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POLYMEG® **Polyols**

Applications

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POLYMEG® Polyol Applications

POLYMEG® polyols are polytetramethylene ether glycols (PTMEG) produced by polymerizing tetrahydrofuron. POLYMEG polyols are linear diols with a backbone of repeating tetramethylene units connected by ether linkages. The chains are capped with primary hydroxyl units.

The primary applications for POLYMEG polyols are as the soft segment of polyurethanes, copolymer polyesters and polyamide elastomers. As a component of urethane elastomers, the polyols are used in the following systems:

- **Thermoplastics for injection molding and extrusion**
- **Thermoset polyurethanes, castable prepolymers, millable gums**
- **Metal and textile coatings/linings and adhesives**
- **Spandex elastic fibers**

POLYMEG polyols are used as the soft segment of elastomers to provide:

- **Good mechanical properties and excellent resiliency over a wide range of temperatures**
- **Superior dynamic properties (minimum heat build-up)**
- **Low temperature flexibility**
- **Good reactivity (bi-functional primary alcohol)**
- **Excellent abrasion resistance**
- **Good tear strength**
- **Superior hydrolytic stability (resistance to high temperature, humidity and salt water)**
- **Good microbial resistance**
- **Good elastomer film clarity**
- **High moisture vapor transmission**

Elastomer Applications

High performance elastomers made with POLYMEG polyols are used in a large number of applications. POLYMEG polyols form the soft segment of polyurethane, copolymer polyester and copolymer polyamide elastomers. Thermoplastic elastomers made with POLYMEG polyols can be processed into finished articles by injection molding or extrusion. Polyurethane articles can also be made by low pressure processes (casting or compression molding) by filling a mold before the polymer viscosity increases from the curing reaction. Common applications are:

<u>Automotive</u>

Body fasteners, electrical boots, suspension system parts, seals and gaskets, belts, taillight assemblies, battery covers, hoses, covers for electronics, adhesives, bushings, bump stops, interlayer for laminates, air bag covers, transmission boots.

<u>Adhesives and Sealants</u>

Shoes, laminated security glazing, aerospace, marine, magnetic media binders, construction.

<u>Coatings</u>

Floor, roof, wire and cable, fiber optics, waterborne, radiation curable, fabric, aircraft, pipe, concrete, vinyl.

<u>Engineered Components</u>

Gears, sprockets, printer rolls, belts, wheels, fork lift tires, escalator wheels, heavy-duty casters.

<u>Industrial</u>

Lined pipe, water valves, pump impellers, hopper car liners, conveyor belts, grain buckets, grain chute liners, marine bumpers, buoys, marine hoses, mining screens, cyclone liners, cattle tags.

<u>Sports</u>

Roller wheels, ski boots, bicycle tires, horseshoes, athletic shoes.

<u>Clothing</u>

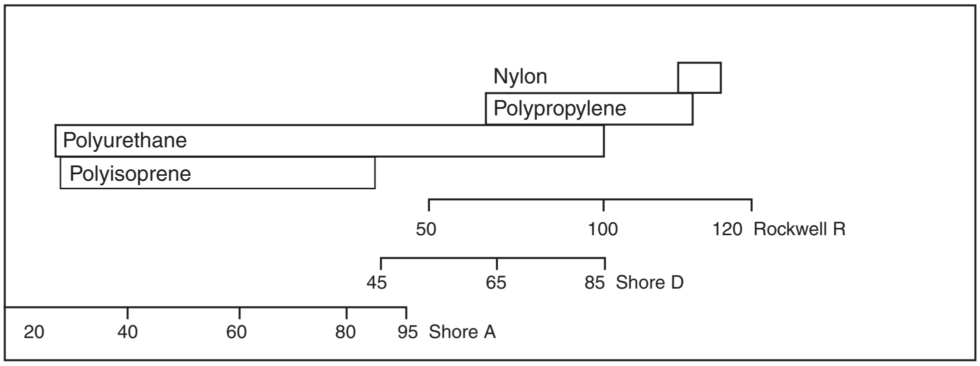
Shoes, upholstery, luggage, fabric coatings, synthetic leather, spandex fiber in sportswear, underwear, fashionwear.

Properties of Polyurethane Elastomers

The composition of polyurethane elastomers can be varied to produce hard and stiff to soft and rubbery materials. The formulator has a wide variety of raw materials that can be used to modify the properties of the elastomer. For systems based upon POLYMEG polyols, the primary variables available to the formulator are the molecular weight of POLYMEG polyols, the type of diisocyanate and the type of extender. As the weight fraction of hard segment (diisocyanate plus extender) is increased, the hardness of the elastomer increases. More subtle changes in the elastomer can be made by varying the isocyanate/hydroxyl ratio; adding crosslinking agents; using a different catalyst; and changing the polymerization process used to produce the elastomer. Figure 1 shows that by changing these variables, polyurethane polymers can be produced which overlap the hardness of soft rubbers to hard thermoplastics.

The largest volume of commercial polyurethane elastomers are made from toluene diisocyanate (TDI) or diphenylmethane-4,4'-diisocyanate (MDI). Typically elastomers made with TDI are extended with an aromatic diamine and elastomers made with MDI are extended with butanediol, except for spandex fibers, which are diamine extended.

Figure 1. Hardness of Polyurethane



Polyurethane Preparation

Polyurethanes made from POLYMEG polyols are prepared by reacting POLYMEG polyols and an extender with a diisocyanate. POLYMEG polyols and the extender can be mixed and added to the diisocyante or the POLYMEG polyols can be reacted first with the diisocyanate to form a prepolymer that is reacted with the extender to form the final polyurethane.

Diisocyanates

The common aromatic diisocyanates used to produce elastomers are MDI and TDI. Smaller amounts of aliphatic diisocyanates (4,4'-methylenebis (cyclohexylisocyanate) HMDI) are used to make low color, light stable polymers. A number of diisocyanates are available for formulating special products (1).

POLYMEG Polyols Molecular Weight

For a simple system of diisocyanate, extender and POLYMEG polyols, elastomers of similar hardness can be made with a POLYMEG polyol of molecular weight 650 to 2000 by keeping the POLYMEG polyol's weight fraction the same in the formulations. The choice of which POLYMEG polyol molecular weight to use for an elastomer is a compromise between properties and processing difficulty. The degree of phase separation of the soft from the hard segment increases as the molecular weight of the POLYMEG polyol increases. The better phase separation gives improved resilience and hysteresis properties and better low temperature ductility. The trade-off is that the viscosity increase associated with the increase in POLYMEG polyol molecular weight makes processing more difficult.

Extenders

Lower molecular weight diols or diamines are used to produce the hard segment of polyurethanes. The hard segment has a high glass transition (T*g*) and melting (T*m*) temperature. Phase separation of the hard segment from the POLYMEG polyols soft segment (-86 T*g*) provides the mechanism for the elastomeric properties of polyurethanes (2). The diols/diamines are called extenders because they are often added to a prepolymer to produce a high molecular weight polyurethane. For an extender to work in an application, it must give a polymer with the desired mechanical properties as well as meet the requirements of the preparation and conversion processes.

