE 9225 begin to build up a high amount of solids as low as 1°C. However they remain stable longer than RUBINATE 1680 because of an excess of 2,4' isomers. The steric hindrance of the 2,4'-isomer allows disruption in the crystalline structure. SUPRASEC 9561 has the ability to suppress crystallization from temperatures down to 1°C. At this temperature, a small amount of fine precipitate has fallen to the bottom of the test tube, however the product remains clear and bright.

The 16% prepolymers have a much greater ability to remain stable at low temperatures. Each prepolymer was stable down to -20°C, with only slight haziness noted.

Table 2: Visual observations of temperature study

	RUBINATE 1680	SUPRASEC 9561	Competitor	RUBINATE 9225	RUBINATE 9433
10°C					
9°C					
8°C					
7°C					
6°C	Small crystals				Small crystals
5°C	Chunks form				Chunks form
4°C	Chunks build up			Small crystals	Chunks build up
3°C	Turning solid			Chunks form	
2°C	90% solid			Chunks build up	
1°C	100% solid	Small crystals	Small crystals	10% solid	50% solid
0°C				25% solid	75% solid

Dimer and haze determination

Aromatic isocyanates undergo dimerization to form uretidinedione. This reaction is quite common even in the absence of a catalyst, and can occur at room temperature during prolonged storage. The tendency for 4,4'-MDI to undergo dimerization most readily is related to its crystalline structure. The molecules of the 4,4'-MDI align in the solid state, with NCO groups in close proximity, which leads to the slow formation of the dimer at room temperature[3].

The percent dimer was tested for the five variants at 25°C and 50°C over a period of 6 weeks. At 25°C the dimer rate was unchanged over time. At 50°C the rate of dimer increased linearly over time for each product. See figure 1. As expected, the products with an increased content of 2,4'-isomer had lower amounts of dimer formation. RUBINATE 1680 and SUPRASEC 9561 had very similar formation rates, while the competitive product showed the highest rate of dimer formation.

In addition to dimer monitoring, % haze measurements were taken over the six weeks as well. Overall, the products at 25°C had a higher % haze after 6 weeks than the products stored at 50°C. See tables 3 and 4. Although it would seem more likely for the samples at 50°C to become hazier due to a higher dimer formation, the opposite occurs. At the higher temperature, the solubility of the dimer actually increases and so the products remain clear.

Viscosity was also tested every two weeks at both 25°C and 50°C. For each product, the viscosity remained stable and unchanged over the six week period.

