



Polyurethane Cast Elastomers with Versalink[®] MCDEA Curative



Obtaining High-Performance Polyurethane Cast Elastomers with Versalink® MCDEA Curative

Introduction

MCDEA curative is now supplied by Air Products under the Versalink® name.

Cast polyurethane technology represents an ideal combination of elastomer performance, processing latitude and economics. Pressures from competitive technologies and demanding applications in the marketplace require manufacturers to seek continuous improvements. In order for cast polyurethane elastomer markets to grow and provide the expanding commercial opportunities that suppliers, processors and end users need, continuing efforts to improve the processability and cost/performance ratio of these materials are required.

One area in which polyurethane elastomers have exhibited significant potential for continued growth is in the dynamic and high-temperature application areas.

Airthane® and Versathane® high-performance TDI prepolymers, when cured with Versalink MCDEA curative, provide significant improvements in dynamic and high-temperature properties compared with commercially available systems. This brochure provides details on:

- Obtaining a 25% improvement in dynamic performance.
- Increasing the service temperature of cast polyurethanes by 25°C or more.
- Obtaining up to a 50% increase in the abrasion resistance of the finished polyurethane elastomer.
- Improving the resilience of the vulcanate by 25% or more.
- Imparting transparent qualities to the finished polyurethane.
- Providing all of these benefits with a low-toxicity material.

Performance

Polyurethane elastomers are composed of long chain polymers which contain regions of differing chemical composition. Those domains containing high concentrations of the isocyanate-curative adduct are referred to as hard segments, while those rich in long chain polyol are called soft segments. If the two regions segregate, the hard segments often crystallize and form domains which act like reinforcing fillers in much the same way that certain types of carbon black reinforce rubber. The performance improvements described here are due in large part to the increased phase segregation obtained in Versalink MCDEA-cured systems relative to MBOCA-cured materials.

Hardness Effects

When a prepolymer is cured with Versalink MCDEA or MBOCA, an obvious difference in the hardness of the final elastomer is observed. As an example, a 2.5% NCO ester-based resin cured with MBOCA produces a 72 Shore A elastomer. However, an 85 Shore A product is obtained when the same resin is cured with Versalink MCDEA curative. Although differences in durometer are often encountered when changing curatives, a variation of this magnitude is surprising. A plausible explanation is that increased phase segregation in the Versalink MCDEA product produces well-defined hard segments which act as reinforcing "filler" and raise both the modulus and the hardness of the elastomer.

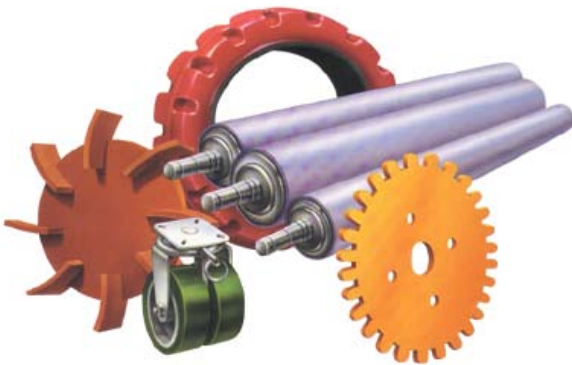
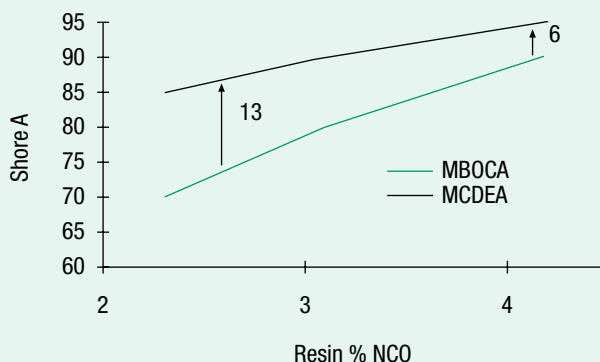
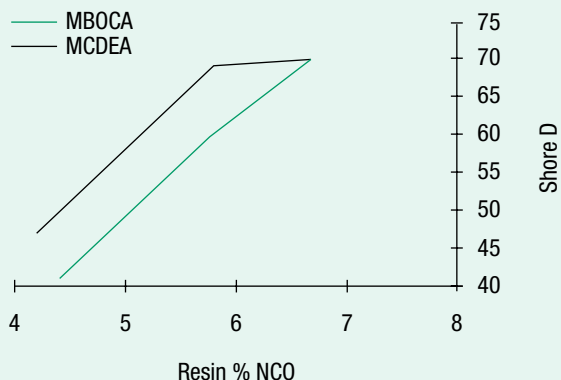
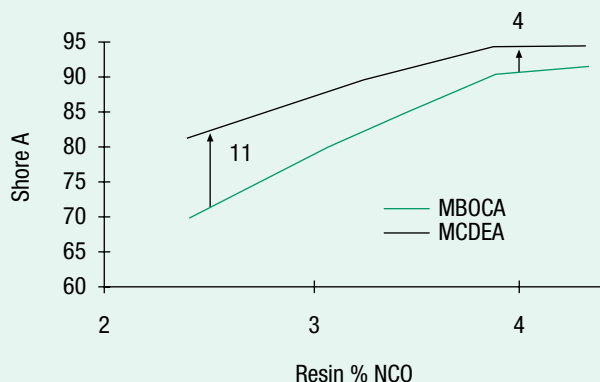
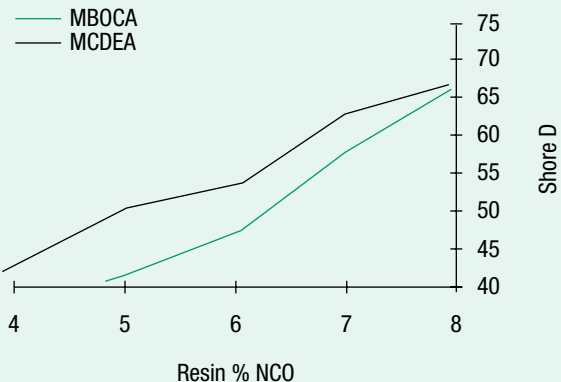