1,4-Butanediol (BDO) is the most common diol used with MDI to produce linear thermoplastic polyurethanes for injection molding, extrusion and cast applications. Polymers with higher temperature resistance can be made with hydroquinone di-(β-hydroxyethyl) ether (HQEE) or resorcinol di-(β-hydroxyethyl) ether. Softer and clearer elastomers can be made with diols which retard crystallization of the hard segment; for example, 2-methyl-1,3-propanediol or 1,5-pentanediol. The cure time of diol-extended polyurethanes is controlled by reaction temperature and addition of catalysts.

Aliphatic diamines are used to produce polyurethanes in solution (spandex and coatings), but are too reactive for cast applications. Isocyanate reactivity is in the order of aliphatic diamines >> aromatic diamines > alcohols ≥ water. Polyurethanes made from diamines have melting points too high to be processed as thermoplastics. Methylene-bis-o-chloroaniline (MOCA) and bis(methylthio)toluenediamine (Ethacure® 300) are commonly used aromatic diamines which give acceptable cure times for cast applications.

Stoichiometry

For polyurethanes, stoichiometry has more than the expected effect for an A-A, B-B step-growth polymerization. Theoretically, the molecular weight of the polymer is highest when the moles of diisocyanate are equal to the moles of diol/diamine. However, polyurethanes are often formulated with an excess of isocyanate to improve several elastomeric properties during post reaction aging. This post reaction improvement in properties is generally attributed to the formation of thermally reversible allophanate bonds or more permanent crosslinks from biuret or cyanurate bonds. Tensile strength, compression set and resilience improve with excess isocyanate. Elongation, tear strength, and abrasion improve with a deficiency of isocyanate. Properties are more sensitive to variations in stoichiometry for extension with diols than with extension with aromatic diamines.

Reaction Rate

The rate of reaction of isocyanate with alcohols or amines can be influenced by a number of variables. Temperature and added catalyst can be used to adjust the reaction rate. Uncontrolled changes in reaction rate can also be caused by impurities in the raw materials used to produce polyurethanes.

As with most reactions, the reaction rate of isocyanates increases with temperature (roughly 2-3 times for each 10° C increase). The temperature increase caused by the heat given off from the reaction must be considered since as the batch size increases more of the released heat will result in increasing the temperature of the batch. Working with prepolymers (3) reduces the problems associated with controlling temperature because most of the heat is liberated in forming the prepolymer.

Tin catalysts are commonly used to increase reaction rate when producing linear elastomers. Tin catalysts are very active catalysts at low concentrations. Tetrabutyl titanate and zirconium chelates are also effective catalysts. Suppliers of catalysts can provide information on selecting a catalyst for a particular application (4).

The reaction rate of isocyanates can be affected by impurities in the raw materials. The most potent impurities are alkali metal salts of weak acids and some transition metal salts (iron salts being the most common). These metal salts can be strong catalysts for linear and branched reactions. Phosphoric acid can be added at 5-20 ppm to inactivate these metals (3). The presence of acids or peroxides in raw materials can also affect reaction rate.

Ethacure® is a registered trademark of Albermarle Corporation.

Thermoplastic Polyurethanes

Linear polyurethanes can be processed into final products by any of the standard thermoplastic processes (injection molding, extrusion, thermoforming) as well as by low pressure cast processes. Diols are used as extenders (amines give too high melting materials) and aromatic (mainly MDI) and aliphatic diisocyanates are used. See the section on MDI Polyurethanes for some typical formulations.

Thermoset Urethanes

Thermoset elastomers differ from the thermoplastics in that irreversible cross-links are formed when the polymers are chemically cured. The prepolymer method, where the polyol and diisocyanate are first co-reacted and then extended with a diamine or glycol, is generally preferred since it provides better control of chemical reactivity and assures that random polymer chains are established prior to cross-linking.

The one-shot method, in which all three components are reacted at one time, can be very economically efficient. The trade-off is the extreme care and sophistication needed to control the ratios of the process streams. Pot life is controlled by temperature and catalysts. This technique is not used with amine extended systems because of the large reactivity difference between the amine groups and the hydroxyl groups with the isocyanate. The one-shot technique is especially useful in MDI systems where higher molecular weights of polyol (e.g. above 1500) are used, and indeed, is frequently as economical as thermoplastic injection molding. With lower molecular weights, the exothermic nature of the reaction may cause thermal breakdown of the polymer except for articles with thin cross-sections.

Millable gums are also produced for subsequent compounding with reinforcing pigments (e.g., carbon black, silica) on a conventional rubber mill or Banbury mixer. They are then cross-linked to a high molecular weight thermoset elastomer using either peroxides or a sulfur-accelerated cure. Generally, cured elastomers produced from the gums have slightly lower mechanical strength properties than cast elastomers in the same hardness range.

Coatings and Linings

The major share of urethane coated textile fabrics is manufactured using solution or waterborne urethane polymers. The coatings are prepared by dissolving thermoplastic urethane granules in solvent prior to use or by polymerizing the co-reactants directly in solvent. Waterborne urethane dispersions are a significant and growing means of coating both flexible textile fabric and rigid metal surfaces. Aqueous urethanes can be produced as non-ionic, anionic or cationic dispersions by chain-extending, an emulsified, neutralized urethane prepolymer in water. In addition, two package urethane elastomer systems are used extensively for in-place urethane coatings and linings of various metal equipment items. Extruded thin TPU film is also commonly used for fabric coatings.

Spandex Fibers

Spandex fibers are the largest and fastest growing application for PTMEG. PTMEG-based spandex is typically produced by first making a prepolymer of PTMEG and MDI and extending the prepolymer in solution (dimethylacetamide) with a diamine (1). Ethylenediamine is often used as the extender with diethylamine used to control molecular weight. Many variations of extender systems are claimed in patents to modify properties of the fiber. Fibers are formed by pumping the spandex solution through a spinneret and removing the solvent by evaporation (dry-spinning process) or extracting with a solvent (wet-spinning process). Melt-spun spandex can be produced in a non-solvent process by extending the prepolymer with a diol. Melt-spun spandex should have lower capital and operating costs, but at present, only a small amount is produced by this method.

Copolymer Elastomers

Elastomers based on aromatic and alicyclic carboxylic acids and aliphatic polyamides are produced with polymer structures similar to thermoplastic urethanes by using crystalline polyesters or polyamide segments instead of urethanes as the hard segment. Adjusting the degree of hard-segment content provides various hardness grades which can range in flexibility from an equivalence to rubber to as stiff as unreinforced nylon. The polymers are high modulus elastomers with good elongation and tear strength, excellent solvent resistance, and a good combination of high and low temperature physical properties. They also provide good creep resistance, excellent dynamic properties, and good dielectric strength and serviceability over a wide temperature range (5).

TDI-Based Urethane Elastomers

High performance elastomers, with durometers values from 75 Shore A to 68 Shore D can be formulated using POLYMEG polyols with TDI and MOCA. The formulations are readily processible via the prepolymer method using machine or hand cast techniques. These elastomers exhibit general toughness, excellent wear and tear properties along with good oil resistance.

Typical TDI prepolymer formulations needed to achieve various hardness elastomers are shown in Table I, (pg. 9).

In TDI elastomer formulations, either the 100 percent 2,4- or the 80/20 percent 2,4-/2,6- isomer may be used. Comparing the two isomer types, the 100 percent is more expensive and exhibits better prepolymer stability. The percent free isocyanate (% FNCO) does not decrease nor does viscosity advance as rapidly at elevated temperatures. It is less sensitive to moisture and has a longer working pot life which better facilitates hand batching.