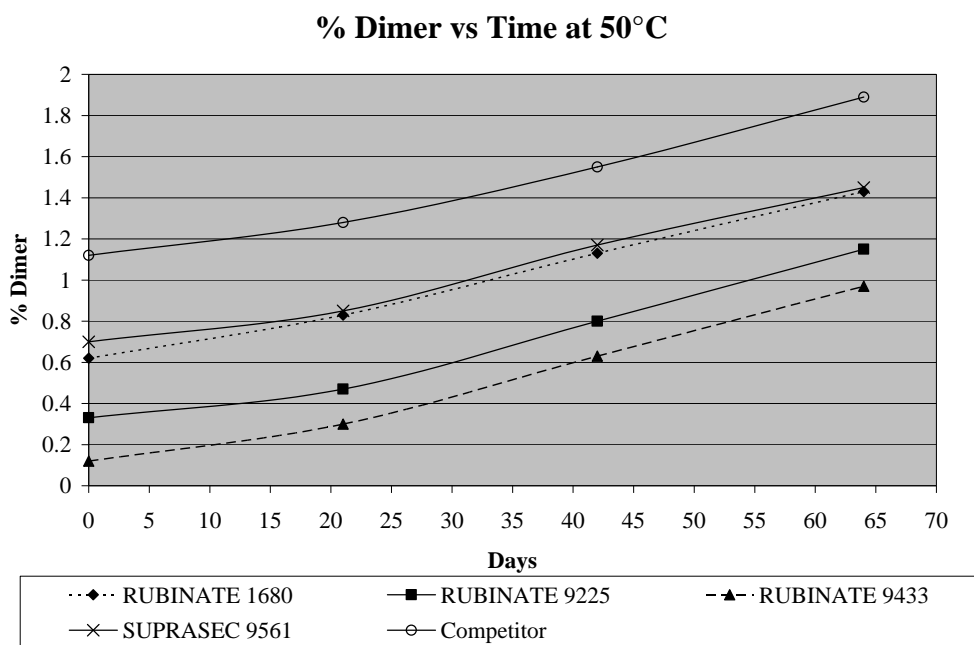


Figure 1: Dimer concentration versus time at 50°C

Table 3: % Haze at 25°C

Days	R1680	S9561	Comp	R9225	R9433
0	9.14	5.33	43.96	34.54	24.41
20	62.25	5.74	85.99	77.46	80.79
40	87.95	7.54	87.66	71.31	80.59
60	88.11	32.72	88.73	72.31	81.95

Table 4: % Haze at 50°C

Days	R1680	S9561	Comp	R9225	R9433
0	7.9	3.09	43.96	2.08	3.36
20	9.14	4.62	52.45	10.16	20.64
40	44.91	5.33	60.74	13.09	24.21
60	64.48	7.07	78.65	34.54	31.20

Elastomers

Three different resin systems were evaluated in order to highlight the broad range of hardness and flexibility that can be achieved with “liquid pure” MDI thru resin selection. Tables 5, 6, and 7 below summarize the raw material components and approximate % hard block of each system. Table 5 provides the formulation for a flexible elastomer with medium hardness. Both “liquid pure” MDI’s and 16% NCO prepolymers were used in the preparation of elastomers using this resin system. 16% NCO prepolymers provided a hard block content around 31% and a final elastomer hardness of approximately 70 Shore A. “Liquid pure” MDI’s had slightly more crosslinking at a hard block content of 37% and corresponding hardness of 80 Shore A. Table 6 provides the formulation for very soft elastomers with low hardness. Only 16% NCO prepolymers were evaluated with this system providing a hard block content of 14% and a 75 shore OO hardness. Table 7 provides the formulation of a resin blend for a very rigid elastomer with high hardness. Only “liquid pure” MDI’s were used to achieve these very hard elastomers providing hard block content of 47% and a 80 Shore D hardness.

It is important to note that hard block content and shore hardness have been listed as an average value for each resin system listed in the tables below.

Table 5: Resin for 70 & 80 Shore A elastomers

<i>Component</i>	<i>Pbw</i>
Jeffol G-31-35	91.5
Ethylene Glycol	8.0
Jeffcat TD 33A	0.25
Fomrez UL-1	0.005
BYK A 535	0.25

Hard block content~31% (70 Shore A elastomers)

Hard block content~37% (80 Shore A elastomers)

Table 6: Resin for 75 Shore OO elastomers

<i>Component</i>	<i>Pbw</i>
Jeffol G-31-35	48.9
Jeffol PPG 3709	48.9
Ethylene Glycol	1.0
Jeffcat TD 33A	1.0
Fomrez UL-1	0.025
BYK A 535	0.25

Hard block content~14%

Table 7: Resin for 80 Shore D elastomers

<i>Component</i>	<i>Pbw</i>
Jeffol G-30-240	94.64
Ethylene Glycol	4.9
Jeffcat TD 33A	0.199
Fomrez UL-1	0.01
BYK A 535	0.25

Hard block content~47%

Physical properties

Figures 2, 4, and 6 show tensile and elongation values for the 70 and 80 Shore A, and 75 Shore OO elastomers. A clear trend is repeated in each figure. Tensile values are consistently highest for RUBINATE 1680 which has the highest functionality and the highest amount of 4,4'-isomer designated by *HH* in each figure. The additional functionality provides extra crosslinking which improves tensile strength. The organized crystallinity provided by the 4,4'-isomer also contributes to the high tensile strength. Functionality has an opposite affect on the % elongation. The elongation consistently increases with a decrease in functionality as displayed in the graphs. For each elastomer set RUBINATE 9433 consistently has the highest elongation value corresponding to its low functionality.