Figure 1**Low % NCO Ester Resins****Figure 2****High % NCO Ester Resins****Figure 3****Low % NCO Ether Resins****Figure 4****High % NCO Ether Resins**

It is interesting to note that the magnitude of the reinforcing effect is a function of both the backbone composition and the isocyanate content of the polyurethane resin. In the previous example, a 13 point hardness difference (85 Shore A vs. 72 Shore A) was obtained with a low % NCO ester-based resin. At higher isocyanate levels, however, the size of the MBOCA-Versalink MCDEA hardness differential decreases. As an example, when a 4.2% prepolymer is cured with MBOCA, an 89 Shore A product results, while Versalink MCDEA curative produces a 95 Shore A elastomer (a hardness increase of 6 Shore A points). The trend

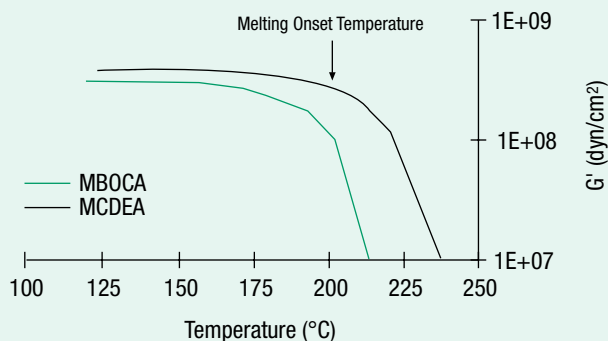
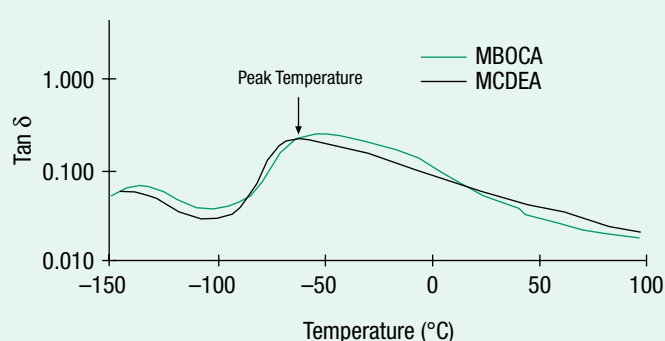
continues with increasing isocyanate content. At an isocyanate level between 6 and 7% NCO, the MBOCA and Versalink MCDEA lines converge and elastomers of equal hardness (70 Shore D) are obtained with both curatives.

These data and trends for ester-based prepolymers cured with Versalink MCDEA and MBOCA are summarized in Figures 1 and 2.