To prepare various hardness elastomers, the % FNCO is varied by changing the NCO/OH ratio when the molecular weight of the POLYMEG polyol is held constant. Increasing the % FNCO permits additional diamine to be used, resulting in higher elastomer tensile, modulus, tear, and compression set values. Elongation and abrasion resistance are decreased.

Since free TDI in a prepolymer formulation increases the risk of physiological problems to the user, the NCO/OH ratio should not exceed 2:1. Therefore, at a constant prepolymer NCO/OH ratio, the elastomer hardness is varied by changing the POLYMEG polyol molecular weight (Table II, pg. 9). The % FNCO is inversely proportional to polyol molecular weight. The property trends are in keeping with a given % FNCO. Generally, at the same NCO/OH ratio, the use of low molecular weight POLYMEG gives higher overall physical properties with the exception of elongation, abrasion resistance, and low temperature performance as shown in Table II. The various commercial molecular weight polyols can be blended to provide intermediate properties.

Full properties may not develop for a week or more at room temperature, and compression set will usually continue to improve over a period of 1-3 months.

Table I
Elastomers Based on POLYMEG Polyol / TDI / MOCA

TDI, Isomer Type	100% 2,4				80/20% (2,4/2,6)	
POLYMEG Polyol Molecular weight	1000			2000	1000	
Prepolymer						
Mole ratio, NCO/OH	2/1[1]	1.67/1	2/1	2/1	1.67/1	2/1
%free-NCO in Prepolymer (%FNCO)	7.5	4.3	6.2	3.5	4.3	6.2
Viscosity: 30°C, cps	1800	16500	5500	11000	18000	6000
100°C, cps	385	400	200	450	400	200
Ratio extender to prepolymer						
MOCA (95% stoich.), g/100 g prepolymer	22.7	13.0	18.7	10.6	13.0	18.7
Processing[2]						
Mix Temperature: Prepolymer, °C	70	90	90	90	70	70
Pot life, Min	2	15	5	18	10	3
Properties[3]						
Hardness, Shore A, (D)	(60)	90	96	84	90	96
Tensile Strength						
100% Modulus, psi	2600	1100	1900	935	1100	1750
300% Modulus, psi	4900	1850	3600	1750	1700	2800
Ultimate psi	7900	5000	5500	4400	4000	5000
Elongation, %	360	500	400	475	490	415
Tear Strength: Die C, pli	740	400	450	345	385	465
Split, pli	-	110	200	70	140	240
Bashore Resilience, %	48	46	45	57	50	48
Compression Set, B, %	30	29	33	25	28	34
Abrasion Resistance, g loss (H-18 1000g/1000rev)	0.15	0.13	0.13	0.09	0.13	0.16
Clash-Berg, T_f, °C	-47	-55	-54	-76	-57	-58

[1] 0.75 eq. POLYMEG Polyol 1000/0.25 eq. 1,3-butylene glycol

[2] Mold Temperatures 110°C, extender at 110°C

[3] Post cure 16 hrs., 110°C

Table II
Effects of POLYMEG Polyol Molecular Weight on Properties of Elastomers

Isocyanate: 100% TDI (2,4 isomer)
Curative: MOCA

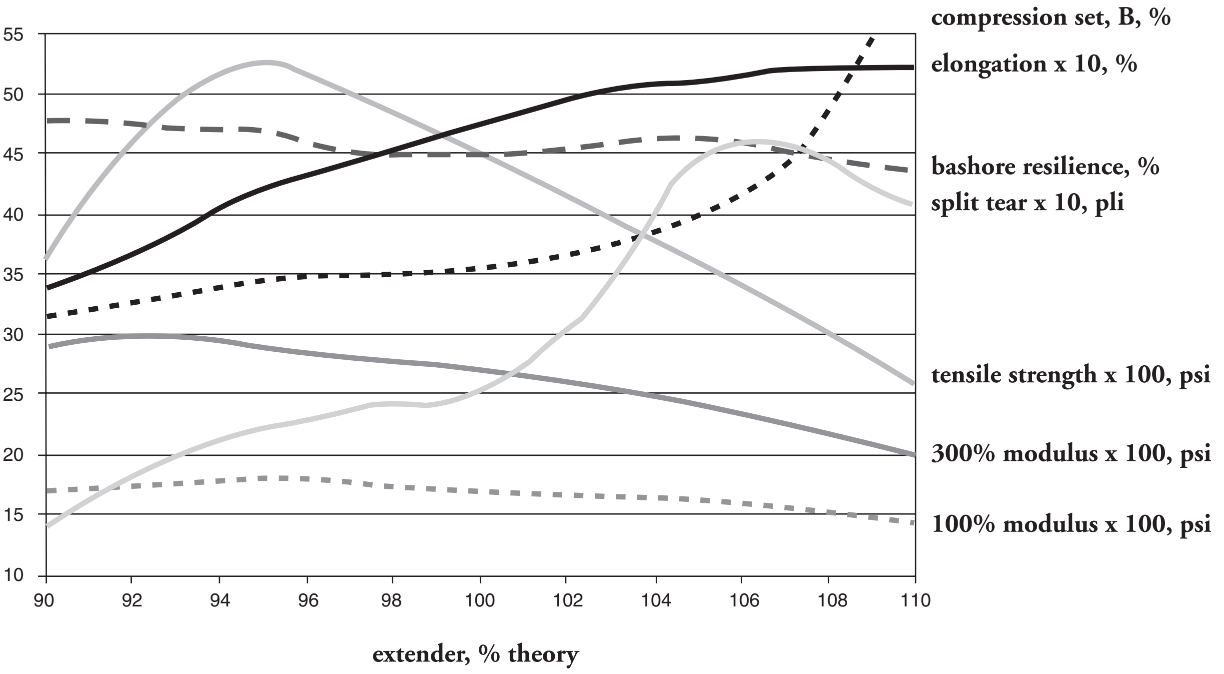
POLYMEG Polyol Molecular Weight	650	1000	1500[1]	2000
Mole Ratio, NCO/OH	2/1	2/1	2/1	2/1
%FNCO	8.3	6.2	4.5	3.5
Curative Level, % Stoich.	95	95	95	91
Hardness, Shore A (D)	(68)	96	92	84
Tensile Strength				
100% Modulus, psi	-	1900	1300	935
300% Modulus, psi	4700	3600	2200	1750
Ultimate, psi	6500	5500	5000	4400
Elongation, %	250	400	450	475
Tear Strength: Die C, pli	715	440	350	345
Split, pli	285	200	130	70
Compression Set, B, %	41	33	30	25
Bashore Resilience, %	52	45	50	57
Clash-Berg, T_f, °C	-18	-54	-72	-76
Abrasion Resistance, g loss (H-18 1000 g/1000 rev)	0.15	0.13	0.10	0.10

[1] Obtained by blending POLYMEG 1000 and 2000 Polyol

Elastomers

At a given elastomer hardness, the properties can be modified by the degree of cross-linking through biuret formation. This is accomplished by using less than the theoretical amount of diamine extender. Figure 2 illustrates how the properties change with extender level. With 4,4'-methylenebis(o-chloroaniline) (MOCA), a theoretical extender level of 95% stoichiometry is used for the best balance of properties.

