What Polyurethane? Where?

Urethane Prepolymers

What Polyurethane? Where?

Selecting the Right Polyurethane Elastomers for Demanding Applications

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One of the keys to functional design success is the selection of the right material to meet the demands of the application. Sometimes steel, aluminum or other metals are the materials of choice; in other cases plastics - ABS, polystyrene, PVC or phenol-formaldehyde resins - are best and, in a growing number of needs, polyurethanes offer superior design and performance characteristics.

You will note that I have cited "polyurethanes" - in the plural. The variety of these elastomers is substantial. Each composition has its attributes and shortcomings. So what is essential, in terms of applications engineering, is to appraise each and then to select the particular polyurethane that meets the criteria of both economics and performance.

The following is designed to serve as a practical macro guideline to the types of PU elastomers that are available, the kinds of physical and environmental resistance properties they have, and typical applications that each will fulfill.

First, let's define just what polyurethane is: The chemical term "polyurethane" can apply to many different kinds of materials.

Types of Polyurethane Materials

Castable Elastomers	Adhesives, Sealants
Foams - Rigid and Flexible	Thermoplastics
Microcellular Shoe Soling	Coatings
Millable Gums	

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There are the castable elastomers, which are the materials of primary importance in this discussion. There are foams, both rigid and flexible types. Rigid foams are used for applications such as insulation while flexible foams are used in upholstery and cushioning. Shoe soling of all types is made from polyurethane microcellular materials, which are special types of foams. These are all very large markets.

Many types of adhesives are also formulated from urethanes. Sealants based on urethane chemistry are widely used for applications such as sealing automobile windows.

Thermoplastic urethanes are materials that are fully reacted and processed by a melting and extrusion or injection molding procedure.

Millable gums are handled in much the same way as conventional rubbers, that is, they are compounded with fillers and other ingredients, are processed on rubber machinery and are cured by vulcanization processes with peroxides or, in some cases, with sulfur. In this way processors can achieve many of the unique properties of urethanes by the same methods used to process conventional rubbers.

Coatings, also widely based on urethane materials, cover a broad range from the types of varnishes and paints that are used on furniture and flooring, to the sprayable elastomeric coatings for high abrasion or corrosion resistance. The latter are not just for protection of the surface from weather, but provide a tough, durable lining for industrial pipe, or added service life for costly mining machinery.

WHY USE URETHANES?

Castable urethanes are made by mixing together two liquids - a prepolymer and a curative- and pouring. These two liquids are blended either by hand mixing or through a processing machine, poured into a mold and allowed to cure into a final shape. The major characteristic of these materials is that they have extraordinary physical properties. They are actually engineering materials and are chosen for use on the basis of these properties.

WHY USE CASTABLE POLYURETHANE ELASTOMERS?

• **Performance**	• **Cost Effectiveness**
- Abrasion Resistance - Toughness - Tear Resistance - Load-Bearing Ability	- Reduced down time in process operations (for example: Mining, Machine parts, Paper Mills) - Lower tooling and equipment costs for small production runs

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Why use castable polyurethane elastomers versus another kind of material? There are really two main reasons: performance and cost effectiveness.

In some cases, performance characteristics of these materials allow them to be used in applications where other materials simply cannot be used satisfactorily or at all due to the tough demands. In other cases, end users select urethanes because they can outperform other materials by a large margin. This is usually a result of their particular properties, abrasion resistance and toughness, that is, resistance to breakage on impact or in rough handling, very high tear resistance and high load-bearing ability. These four properties, although certainly not the only outstanding properties of urethanes, are the ones that usually make them stand out far above other materials in many applications.

Cost effectiveness is the second reason. Even though polyurethanes are often more expensive than other materials - including various rubbers - the extra cost is frequently justified in terms of less downtime in actual service. This is particularly critical, for instance, in mining and paper mills. Downtime in these operations is very expensive. If a mining operation has to be shut down for replacement of a part that has failed or worn out, the cost can run to thousands of dollars per hour. The higher initial cost of a urethane part that will last two, four or even ten times as long as a part made from another material is clearly more than justified.