The influence of backbone composition on hardness can be seen by comparing the durometer of ether-based resins similar to the ester-based resin discussed above. If a 2.5% NCO ether resin is cured with MBOCA, a

70 Shore A material is obtained. The Versalink MCDEA-cured composition produces an 81 Shore A elastomer and an 11 point differential relative to MBOCA with the same resin. As in the case of ester resin, the MBOCA and Versalink MCDEA durometers converge with increasing isocyanate content. Consequently, a 4.2% NCO resin produces 90 and 94 Shore A elastomers with MBOCA and Versalink MCDEA curative, respectively.

These data for ether-based resins are summarized in Figures 3 and 4.

Figure 5**Storage Modulus, 4.2% NCO Ether Resin****Figure 6****Tangent Delta, 4.2% NCO Resin****Dynamic Properties**

The consistently higher durometers obtained from resins cured with Versalink MCDEA curative are attributed to improved phase segregation obtained with this curative, relative to MBOCA. The hard domains, which serve to reinforce the elastomer, produce higher hardnesses. The hardness of a material is a function of the storage modulus (G'). In Figure 5, it can be seen that the same resin produces a higher modulus, and consequently, a higher hardness with Versalink MCDEA curative. Better phase segregation also produces a purer and higher melting hard segment. Evidence for this effect is seen in the storage modulus curve, which exhibits a higher melting onset temperature for Versalink MCDEA curative relative to the MBOCA-cured elastomer. Additional evidence for improved phase segregation is found in the tangent delta ($\tan \delta$) curves of Versalink MCDEA and MBOCA-cured resins. In Figure 6, the $\tan \delta$ of a Versalink MCDEA-cured resin is at a maximum at a lower temperature than the MBOCA-cured counterpart. This observation is consistent with improved phase segregation, which leads to a lower transition temperature for the soft segment.

Service Temperature

If comparisons between Versalink MCDEA and MBOCA-cured resins are made on an equal hardness basis, it is still apparent that better phase segregation exists. For example, the storage modulus and $\tan \delta$ of a Versalink MCDEA and a MBOCA-based 95 Shore A elastomer are compared in Figures 7 and 8.

Although the elastomers are of similar hardness (and modulus), the temperatures at which the moduli decrease differ significantly. This improved temperature stability is attributed to a more crystalline hard segment and an improved phase segregation in the Versalink MCDEA-cured system relative to the MBOCA-cured material.

Similar arguments can be made regarding the soft segment based upon the $\tan \delta$ spectra of the Versalink MCDEA and MBOCA cured resins. In phase mixed systems, the $\tan \delta$ curve becomes broad in much the same way that impurities broaden the melting range of chemical compounds. The position of the $\tan \delta$ maximum, associated with the glass transition temperature and the beginning of the rubbery/elastomeric region, is also affected by phase mixing. A pure soft segment will generally have a lower glass transition temperature than a phased mixed one. Thus, the purer soft segments obtained with resins using a Versalink MCDEA curative exhibit sharper and lower glass transition temperatures.

This lower glass transition temperature and the higher melting point described above are characteristics of Versalink MCDEA-cured elastomers, and they translate into a broader service temperature for these materials (see Table 1).