Figure 2. 95 Shore A Elastomer Properties vs Extender Stoichiometry; POLYMEG 1000 Polyol / TDI / MOCA



MOCA is a high melting solid (mp 110°C) and requires processing at elevated temperatures. A unique method of producing a liquid extender is to dissolve MOCA with POLYMEG 650 polyol at 90°C producing a glycol diamine blend. The most stable blend is a NH_2/OH ratio of 1:1 exhibiting excellent room temperature stability. Higher NH_2/OH ratios may be used (e.g., 1.5:1 or 2:1) but stability is reduced to 7 weeks and 1 week respectively.

To produce low hardness elastomers using TDI technology, glycols such as 1,4-butanediol (BDO) may be used. Since allophonate cross-linking is more difficult in this system, the use of a trifunctional glycol, such as trimethylolpropane (TMP) is recommended. The reactivity of a diol/triol extender is lower than that of MOCA and therefore demolding times are longer. Catalysts, such as amines and metal salts, can be used to shorten demolding times.

Table III shows the expected elastomer physical properties for a 6.2% NCO POLYMEG 1000 / 80-20 TDI prepolymer extended with POLYMEG 650 polyol/MOCA blends and with a 1,4-BDO / TMP blend.

Table III
Elastomers Based On POLYMEG 1000 Polyol and 80/20 TDI With Various Extender Blends

Prepolymers			
Mole Ratio, NCO/OH	2/1	2/1	2/1
%FNCO	6.2	6.2	6.2
Extender Blends			
POLYMEG 650 Polyol, equiv.	1	1	-
MOCA*, equiv.	1	2	-
1,4-Butanediol*, equiv.	-	-	5
Trimethylolpropane, equiv.	-	-	1
Properties			
Hardness, Shore A	86	91	60
Tensile Strength			
100% Modulus, psi	635	800	250
300% Modulus, psi	1100	1250	450
Ultimate, psi	4000	4800	2900
Elongation, %	615	575	560
Tear Strength: Die C, pli	315	350	170
Split, pli	50	80	10
Bashore Resilience, %	52	48	43
Compression Set, B, %	26	26	12
Clash-Berg, T_f, °C	-58	-54	-53

*@ 95% Stoichiometry

There are alternative extenders available. Some provide useful physical properties and desirable processing characteristics with minimal sacrifice in elastomer properties. Some of the alternatives are:

Ethacure® 300, a mixture of 3,5-bis(methylthio)-2,4 and 2,6-toluenediamine (80/20 ratio), is a low viscosity liquid. At the 95% stoichiometric level, it gives elastomeric properties in line with the MOCA system.

Other extenders used are methylene-bis-aniline (MDA), Versalink® 740M, and Lonzacure® (M-CDEA).

Ethacure® is a registered trademark of Albermarle Corporation.
Versalink® and Lonzacure® are registered trademarks of Air Products.

MDI Formulations

With concern for the use of MOCA as an extender with TDI prepolymers, alternative prepolymer systems, based on diphenylmethane-4,4-diisocyanate (MDI) and 1,4-butanediol (BDO) extension, have been formulated.

Tables IV (pg. 13) and V (pg. 14) illustrate various MDI/POLYMEG polyol/BDO elastomer properties. These elastomers exhibit equivalent physical properties, such as tensile strength, elongation, compression set, and resilience; and almost equivalent tear strength when compared to equivalent hardness TDI-based elastomers. Hydrolytic stability, low temperature flexibility, rebound, and impingement abrasion resistance are greatly enhanced. To achieve the same hardness values, the MDI/POLYMEG polyol NCO/OH ratio must be higher than those for TDI. For example, 95 Shore A material based on TDI has a 2:1 ratio, while the MDI based material requires 3:1. As in TDI technology, the 95% extender stoichiometry is used to achieve the best balance of overall physical properties.

When extending with 1,4-butanediol (BDO), MDI/POLYMEG polyol prepolymers require higher-shear mixing than TDI/POLYMEG polyol prepolymers extended with MOCA. Incomplete mixing is characterized by streaks and inferior properties in the final elastomer. Proper casting techniques are required for each mold configuration in order to obtain bubble-free castings. A mold temperature up to 130°C with 150°C as maximum may be required to prevent the occurrence of stars in the cured elastomer. Molding and post-cure temperature guidelines are listed in Tables IV and V. After the initial oven cure, a 7-14 day post-cure at room temperature is necessary for the urethane elastomer to achieve optimum physical properties.

Aromatic diols such as hydroquinone di-(beta-hydroxyethyl) ether (HQEE) and resorcinol di-(beta-hydroxyethyl) ether (HER) are used as extenders for MDI/POLYMEG polyol prepolymers to impart high modulus and tear properties to the elastomer over that of short chain aliphatic diols. With HER's lower melting point, the final elastomer is less likely to have evidence of star formation.

Table IV
Elastomers Based on POLYMEG 1000 Polyol / MDI / Glycol Extended

Hardness, Shore A, (D)	**(75)**	**(60)**	**95**	**95**	**90**	**85**	**80**	**70**	**60**
Prepolymer									
Mole Ratio, NCO/OH	7/1	4/1	3/1	2/1	2.4/1	2/1	3/1	3/1	3/1
%FNCO	18.0	12.5	9.4	5.3	7.3	5.3	9.4	9.4	9.4
Viscosity: 30°C, cps	380	2500	7000	34000	15000	34000	7000	7000	7000
100°C, cps	-	180	240	750	450	750	240	240	240
Extender (95% stoich), g/100 g prepolymer									
POLYMEG 1000 Polyol	4.2	-	-	-	-	-	36.3	64.0	95.0
1,4-BDO	1.8	12.7	9.5	-	7.3	5.4	6.3	3.8	0.76
TMP	-	-	-	-	-	-	-	-	0.18
HQEE	-	-	-	11.9	-	-	-	-	-
Niax® Polyol HL-565	11.7	-	-	-	-	-	-	-	-
Processing with Mold Temperature 120°C									
Reactants °C	45	80	80	120	80	80	80	80	80
Pot Life, Min	2.5	1.5	4	5	6	9	16	24	20
Properties[1]									
Tensile Strength									
100% Modulus, psi	3250	2350	1380	1800	1020	770	580	400	500
300% Modulus, psi	4100	3700	2400	2650	2100	1660	1100	780	620
Ultimate, psi	4500	6200	5500	4100	5310	4800	4400	3300	2440
Elongation, %	310	420	510	550	480	460	490	500	575
Tear Strength: Die C, pli	890	700	490	590	350	295	280	230	150
Split, pli	-	300	175	240	90	45	38	15	12
Bashore Resilience, %	38	42	45	47	47	50	53	59	71
Compression Set, B, %	24	31	27	21	30	30	30	27	26
Abrasion Resistance, g loss	0.10	0.08	0.08	0.17	0.09	0.06	0.04	0.03	0.02
Clash-Berg, T_f, °C	-26	-37	-43	-45	-46	-49	-50	-52	-56