Figures 3, 5, and 7 show tear values for both the 70 and 80 Shore A, and 75 Shore OO elastomers. It is easily seen that as functionality decreases and 2,4'-isomer ratio increases, the values of Die C are improved. This is mainly due to the disorganized hard blocks formed by the 2,4'-isomer which provide additional resistance to tear.

Figures 6 and 7 present Heat Deflection Temperature (HDT) and Charpy Impact which are two very common tests for very hard, highly crosslinked elastomers. The HDT results demonstrate that the higher functional isocyanates have higher crosslinking and therefore withstand higher temperatures before deflecting. As functionality decreases, the temperature required for deflection decreases as well. The impact test also reflects this trend in a similar way. More highly crosslinked isocyanates display higher impact strength as presented in the graph.

Table 8 below shows the glass transition temperature data for the very hard, highly crosslinked elastomers. The data corresponds well to the HDT results. RUBINATE 1680 (*HH*), with high functionality and high 4,4'-isomer has the highest glass transition temperature. As expected, the least crosslinked isocyanate RUBINATE 9433 (*LL*), with low functionality and low 4,4'-isomer has the lowest glass transition temperature.

Reactivities

Table 9 presents gel times for each set of elastomers. Regardless of which resin blend is used, RUBINATE 1680 has the quickest reactivity followed by SUPRASEC 9561 and the competitor product. The reactivity of the elastomer is greatly affected by the amount of 2,4'-isomer present in the isocyanate. As a general rule the 2,4'-isomer is significantly less reactive than the 4,4'-isomer. The higher levels of 2,4'-isomer in both RUBINATE 9225 and RUBINATE 9433 cause a significant decrease in gel time compared to the other MDI's and prepolymers.

Table 8: Glass transition temperature in (°C)

	Tg
R 1680, HH	53.1
S 9561, MM	51
Comp, MM	51.1
R 9225, LL	48.6
R 9433, LL	48.5

Table 9: Gel time in seconds

	70 shore A	80 shore A	75 shore OO	80 shore D
R1680, HH	71	55	90	120
S 9561, MM	80	59	92	125
Comp, MM	90	60	98	123
R9225, LL	120	72	100	141
R 9433, LL	135	75	144	155