Figure 7

Storage Modulus, 95 Shore A Elastomers

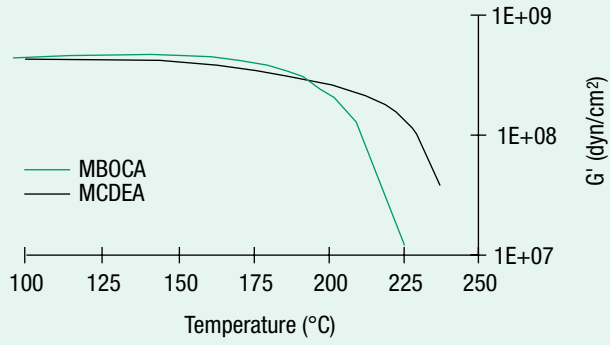


Figure 8

Tangent Delta, 95 Shore A Elastomers

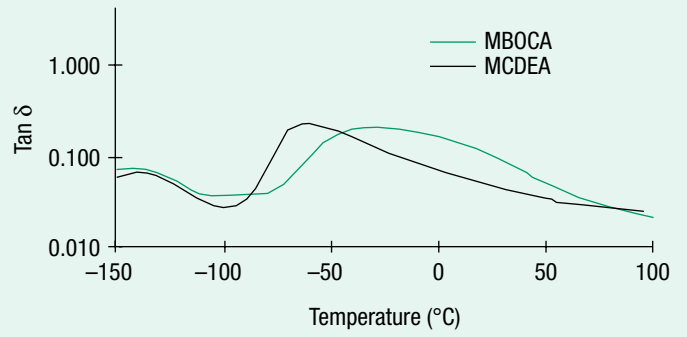
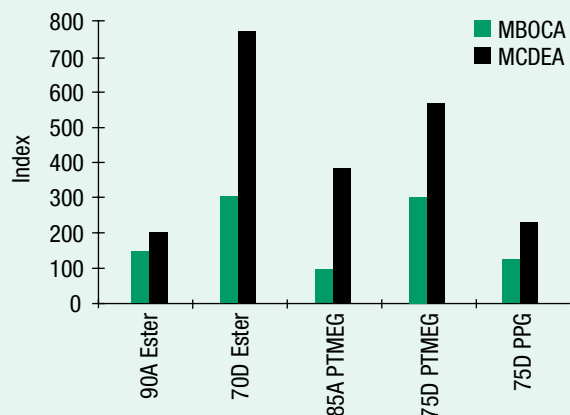
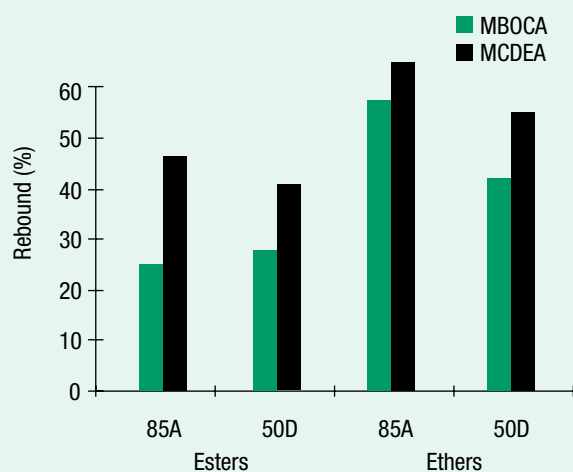


Table 1

Thermal Transitions of MCDEA and MBOCA-Cured Elastomers

		Elastomer System			
		Ether		Ester	
Elastomer Hardness	Transition	MCDEA	MBOCA	MCDEA	MBOCA
85A	T _g (°C)	-70	-67	-25	-23
	T _m (°C)	197	155	195	157
95A	T _g (°C)	-67	-37	-29	5
	T _m (°C)	240	213	237	185
70D	T _g (°C)	-41	-33	4	23
	T _m (°C)	235	215	235	190

Figure 9**Abrasion Index Comparison****Figure 10****Rebound of MCDEA and MBOCA-Cured Resins****Abrasion Resistance**

The use of Versalink MCDEA curative also results in a marked improvement in the dry-sliding abrasion resistance of the final elastomer, as measured by the NBS Abrasion Index (ASTM D1630). Data comparing the performance of Versalink MCDEA and MBOCA-cured ether and ester prepolymers are summarized in Figure 9.

Abrasive wear is a complex phenomenon dependent upon the tear, rebound and high temperature stability of the elastomer in question. Since Versalink MCDEA-cured elastomers exhibit a general improvement in these properties relative to MBOCA-cured systems, it is reasonable that improved abrasion should be obtained.

Rebound

Rebound, or resilience, is a reflection of the energy storage and loss properties of a material. Intuitively, it seems clear that a material with high resilience is able to store energy efficiently, while a low-resilience material absorbs the energy and converts it to heat. Rebound is often a useful predictor of the rolling resistance and heat buildup in dynamic applications such as wheels and rollers.

When compared on an equal hardness basis, Versalink MCDEA-cured elastomers show a clear increase in resilience relative to MBOCA-cured materials (Figure 10). This improvement is consistent with the general elevation of dynamic properties seen in Versalink MCDEA-cured systems.

Clarity

It has been observed that Versalink MCDEA-cured elastomers are often more transparent than the corresponding MBOCA-cured systems. Optical properties are affected by the polymer morphology. If hard and soft block segments form domains which are large enough to interact with light, the bulk polymer is opaque. The dynamic data discussed previously suggests that Versalink MCDEA-cured systems are phase segregated. If these elastomers have reduced phase mixing and are transparent, the domain sizes must be small compared with the wavelength of visible light.