[1] Post cure at 16 hr. @ 110°C

Niax® is a registered trademark of Union Carbide

Table V
Elastomers Based on POLYMEG 2000 Polyol / MDI / Glycol Extended

Hardness, Shore A, (D)	**(60)**	**95**	**90**	**85**	**70**	**70**	**60**
Prepolymer							
Mole Ratio, NCO/OH	8.2/1	4.6/1	3.55/1.0	2.8/1	8.2/1	4.6/1	2.8/1
%FNCO	14.9	9.5	7.3	5.35	14.9	9.5	5.35
Viscosity: 30°C, cps	2,000	8,000	13,000	23,000	2,000	8,000	23,000
100°C, cps	100	289	400	700	100	280	700
Extender (95% stoich), g/100 g prepolymer							
POLYMEG 2000 Polyol	-	-	-	-	157.1	132	121.0
1,4-BDO	15.2	9.6	7.5	5.5	8.1	-	-
HQEE	-	-	-	-	-	8.1	-
Processing with Mold temperature at 120°C							
Prepolymer/extender, °C/°C	50/50	80/80	80/80	80/80	80/80	100/110	80/80
Pot Life, Min	2.5	4.5	7	16	45	35	48
Properties[1]							
Tensile Strength							
100% Modulus, psi	2790	1375	960	770	425	390	225
300% Modulus, psi	3450	1300	1875	1500	795	905	350
Ultimate, psi	4500	5500	5450	4875	3750	3200	1300
Elongation, %	440	480	600	540	510	545	785
Tear Strength: Die C, pli	650	545	425	360	225	240	130
Bashore Resilience, %	48	50	57	65	72	70	79
Compression Set, B, %	37	32	30	27	28	40	18
Abrasion Resistance, g loss	0.15	0.11	0.09	0.07	0.02	0.02	0.01
Clash-Berg, T_f, °C	-60	-66	-68	-71	-72	-73	-78

[1] Post cure at 16 hr. @ 110°C

Alternative Urethane Elastomers

Systems based on POLYMEG polyol, 4,4'-methylenebis(cyclohexylisocyanate) (HMD) and methylenedianiline (MDA) are used for applications requiring a high degree of UV resistance and maximum hydrolytic stability. The formulation for a 50 Shore D elastomer is illustrated in Table VI. Glycol extension with catalysts is utilized for specialized ambient temperature applications and as a base for thermoplastic formulations requiring the maximum degree of environmental stability.

Table VI
Elastomer Based on POLYMEG 1000 Polyol
Methylenebis (cyclohexylisocyanate)-Methylenedianiline

Prepolymer	
Mole Ratio, NCO	2/1
%FNC	5.5
Viscosity: 30°C, cps	17,660
100°C, cps	5780
Compound	
Prepolymer, g	100
Methylenedianiline, g. at 95% Stoichiometry	12.3
Processing and Curing	
Mix Temperature, °C	100
Mold Temperature, °C	110
Pot life, Mins	3.5
Post-Cure, Hrs./°C	16/110
Properties	
Hardness, Shore D	50
Tensile Strength	
100% Modulus, psi	1800
300% Modulus, psi	4650
Ultimate, psi	5400
Elongation, %	320
Tear Strength, Die C, pli	345
Bashore Resilience, %	47
Compression Set, B, %	45

Low Temperature Properties

Many applications require that the elastomer retain its elasticity at temperatures as low as -40°C (-40°F). Table VII shows results from a study that showed the best low temperature performance was obtained using the polytetramethylene ether glycol (POLYMEG polyols) in three isocyanate-extender systems (6). This test was run by measuring the apparent modulus of rigidity at 45,000 psi (T_f) with the Clash-Berg torsional apparatus. An alternative method of measuring low temperature performance is to view compression-deflection curves over a broad temperature range. The ideal elastomer would exhibit essentially a constant compression-deflection or a minimal change in compressive behavior between 180°F and –40°F. The study showed that the various polyols were found to be similar at higher temperatures with significant differences found in low temperature performance. The elastomers prepared from POLYMEG polyols exhibited the least change in compression-deflection over the total temperature range.

Table VII
Comparison of Low Temperatures Elastomer Properties:
Various Polymeric Diol / Diisocyanate / Extender Systems

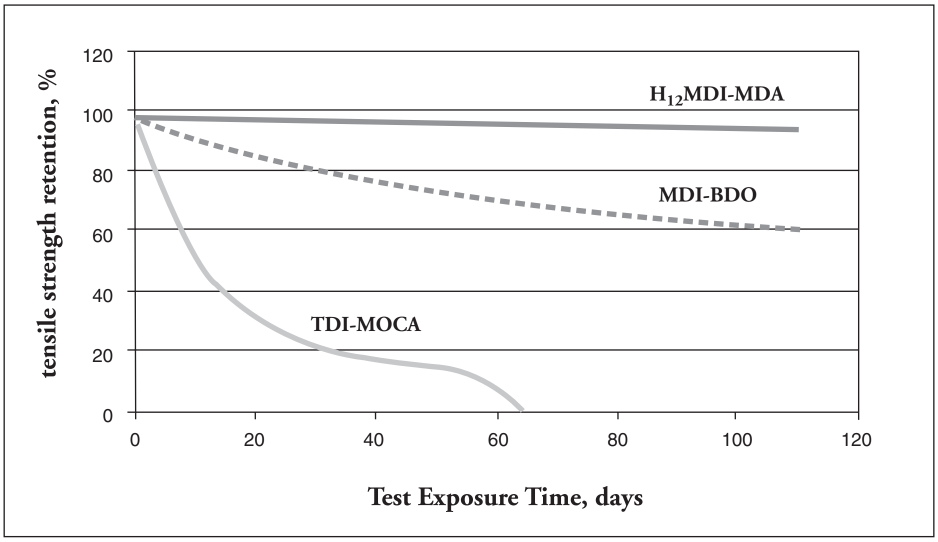
Polymeric Diol	Clash-Berg T_f(°C)	Clash-Berg T_4(°C)	Hardness Break (°F)	Rebound Minimum (°F)	Compression Deflection (180°F to -40°F) % Change 25%	Compression Deflection (180°F to -40°F) % Change 50%
TDI-MOCA System						
POLYMEG 1000 Polyol	-53	-5	10	10	205	203
POLYMEG 2000 Polyol	-75	-43	20	5	211	174
PCL 1250	-34	-15	20	35	558	392
PCL 2000	-44	-32	25	5	480	363
PEPAG 1000	-16	10	45	>77	900	530
PEPAG 2000	-32	-18	10	15	955	700
MDI-1,4 BDO System						
POLYMEG 1000 Polyol	-47	-10	10	15	320	343
POLYMEG 2000 Polyol	-73	-57	15	0	137	180
PCL 1250	-34	-14	10	25	810	610
PCL 2000	-47	-35	25	25	400	294
PEPAG 1000	-27.5	-15	15	20	505	425
PEPAG 2000	-44	-29	20	30	460	385
HMDI-MDA System						
POLYMEG 1000 Polyol	-57	-2	20	-	366	320
PBAG 1000	-35	15	25	-	840	720

PCL = Polycaprolacetone
PEPAG = Polyethylene propylene adipate glycol
PBAG = Polybutylene adipate glycol

Hydrolytic Stability

The results of a study comparing the hydrolytic stability of different polyether and polyester based elastomers with various diisocyanate-curative systems indicate that polyester based elastomers are four times more susceptible to the hydrolytic attack than polyether-based elastomers (7). Among the polyethers tested, the POLYMEG polyol based elastomers showed the greatest degree of hydrolytic stability. Figure 3 graphs the hydrolytic stability as percent tensile strength retention versus aging time of POLYMEG polyol-based elastomers with three different diisocyanate-curative systems. The use of MDI and BDO with POLYMEG 1000 polyol improves hydrolytic stability 12 fold over that of the TDI and MOCA system. With the HMDI and MDA system, the POLYMEG polyol-based elastomer shows very slight degradation.