Another area where urethane's cost effectiveness is of interest is in the cost of tooling and equipment. Tooling for urethanes is not expensive because molds can easily be made out of plastic, metal, urethane itself or fiberglass reinforced epoxy - in short, almost anything that does not hold moisture and can take the modest heat and pressure of casting operations. Tooling for rubber molding, on the other hand, is relatively expensive because it has to withstand the high pressures developed in compression molding operations and the high temperatures of curing. Therefore, even though the cost of the materials in small production runs with urethane may be more expensive, the cost of setting up to do the job may easily offset that cost.

What are some of the materials that urethanes compete against? In general, urethane competes in various applications with metals, plastics and rubbers.

ADVANTAGES VERSUS METAL

- Lighter Weight
- Less Noise
- Better Wear
- Cheaper Fabrication
- Corrosion Resistance

One of the advantages of urethanes versus metal is lighter weight. Parts fabricated from urethane weigh far less than metal parts and are much easier to handle and, typically, result in having to move less mass in machinery. In addition, metal parts tend to generate noise while urethane absorbs noise. The reduction of this "noise pollution" in the workplace when urethanes replace metal can often be dramatic.

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Urethanes will also outwear metals in many applications and can be easily cast in inexpensive tooling as discussed earlier. In contrast, making metal parts requires foundry operations, welding and machining and, as a result, can be very costly, particularly with high hardness alloys.
Urethanes are also corrosion resistant. For example, in many mining operations, highly corrosive solutions cause rapid deterioration of steel. Wherever there is a combination of abrasion and corrosion at the same time - such as in copper mining slurry pipelines - the lifetime of metal parts can be remarkably short. Urethanes, because they have high resistance to abrasion and to corrosion outlast metal by a large margin. This application embodies many of the advantages versus metals described above.

Another group of materials that are sometimes used in some of the same types of applications as urethanes are the plastics.

ADVANTAGES VERSUS PLASTICS

- Non - Brittle
- Elastomeric Memory
- Abrasion Resistance

One advantage of urethane elastomers over plastics is that they are not brittle. Many plastics, particularly in the higher hardnesses, tend to crack and break under impact and shock loading.

Urethanes remain true elastomers maintaining their high impact resistance even up to very high hardnesses. Urethanes also have elastomeric memory; that is, they can be stretched even at high hardnesses to substantial elongation and will return to their original dimensions. Most plastics, once they have been stretched beyond a certain point, remain permanently stretched. Finally, plastics, as a class, do not have the high abrasion resistance of polyurethanes.

The third major types of material competing with urethanes are the various natural and synthetic rubbers.

ADVANTAGES VERSUS RUBBERS

- Abrasion Resistance
- Oil Resistance
- Harder Durometer Range
- Non-Marking, Non-Staining
- Ozone Resistance
- High or Low Hysteresis
- Cut and Tear Resistance
- Higher Load Bearing
- Clarity; Translucence
- Pourable; Castable
- Microorganism Resistance
- Versatility

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The main advantages of urethanes versus rubber are the higher abrasion resistance, greater cut and tear resistance, and higher load bearing ability

In addition, most cast urethanes have natural colors ranging from completely clear to opaque white or amber. Their ready acceptance of a wide variety of pigments and dyes also permits coloring ranging from black to brilliant fluorescent oranges, reds or greens. This is especially useful in color-coding of parts. A good example is in business machines where rolls and belts can be color-coded so that correct replacement can be easily made.

Rubber is subject to ozone cracking, particularly around electrical equipment where ozone concentrations can be high. Polyurethanes have no ozone-cracking problem.

The fact that urethanes are pourable and castable, which was mentioned earlier makes for cheaper tooling and makes possible the fabrication of complicated parts. Moreover, most rubber compounds when compounded up to 90 or 95A durometer have sacrificed a good deal of their physical properties. On the other hand, polyurethanes in the 80 to 95A durometer range are approaching the peak of their properties and give extremely good performance at these hardnesses.

So far we have discussed the advantages of polyurethanes compared to other materials. Naturally, as with anything, there have to be some disadvantages as well.

LIMITATIONS OF POLYURETHANE

- High Temperature Service
- Moist Hot Environments
- Certain Chemical Environments

The limitations of polyurethanes are chiefly three. Polyurethanes are not high temperature materials. Owing to certain thermoplasticity in their nature, properties tend to fall off at elevated temperatures. Generally speaking, urethanes are not useful materials under heavy service loads at temperatures above approximately 220-225 °F (105-107 °C).