Toxicity

Table 2 shows a comparison of the properties of Versalink MCDEA and MBOCA with regard to toxicity. The comparison shows that the structures are similar and that they are both aromatic diamines which contain chlorine. Versalink MCDEA curative also contains ethyl groups which hinder the reactivity of the amine. In addition, Versalink MCDEA curative has not been shown to be mutagenic or genotoxic in a battery of tests.

Please refer to the Versalink MCDEA curative Material Safety Data Sheet (MSDS), available on request from Air Products, for all safety and handling information for this product.

Table 2**Health and Safety Comparison—MCDEA Curative vs. MBOCA**

	MCDEA	MBOCA
Chemical Name	4,4' methylene bis (3-chloro-2,6 diethyl aniline)	4,4' methylene bis (2-chloro aniline)
Chemical Structure		
Acute Toxicity <ul style="list-style-type: none"> • Oral LD50 (rat) • Dermal LD50 (rat) • Ames 	>5000 mg/kg >2000 mg/kg Negative	750 mg/kg No data Positive
OSHA PEL ACGIH TLV	No PEL or TLV has been established.	No PEL has been established. TLV-TWA 0.01 ppm
HMIS Code <ul style="list-style-type: none"> • Health • Flammability • Reactivity 	1 1 0	2 1 1
CA Proposition 65	Not regulated	Regulated
TSCA	CAS #106246-33-7 Included on inventory	CAS #101-14-4 Included on inventory
DOT	Not regulated	RQ – hazardous substance, solid N.O.S., ORM-E, NA9188
EPA SARA Title III Section 313 (40 CFR 372)	No requirements	Subject to reporting requirement
Carcinogenicity <ul style="list-style-type: none"> • IARC • ACGIH • NTP 	Not Listed Not Listed Not Listed	1 (Carcinogenic to humans based on mechanistic and other relevant data) A2 (suspected human carcinogen) Anticipated carcinogen

Alternative Systems

Vulkollan® castable polyurethane is recognized as the leader in the area of dynamic polyurethane elastomer performance. This product is prepared by the reaction of naphthalene diisocyanate (NDI) with one of several adipate ester polyols to produce a prepolymer which is then cured with short chain diols like 1,4 BDO. The resulting network has been remarkably successful in high-load and high-temperature applications.

However, there are drawbacks with the use of the Vulkollan System. First, NDI does not produce shelf-stable prepolymers—the pro-

cessor is required to react the isocyanate and polyol to make the prepolymer on-site. The curative is then added to the newly produced prepolymer to make a finished elastomer. Gel times are rapid, so machine processing is essential. Additionally, cure schedules can be complex. Thick profiles require complex cure schedules with cycles of cure temperature at 100°C for 12–24 hours followed by 1–5 days at room temperature. Additionally, shrinkage can be substantial, resulting in part cracking when complex geometries or long dimensions are involved. Added complications in the processing of NDI-based systems include

health and safety concerns associated with the isocyanate. The data in Table 3 show that Airthane-Versalink MCDEA elastomers compare favorably with Vulkollan. Static properties such as tensile, tear, compression set and rebound are nearly equal to those of Vulkollan. High-temperature performance is also similar, with the hard segment melting point being equal. Although actual service temperatures must be measured in the field, the hard segment melting point does give an indication of the level of performance.

Table 3

Comparison of Elastomers Based on MCDEA-Cured Airthane with Vulkollan 27

Elastomer System	Vulkollan 27	Airthane PET-91A/MCDEA	Airthane PST-90A/MCDEA
Type	NDI-Ester	TDI-Ether	TDI-Ester
Hardness (Shore A)	93	92	95
Tensile Strength (psi)	5730	5195	8285
Tensile Tear (pli)	640	582	785
Split Tear (pli)	163	57	151
Compression Set (%)	18	20	23
Rebound (%)	50	57	43
Stress at 10% Deflection (psi)	455	610	840
Loss Compliance Area			
0 → 150°C	67	142	209
-78 → 150°C	101	270	259
Hard Segment Melting Point (°C)	239	240	237

The loss compliance is a function of the loss and storage moduli. The area under the loss compliance curve (Figure 11) is an indicator of the tendency of the material to convert mechanical energy to heat. The smaller the area, the less mechanical energy is converted to heat and the better the dynamic performance of the elastomer. Low loss compliance values for Vulkollan indicate superior dynamic performance. The Airthane-Versalink MCDEA elastomers are superior to conventional MBOCA-cured systems and generate approximately 85% of the dynamic performance obtained with Vulkollan.