Figure 3: Hydrolytic Stability of POLYMEG 1000 Polyol-based Elastomers: Comparison of Various Diisocyanate / Curative Systems (80° C – 95% RH Environmental Chamber)



Oil and Solvent Resistance

Like most polyether-based elastomers, POLYMEG polyol-based elastomers will swell in solvents because they are less polar in nature.

The data in Table VIII shows that POLYMEG polyol-based elastomers have excellent resistance to acids and bases.

Table VIII

Oil and Solvent Resistance
For 50 Shore D POLYMEG Polyol Based Urethane Elastomers

Medium	Water[1]	20% HCl[3]	20% H_2SO_4[3]	20% HNO_3[4]	50% NaOH[3]	Conc. NH_4OH[3]	20% Acetic Acid[3]	ASTM[2] Oil #1	ASTM[2] Oil#3	Ref.[1] Fuel B
POLYMEG 1000 Polyol / TDI / MOCA										
Swell, %	1.3	1.3	4.3	7.0	0.3	1.6	9.0	1.0	12.0	25.0
Property Retention, %										
Tensile Strength										
100% Modulus	81	-	111	28	139	89	59	126	115	89
300% Modulus	97	-	125	-	164	83	55	127	99	-
Ultimate	63	-	83	15	152	56	34	131	101	46
Elongation	79	-	83	50	100	113	100	121	142	58
POLYMEG 1000 Polyol / MDI / 1,4-BDO										
Swell, %	1.2	1.5	1.0	4.2	1.0	1.9	6.5	0.5	13.0	22.0
Property Retention, %										
Tensile Strength										
100% Modulus	89	-	96	61	117	89	78	94	-	90
300% Modulus	110	-	112	-	123	97	77	104	-	97
Ultimate	85	-	105	24	170	89	73	141	154	75
Elongation	81	-	93	35	116	93	97	116	151	76
POLYMEG 1000 Polyol / HMDI / MDA										
Swell, %	1.5	1.6	1.3	Dissolved	0.4	1.8	12.0	2.7	32.0	30
Property Retention, %										
Tensile Strength										
100% Modulus	73	-	100		128	89	45	122	-	60
300% Modulus	-	-	-		-	-	-	-	-	-
Ultimate	69	-	92		101	77	35	119	66	54
Elongation	85	-	82		78	95	100	98	117	98

[1] 1 week @ 50°C

[2] 70 hours @ 100°C

[3] 30 days @ 25°C

[4] 8 days @ 25°C

Stabilization of Polyether-Urethanes and Polyether Block Copolymers

Polymers are susceptible to degradation primarily caused by thermooxidative, thermal, or UV initiated degradation. In thermooxidation of polyurethanes, the urethane group is relatively stable and the degradation starts in the polyether chain, particularly the CH_2 group adjacent to or in the alpha position to the ether linkage. In MDI-based polyurethanes, the methylene bridge between the two aromatic rings of the MDI is also a point of photooxidative attack. This can lead to badly discolored and degraded polymers unless stabilizers are used.

Stabilizers are added to the raw materials used to make polyurethanes and are also added as additives during the production of polyurethanes. The stabilizers are added to primarily retard the effects of thermooxidation and photooxidation of either the raw materials or the finished polymer. Development of color and reductions in mechanical properties are common problems that result from oxidative degradation of polyurethanes.

PTMEG as well as aromatic isocyanates typically contain butylated-hydroxytoluene (BHT) to retard oxidation during storage. BHT is an effective thermooxidative stabilizer; however, higher molecular weight hindered phenols are usually used in polyurethanes because of color or volatility problems with BHT (8). Trace levels of transition metal compounds in polyurethane raw materials can strongly catalyze oxidative reactions and for this reason low levels of phosphoric acid are often added to passivate these metals.

Aromatic isocyanates easily form highly yellow colored compounds via the oxidation of intermediate aromatic amines. This color formation can be retarded by the use of stabilizers (9) but aliphatic isocyanates are usually used for light stable applications. Aliphatic-based polyurethanes give light stable products but stabilizers must be used to retard loss of mechanical properties.

PTMEG QC Tests

Molecular Weight

- Accurate molecular weight is critical for thermoplastic polyurethane properties
  - The high hydroxyl-side gives lower mechanical properties, sticky and/or hazy product
  - The high isocyanate-side can give crosslinked product
- Lyondell Chemical Company uses a near IR method to ensure accurate MW measurements
  - For P-1000, MW standard deviation is 1.5
- Hydroxyl number = 112,200/MW

Acid Number

- Simple titration of sample with sodium hydroxide
- All commercial PTMEG has less than 0.04 mg KOH/g acid number unless the sample has been oxidized

Alkalinity Number

- Acid/base titration developed in the 60's to measure low levels of sodium/potassium weak acid salts
- Test was modified to measure very low levels of acid in PTMEG
  - A negative alkalinity number means the sample is acidic
  - To convert to acid number multiply by -0.001867
- The target is to be near zero alkalinity number (test has standard deviation of about 0.2)

APHA Color

- Slight yellow color is detectable by eye when APHA number exceeds about 25 in a quart jar
- Most commercial PTMEG has APHA below 30
- Color of polyurethanes does not correlate with PTMEG APHA color when numbers are below 30

Water

- High water in PTMEG can cause bubbles, color and stoichiometry problems in polyurethanes
- Karl-Fisher titration is used for test. Proper sampling/handling is needed to get accurate numbers

Volatiles

- GC method for organic volatiles

Ash

- Originally determined by weight left after ashing with sulfuric acid
  Gravimetric method is difficult to use for low (<20 ppm) ash samples
- Lyondell Chemical Company uses atomic absorption to quantify sodium, calcium, magnesium, iron.
  Low ash is needed to prevent urethane crosslinking reactions

Molecular Weight Ratio

- Weight average MW/number average MW
- The weight average MW is calculated from the viscosity of the sample at 40° C (MW = 10^(0.493 log(poise) + 3.0646)
- Target is to be below 2.1
- Higher MW ratios give higher viscosities for prepolymers and possibly haze in clear polyurethane applications

Carbonyl Ratio

- Number calculated from an IR spectra which reflects the amount of carbonyl groups in PTMEG
- Carbonyl groups show up in PTMEG which has been exposed to oxygen and heat

The carbonyl ratio is typically less than 2 for non-oxidized PTMEG

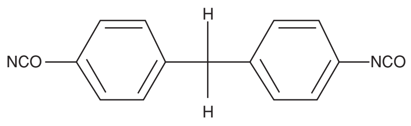
Peroxide

- Determined by thiosulfate titration of peroxide liberated iodine
- Peroxides form in PTMEG which has been exposed to oxygen and heat. Peroxides can affect catalyst and other additives in polyurethanes

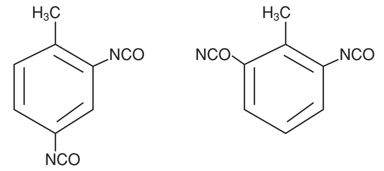
Polyurethane Chemistry

Structures of common chemicals used in making polyurethane elastomers are given below.