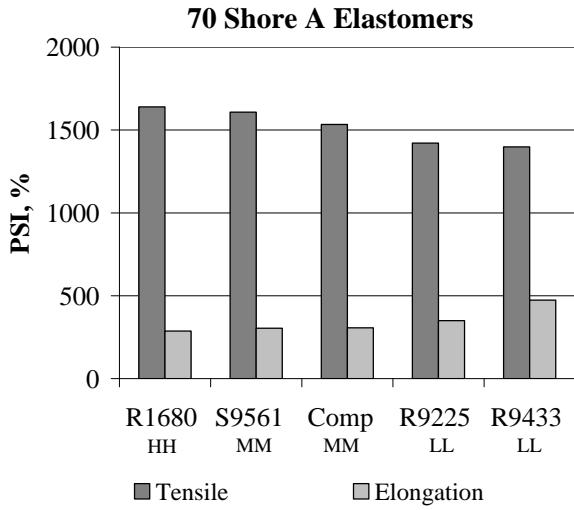


Figure 2: Tensile and elongation

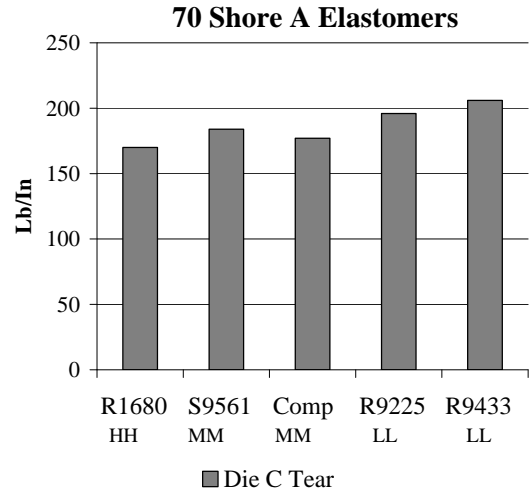


Figure 3: Die C tear

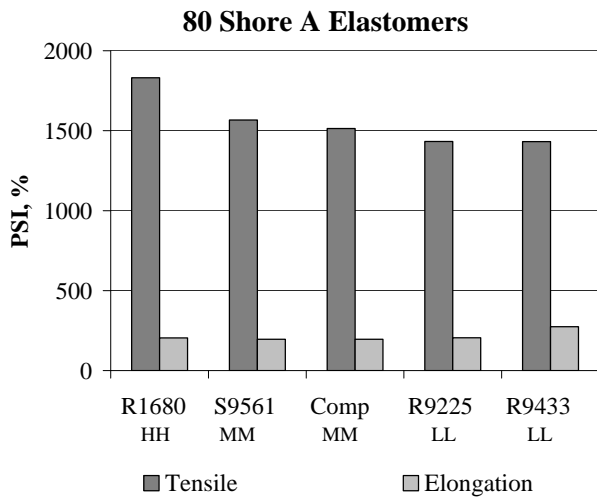


Figure 4: Tensile and elongation

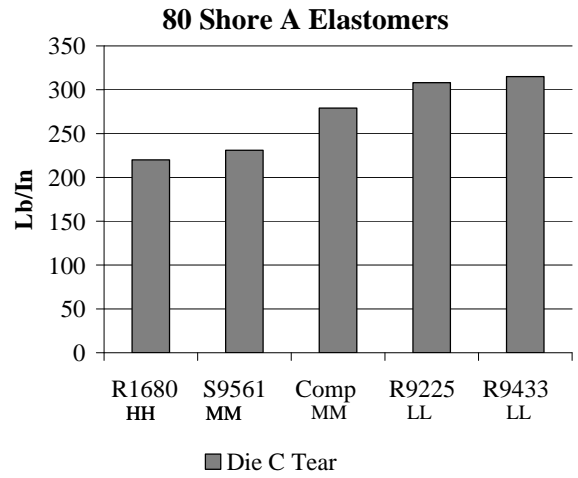


Figure 5: Die C tear

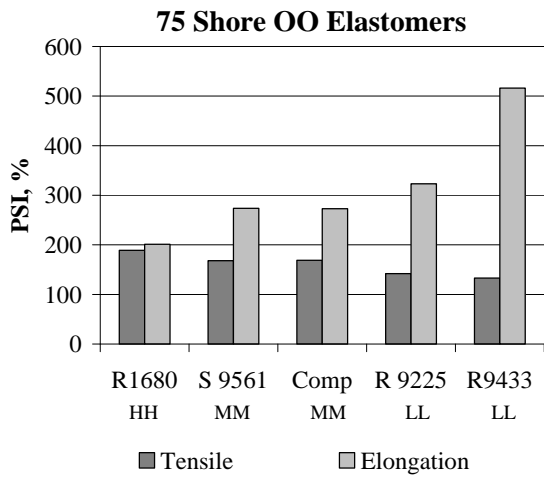


Figure 6: Tensile and elongation

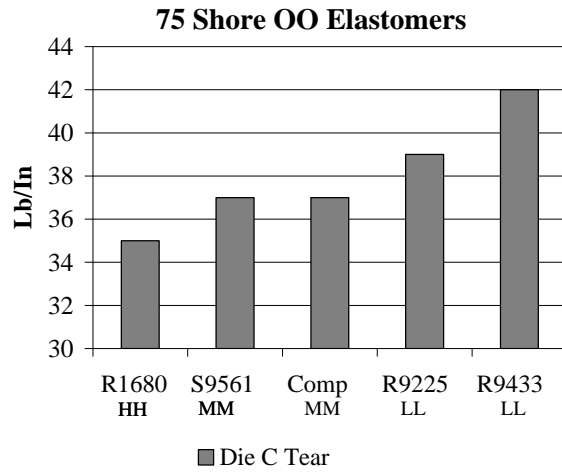


Figure 7: Die C tear

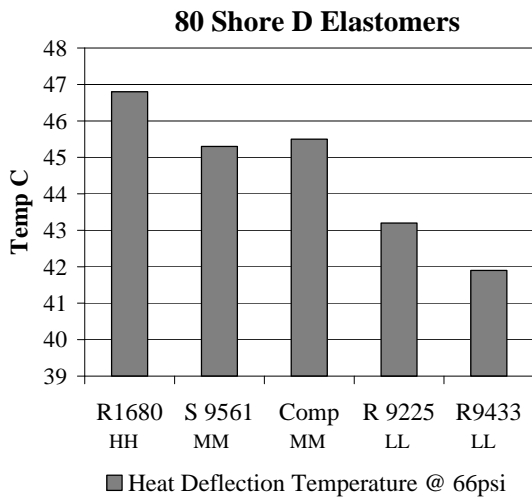


Figure 8: Heat deflection temperature

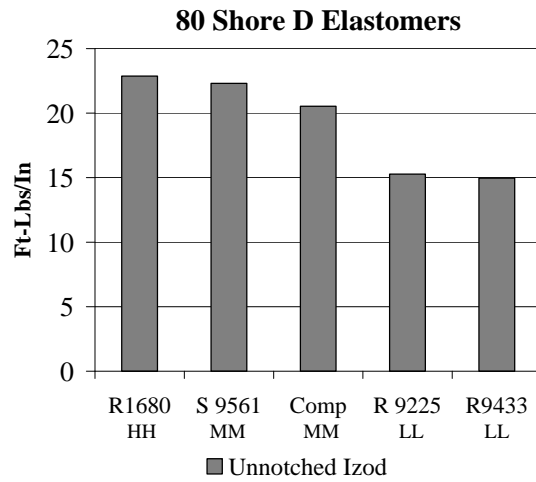


Figure 9: Unnotched Izod

CONCLUSIONS

In continued efforts to improve the overall stability performance of its "liquid pure" products, Huntsman has developed a new modified liquid pure MDI, SUPRASEC 9561 which has improved storage stability, temperature stability, and extended clarity. Under rigorous low temperature stability testing SUPRASEC 9561 demonstrated the ability to remain liquid at temperatures as low as 1°C. In long term stability tests of dimer concentration and haze % at 25°C and 50°C, SUPRASEC 9561 was similar to RUBINATE 1680 in dimer formation and had % haze values lower than any other product for both temperatures. Elastomers prepared from SUPRASEC 9561 maintained high physical properties within close proximity of RUBINATE 1680 in tensile strength, heat deflection temperature, and izod impact test. These qualities make SUPRASEC 9561 a product of choice for a variety of elastomer applications where shelf stability and low temperature performance are critical requirements.

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BIOGRAPHIES

Katie L. Skok



Katie L Skok is currently a Chemical Engineer within the ACE technical service business in Auburn Hills, MI. She has been part of the Polyurethanes business at Huntsman since 2004 and has worked within the Footwear and ACE teams. Katie has a Bachelors Degree in Chemical Engineering from the University of Detroit Mercy. During her years at UDM, Katie worked as a co-op student for three consecutive terms in the ACE group within Huntsman.

Roeland J. Tuinman



Roeland Tuinman received his M.Sc. from the University of Leiden. After receiving his Ph.D. in Organic Chemistry from the University of Michigan, Ann Arbor he joined BASF in 1996 and worked on a variety of CASE projects. In 2001, he joined Foamex International as a Technical Director responsible for R&D in their Technical Products Group. He joined Huntsman Polyurethanes in 2004 and currently serves as the Technical Service Manager for the ACE and Footwear business at their Auburn Hills, MI facility.