Prepolymers based upon pPDI (paraphenylene diisocyanate) also offer dynamic performance improvements. However, they have unfavorable cost/performance characteristics and processing drawbacks similar to NDI. They pose serious safety concerns with respect to free monomer. The pPDI monomer is considered a Class B poison and has a vapor pressure similar to TDI. Since all pPDI prepolymers contain unreacted pPDI, it is possible to vaporize the free monomer upon heating. Exposure to pPDI can cause severe irritation to eyes, skin, mucous membranes and the respiratory system. Therefore, care should be taken to operate in well-ventilated areas and to wear appropriate protective clothing. Although pPDI and TDI have similar vapor pressures, not all TDI prepolymers are high in free monomer content. Airthane prepolymers contain less than 0.1% free TDI monomer—therefore they are considered nonhazardous.

The properties obtained with a commercial pPDI-polyester prepolymer compared with ether and ester-based Airthane-Versalink MCDEA systems are summarized in Table 4. The data show the static properties of the materials to be similar. The dynamic performance comparison, as measured by the area under the loss-compliance curve, remains slightly more favorable for the pPDI product compared with the Versalink MCDEA-cured elastomers. A critical difference between the systems is the high-temperature properties. The Airthane-Versalink product has a higher hard segment melting point than the pPDI-based material. This 50°C difference implies that higher service temperatures are obtainable with the former material. Preliminary field testing corroborates this prediction.

Figure 11

Representative Loss Compliance Area

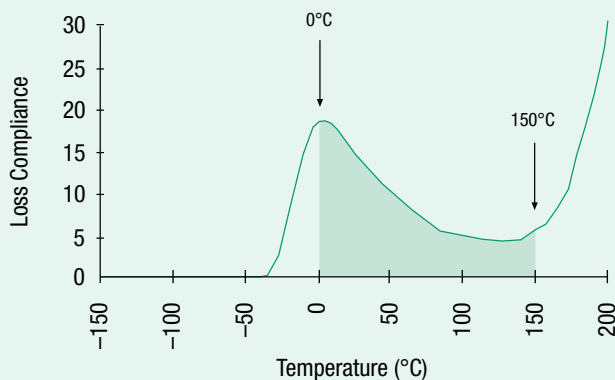


Table 4

Comparison of Elastomers Based on MCDEA-Cured Airthane with pPDI Ester Properties

Elastomer System	Adiprene® PP1095	Airthane PET-91A/MCDEA	Airthane PST-90A/MCDEA
Type	pPDI-Ester	TDI-Ether	TDI-Ester
Hardness (Shore A)	95	92	95
Tensile Strength (psi)	6300	5195	8285
Tensile Tear (pli)	705	582	785
Split Tear (pli)	—	57	151
Compression Set (%)	37	20	23
Rebound (%)	55	57	43
Stress at 10% Deflection (psi)	675	610	840
Loss Compliance Area			
0 → 150°C	151	142	209
-78 → 150°C	231	270	259
Hard Segment Melting Point (°C)	185	240	237

Elastomer Properties for Versalink MCDEA and Airthane/Versathane TDI Prepolymers

Air Products does not produce finished elastomer or fabricated parts. Rather, we supply both polyester and polyether prepolymers under the names Airthane and Versathane polyurethane

prepolymers. We also supply a variety of high performance curatives, including Versalink MCDEA. These materials are used by fabricators to produce molded polyurethane elastomers.

The following tables (Table 5 and 6) summarize the most important physical properties

obtainable using Versalink MCDEA and selected products from our two prepolymer product lines: Airthane and Versathane. Note that all elastomers listed in these tables have been post cured using the recommended conditions for Versalink MCDEA discussed in the Processing Guidelines section on the following pages.