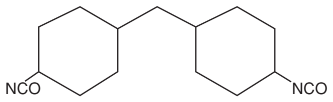
POLYMEG Polyol $HO\text{-}(CH_2CH_2CH_2CH_2\text{-}O)_n\text{-}H$



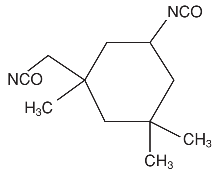
MDI



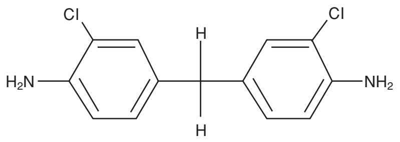
TDI isomers



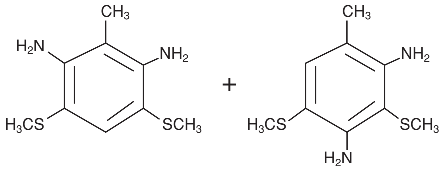
HMDI



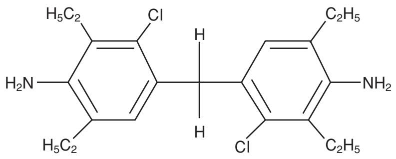
Isophorone diisocyanate (IPDI)



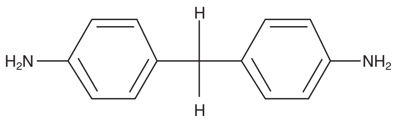
MOCA



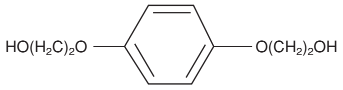
Ethacure® 300



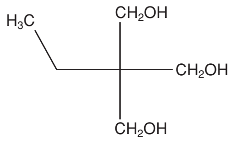
M-CDEA



MDA

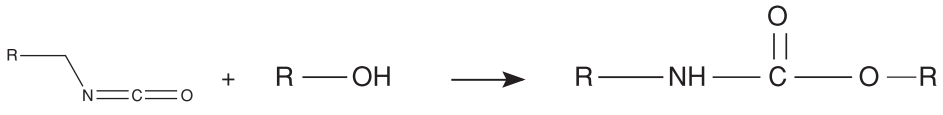


HQEE

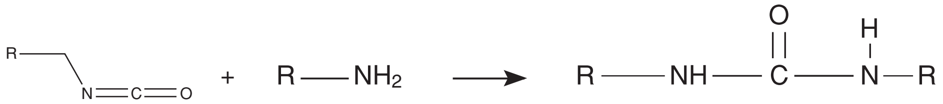


trimethylol propane (TMP)

Primary Reactions of Isocyanate

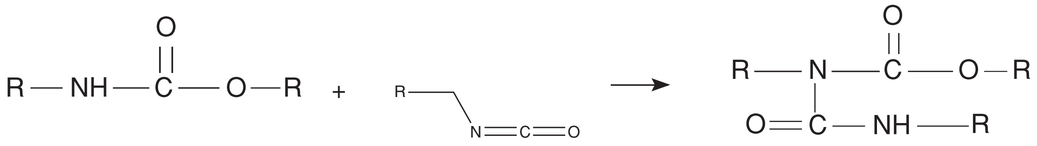


isocyanate alcohol urethane

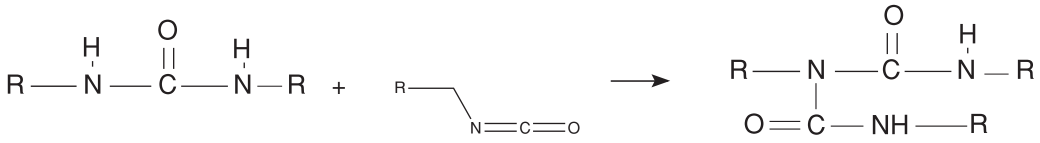


isocyanate amine urea

With excess isocyanate, urethane and urea bonds can react to form allophonate and biuret bonds.

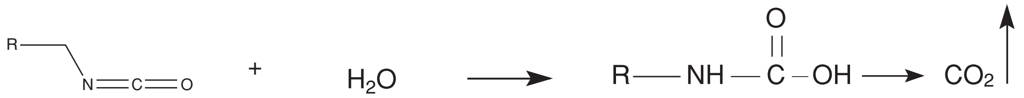


urethane excess isocyanate allophonate

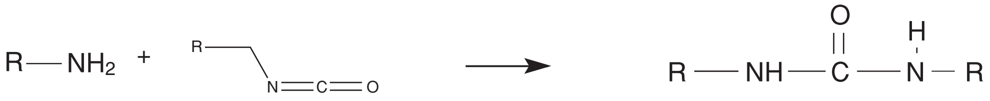


urea excess isocyanate biuret

Water reacts with isocyanates to give carbon dioxide plus a primary amine. The amine quickly reacts with another isocyanate to form a urea bond. The released carbon dioxide causes bubbles in elastomers.



isocyanate carbamic acid



amine isocyanate urea

Formulation Calculations

A common problem is to determine the weight percent of POLYMEG polyol, extender and diisocyanate needed to get an elastomer of a target hardness. This can be done for the TDI and MDI systems by looking at the tables in this brochure. From the mole ratio of NCO/OH (isocyanate/hydroxyl) for the prepolymer, the % NCO for a prepared or purchased prepolymer is calculated by:

% NCO = (equivalents isocyanate-equivalents POLYMEG polyol) * 4200/(weight of prepolymer)

equivalents POLYMEG polyol = P_w * weight of prepolymer/(POLYMEG polyol equivalent weight)
POLYMEG polyol equivalent weight = 56100/(POLYMEG polyol hydroxyl number)
P_w = (P_n * POLYMEG polyol eq wt)/(P_n * POLYMEG polyol eq wt + I_n * isocyanate eq wt)
P_n = OH mole ratio/(OH mole ratio + NCO mole ratio)

equivalents isocyanate = I_w * weight of prepolymer/(isocyanate equivalent weight)
I_n = NCO mole ratio/(OH mole ratio + NCO mole ratio)
I_w = (I_n * isocyanate eq wt)/(P_n * POLYMEG polyol eq wt + I_n * isocyanate eq wt)
Isocyanate equivalent weight = isocyanate molecular weight/(functionality)
Functionality usually = 2

The table below lists the molecular weight of some common diisocyanates and extenders.

Compound	Molecular weight
MDI	250
TDI	174.2
HMDI	262.2
Isophorone diisocyanate	222.2
MOCA	267.2
Ethacure 300	214.4
MDA	198.3
M-CDEA	379.4
HQEE	198.2
1,4-butanediol	90.0
Trimethylol propane	134.2

A prepolymer that is made or purchased should be analyzed (10) for the % NCO since it will often differ slightly from the calculated value. The measured % NCO value gives the weight of extender to add by:

Weight of extender = (% NCO * weight of prepolymer * extender equiv. wt) * F/4200

F = mole fraction of stoichiometry, often F = 0.95

For example, to make a 95 Shore A elastomer with MDI, Table IV shows that a NCO/OH of 3/1 is needed. The mole fraction of POLYMEG polyol in the prepolymer is P_n = 1/4 = 0.25 and for MDI I_n = 3/4 = 0.75. For a POLYMEG polyol with hydroxyl number 112.2 (500 eq. wt), the weight fraction of POLYMEG polyol in the prepolymer is P_w = (0.25 * 500)/(0.25 * 500 + 0.75 * 125) = 0.57. For 100 parts of prepolymer the equivalents of POLYMEG polyol = 0.57 * 100/500 = 0.114 and the equivalents of isocyanate = 0.43 * 100/125 = 0.344. The prepolymer % NCO is:

% NCO = (0.344-0.114) * 4200/100 = 9.65

The weight of butanediol extender/100 parts prepolymer = 9.65 * 100 * 45 * 0.95/4200 = 9.82 (for 0.95 stoichiometry).