Table 5

	Airthane® TDI Prepolymers					
	Polyether Grades				Polyester Grades	
	PET-95A	PET-93A	PET-91A	PET-80A	PST-90A	PST-80A
Prepolymer Properties						
Processing Conditions						
Curative Level, 95% Stoichiometry (pph)	26.6	21.9	17.1	11.2	17.9	12.7
Airthane Prepolymer Temperature (°C)	55	55	80	80	80	85
Pot Life (min)—85°C	2	3	4	5	3	3.5
Mold Temperature (°C)	100	100	130	100	130	100
Demold Time (min)	15	20	30	60	30	60
Post Cure (hrs/temp °C)	48/130	48/130	48/130	48/130	48/130	48/130
Elastomer Properties						
Hardness						
Shore A		96	92	85	95	90
Shore D	60	49	42		45	
Modulus (psi)						
100% Elongation	3065	2055	1270	900	1535	1200
200% Elongation	5410	3035	1485	1100	1695	1500
300% Elongation			1870	2000	2065	2000
Tensile Strength (psi)	6710	4535	5195	3700	8285	8200
Elongation (%)	209	258	479	535	566	540
Tear Resistance (pli)						
Die C	562	462	582	347	785	540
Split	69	52	57	44	151	130
Trouser			86		350	
Compressive Stress (psi)						
5% Deflection			370		530	
10% Deflection			610		840	
15% Deflection			840		1135	
20% Deflection			1110		1500	
25% Deflection			1460		1730	
Compression Set (%)	25	25	20	17	23	31
Rebound (%)	59	57	57	70	43	40
NBS Abrasion Index	280	240	220	260	219	200

Table 6

	Versathane® TDI Prepolymers			
	Polyether Grade	Polyester Grades		
	2070	A-7QM	A-85	A-9
Processing Conditions				
Curative Level, 95% Stoichiometry (pph)	10.2	10.3	14.7	18.0
Versathane Prepolymer Temperature (°C)	80	85	100	80
Pot Life (min)— 80°C	5	3.5	1.5	3
Mold Temperature (°C)	100	100	100	130
Demold Time (min)	60	60	60	30
Post Cure (hrs/temp °C)	48/130	48/130	48/130	48/130
Elastomer Properties				
Hardness				
Shore A	85	87	95	95
Shore D				50
Modulus (psi)				
100% Elongation	700	800	1400	1630
200% Elongation	900	1000	1700	1835
300% Elongation	1300	1300	2300	2335
Tensile Strength (psi)	3400	4900	7900	8415
Elongation (%)	460	580	550	567
Tear Resistance (pli)				
Die C	350	450	621	633
Split	55	110	159	157
Trouser	—	—	—	290
Compressive Stress (psi)				
5% Deflection				630
10% Deflection				950
15% Deflection				1270
20% Deflection				1675
25% Deflection				2200
Compression Set (%)	27	27	32	25
Rebound (%)	66	46	41	43
NBS Abrasion Index	210	160	250	260

Processing Guidelines

Appearance and Form

Versalink MCDEA curative is an off-white solid with a minimum purity of 98%. It can be handled similarly to other solid aromatic diamines like MBOCA, where solid is melted in appropriate processing equipment.

Melting

The melting point of Versalink MCDEA curative is 88–90°C, and it is typically processed at 100°C. These temperatures are lower than the 101°C melting point and 120°C processing temperature associated with MBOCA. Like MBOCA, however, Versalink MCDEA curative can be supercooled and the material will remain liquid for brief periods below the melting point.

Equivalent Weight

Versalink MCDEA curative has an equivalent weight of approximately 190 gm/eq. Compared with the equivalent weight of 133 gm/eq. for MBOCA, roughly 40% more Versalink MCDEA curative by weight is required when using prepolymers with the same % NCO content. For example, a 5% NCO prepolymer processed at 95% stoichiometry would require 15 pph of MBOCA or 21 pph of Versalink MCDEA curative. A lower % NCO product is often used with Versalink MCDEA since this curative produces elastomers with higher hardnesses than MBOCA. Please consult Air Products' data sheets for specific physical properties.

Pot Life

The pot life for Versalink MCDEA curative-based systems can be as much as 50% shorter than that of MBOCA. Machine processing may be required for high-hardness systems. In order to offset the faster pot life, it is recommended that lower viscosity products be used, such as Airthane prepolymers. Using Airthane prepolymers allows the processor to reduce the resin temperature from 90°C to 70°C for polyethers, and from 100°C to 85°C for polyesters. The lower temperatures will increase the working life of Versalink MCDEA curative-based systems to a manageable level.

Post-Cure

Post-cure conditions have a dramatic impact on elastomer properties.

The processor can post-cure an Airthane or Versathane TDI prepolymer-Versalink MCDEA curative system using the traditional 16 hours at 100°C. However, changing the post-cure conditions to 48 hours at 130°C will provide the optimum balance of physical properties such as abrasion resistance, dynamics, tensile, tear and compression set.

Table 7 highlights the changes in elastomer properties which occur with extended high-temperature post-curing.

Table 7

Effect of Post-Cure on the Properties of Airthane PST-90A Prepolymer Cured with MCDEA Curative

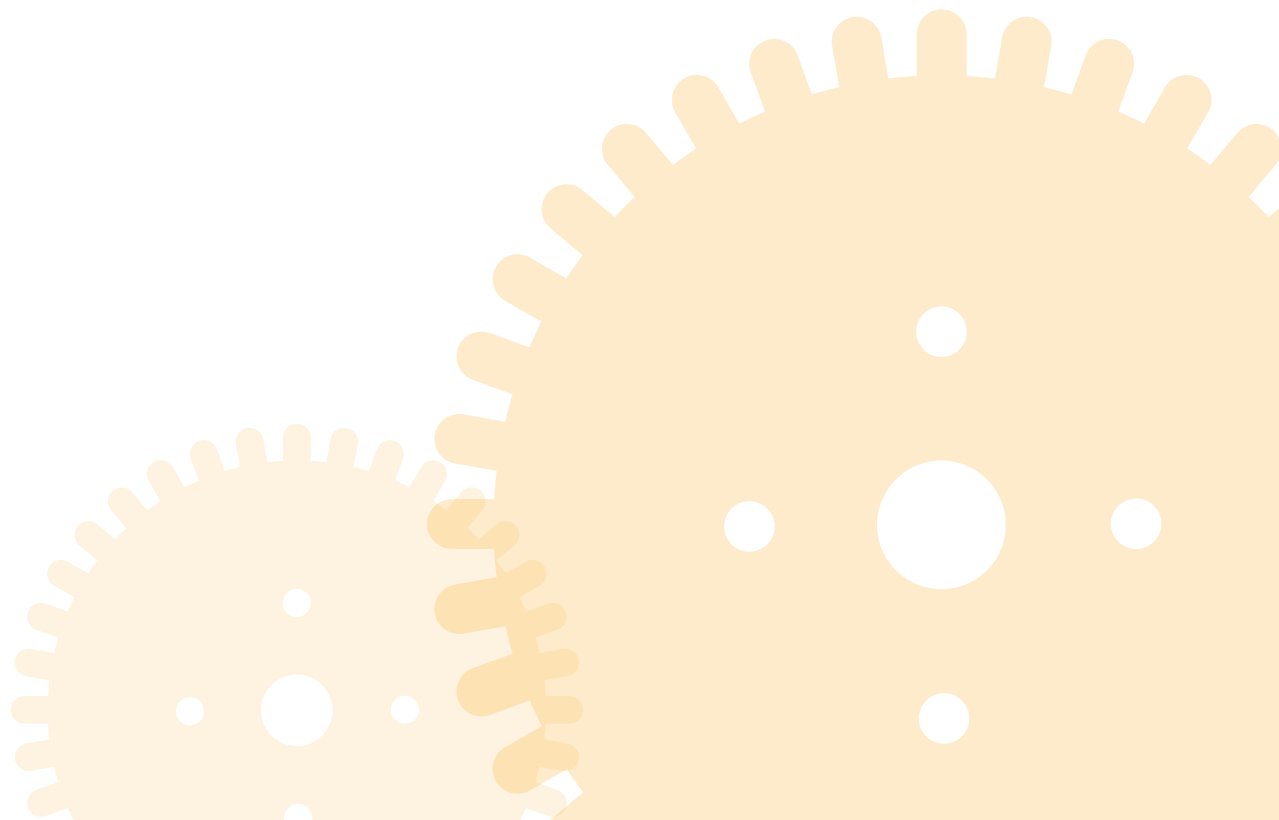
Post-Cure Conditions (Hours/Temperature °C)	48/130	16/100
Hardness (Shore A)	95	94
Tensile Strength (psi)	8285	6900
Tensile Tear (pli)	785	719
Split Tear (pli)	151	132
Compression Set (%)	23	33
Rebound (%)	43	44
NBS Abrasion Index (%)	219	162
Stress at 10% Deflection (psi)	840	915
Loss Compliance Area		
0 → 150°C	209	274
-78 → 150°C	259	329
Hard Segment Melting Point (°C)	237	242



“Your Air Products PSP team has a basic, all-important mission:

To understand your needs so that we meet and/or exceed your expectations, adding value wherever we can all along our global supply chain.”

*Dr. Mark Conner
Technical Director*



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