Viscosity and Density Calculations for POLYMEG Polyols

The formulas listed below can be used to calculate the viscosity and density of POLYMEG polyol grades.

POLYMEG Polyol Grade	Log 10 viscosity in cp
650	$9\text{x}10^{-5}$ (temp °C)^2 -0.0257 (temp °C) + 3.11
1000	$9\text{x}10^{-5}$ (temp °C)^2 -0.026 (temp °C) + 3.3662
2000	$9\text{x}10^{-5}$ (temp °C)^2 -0.026 (temp °C) + 3.994

POLYMEG Polyol Grades	Density, g/cc
650	-0.0007 (temp °C) + 1.0047
1000 to 2000	-0.0007 (temp °C) + 1.0025

Testing of Polyurethane Elastomers

There are two ways to evaluate a polyurethane elastomer used by most application chemists. One can test the final part and/or one can test the polyurethane material.

Testing of the final parts can be quite complex and the tests results can be narrowed depending upon the specific size and shape of the part to be tested. Material testing usually involves a set of standardized test methods with simple specimens. Such test results are very important in the development of polyurethane materials with targeted properties and can be utilized in predicting the properties of the final parts. As the final product cures, the mechanical properties are subject to change due to curing and crystallization of the material. Various industrial users will develop additional specifications based upon product needs.

Hardness ASTM D2240

The hardness test measures the indentation into the polymer of the indenter under a load. It is measured on a scale of 0 to 100. Hardness is typically measured on the Shore A or the Shore D scale. A reading above 90 on the Shore A scale will generally overlap with readings below 20 on the D scale. Further information may be found by reading the ASTM D2240 Durometer Hardness test methods.

Stress/Strain Modulus ASTM D412

Typically, the stress/strain modulus is measured as the force needed to stretch a sample at 100, 200, and 300% of elongation. These measured parts are generally 2 mm thick and 6 mm wide and prepared using a Die “C” mold.

Tear Strength ASTM D3574

The tear strength of a sample measures the energy requirements needed to tear a partially slit sample at a specific rate of separation.

Die C Tear ASTM D 624C

This test uses an un-nicked 90 deg. angle specimen and provides a good measure of tear initiation and propagation.

Rebound ASTM D2632

The rebound test determines the amount of energy a sample will absorb. A sample of material 28 mm in diameter and 12-13 mm thick has a plunger dropped from a specific height. The lower the plunger rebounds (more energy absorbed by the sample), the lower the value.

Compression Set ASTM D395

The compression set determines the extent a polymer will be permanently deformed by a prolonged compressive load.

NBS Abrasion ASTM 1630

Materials are exposed to two types of abrasion: sliding and impingement. Sliding is the passing of one surface across the surface of the polymer. Impingement tests the wear of a polymer surface as exemplified by sand particles striking the surface.

DIN Abrasion DIN-53516

This is a specialized test of a polymer 10 mm thick and 12 mm in diameter placed under force on a roll with sandpaper.

DeMattia Flexer ASTM D430

The DeMattia Flex test is designed to bend a polymer to produce cracking as a measure of performance.

Ross Flexer ASTM D1052

The Ross Flexer test point determines the resistance of an elastomer to cut growth when subjected to repeated bending.

Vicat Softening ASTM D1525

The Vicat softening point is a useful method to compare the heat-softening characteristics of various polymers.

The test methods which are used to determine the properties of elastomers are in most cases standardized methods, such as ASTM (American Society for Testing and Materials), DIN (Deutsche Industire Norms), and ISO (International Standardization Organization). ISO standards are more and more utilized due to the easier communication on the international level.

Storage and Handling

POLYMEG polyols are shipped in 55-gallon (208L) closed-head steel drums, coiled and insulated tank cars, and tank trucks. All shipping containers undergo a rigorous inspection in accordance with the standard procedure used for shipping product for food applications. The product is loaded and bulk shipped at a minimum of 65°C (150°F). Normal precautions should be maintained in handling hot liquids during the unloading of bulk shipping containers and warmed drums.

POLYMEG polyols are stabilized to prevent degradation in storage and during normal handling. Prolonged heating under a nitrogen blanket at 50-65°C (125-150°F) is recommended. However, the presence of air will result in partial oxidation and degradation. The first indication of improper heating is an increase in APHA color, followed by a moderate increase in both peroxide content and acid number. Thermal decomposition will occur under anaerobic conditions at 210-220°C (410-430°F) with the tetrahydrofuran as the major decomposition product.

When stored in tanks, POLYMEG polyols must be blanketed with dry nitrogen to prevent moisture pickup and possible discoloration in the final polymer product. Storage tanks should provide for adequate circulation of the contents and be equipped with proper instrumentation to control the storage temperature—generally at 55-65°C (130-150°F). Low-pressure steam and/or electric coils should be used as the heat source for the tank contents and heat tracing of pipe lines. POLYMEG polyols are completely stable for at least one year when stored under a nitrogen atmosphere at a maximum temperature of 55°C (130°F). At a temperature of 100°C (212°F), stability is limited to a few days.

POLYMEG polyols are hygroscopic and can absorb as much as 2% moisture in an unprotected environment. Gross amounts of water are removed by azeotropic distillation with toluene. Further reduction in water content can be achieved by heating for several hours at 120-150°C (248-302°F) under reduced pressure (less than 20mm Hg). The apparatus must be cleaned and free of air, oxides and acids to minimize contamination and oxidation.

Drums may be warmed to about 70°C (160°F) for about 24 hours to melt the contents. Thereafter, storage at 38°C (100°F) will prevent re-solidification. Open drums with partially used contents should be blanketed with nitrogen. If partial solidification occurs, it is recommended that the material be remelted to prevent stratification and to facilitate handling.

Alternative methods to melt drum contents:

1) Steam chest with free steam at 100°C (212°F) for 9-16 hours.
2) Plate coil drum heater using low-pressure steam in coils to heat until the drum skin temperature is about 95°C (200°F).
3) Mantle drum heaters using a thermostat to ensure that the drum skin temperature does not exceed 95°C (200°F).
4) Band drum heaters placed on lower part of the drum. Control with a thermostat to ensure that the drum temperature does not exceed 95°C (200°F).
5) Place a tarp over a series of drums. Free steam under the tarp will melt the drums overnight.

More detailed safety and disposal information about this product is contained in the Material Safety Data Sheet (MSDS). All users of our products are urged to retain and use the MSDS. A MSDS is automatically distributed upon purchase/order execution. You may request an advance or replacement copy by going to our website: www.lyondell.com or www.lyondelleurope.com or by calling our MSDS hotline at (800) 700-0946 (U.S. and Canada), European Technical Services at (33) 3 44 24 92 05, or Asian Headquarters at (852) 2882-2688.

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