Another limitation is that all polyurethanes are subject to hydrolysis in the presence of moisture and elevated temperatures. The combination of the two factors creates a problem. While at lower temperatures, most polyurethanes can withstand continual contact with water for many years, no polyurethane as yet can stand prolonged contact with live steam. In between, there is a wide range of temperature and moisture conditions under which polyurethanes may, or may not be suitable for use. Newer developments in polyurethane chemistry show promise to push these limits further, however.

Lastly, there are certain chemical environments that are unsuitable for polyurethanes. Very strong acids and bases generally are detrimental, as are certain solvents, specifically the aromatic solvents such as toluene or ketones such as MEK or acetone; and esters such as ethyl acetate. (There are many solvents, on the other hand, which urethanes resist very well and are suited for in-contact service. These include many oils and petroleum-based materials).

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SELECTING A POLYURETHANE ELASTOMER

Now that we have reviewed some of the most important advantages and disadvantages of urethanes compared with other materials, what is the basis that we should use to choose a specific polyurethane elastomer for a particular application?

BASIS OF SELECTION OF POLYURETHANE ELASTOMER FOR A SPECIFIC APPLICATION

- **PROPERTIES NEEDED FOR JOB**
- **PROCESSING CHARACTERISTICS**
  - **Pot Life**
  - **Viscosity**
  - **Ratio Control**
  - **Demold Time**
  - **Process Temperature Required**

There are two major considerations: first, what is required for the job in terms of physical properties and environmental resistance; and second, what are the processing characteristics of the polyurethane system chosen? Significantly, and often overlooked, is that when you choose a particular polyurethane system you have to make sure that it not only has the properties needed to perform in the application, but that it also has processing characteristics that you can deal with. These include pot life, viscosity, ratio control, demold time (how many times you must turn each mold per day to have a cost-effective production system) and the process temperature required.

What controls the properties of these urethane elastomers? In part, properties are controlled by the chemical nature of the material being worked with and, in part, by the way in which it is handled.

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WHAT CONTROLS PROPERTIES?

Type of Prepolymer

Isocyanate Type

- TDI
- MDI
- Other (PPDI,Aliphatic, etc.)

Polyol Type

- PTMEG Premier Polyether
- Polyester
- PPG Low-Cost Polyether
- Other (Caprolactone, etc.)

Processing Conditions

- Curative Ratio
- Temperatures

Type of Curative

- Diamine (MOCA, E-300, A153, etc.)
- Diol (1,4-BD, HQEE, etc.)
- Triol (TMP, TIPA, etc.)

- **Additives**
  - Plasticizers
  - Fillers
  - Protectants

Polyurethane prepolymers consist of two major chemical structures: One is the diisocyanate. Most of the commercial materials are based either on MDI (4,4'-diphenylmethane diisocyanate) or TDI (tolylenediisocyanate).
Each of these diisocyanate gives different properties to the final prepolymer and each requires different curing systems and, in many cases, different processing systems as well. There are several other diisocyanates used in the casting industry, such as aliphatics, the newly commercialized PPDI (para-phenylenediisocyanate), and NDI (naphthylene diisocyanate).

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The other component is a polyol. There are three major types: PTMEG (polytetramethylenether glycol), the so-called premium type of polyether spine; PPG (polypropylene glycol), a low-cost polyether type; and adipic acid-based polyesters. Again, there are other polyols, such as polycaprolactones, but their use is relatively minor. With three possible types of polyols and two possible types of isocyanates there are six major classes of polyurethane prepolymers available.

The second part of the system is the curative. A polyurethane casting involves a chemical reaction. When you mix the two components together (the prepolymer and the curative) the reaction has no way to go but forward. Curatives also determine the structure of the polymer molecule and its properties. The most commonly used diamine curative is MBCA, predominantly used with TDI systems, although another material, ETHACURE® 300 Curative, is gaining wider acceptance as a MBCA alternative. Diol curatives such as 1,4-butanediol and HQEE are predominantly used with the MDI systems. Triols are sometimes used in combination with diols with MDI polymers. But the most common use for triol curatives is in a special situation where TDI ester prepolymers are used to produce low durometer rolls for the printing and metal coating industries.

The other factors that can influence the properties of the final product concern the processing conditions. Probably the most important condition is the curative ratio. The relative amounts of prepolymer and curative have to be determined and held within close tolerances to get the desired physical properties.

There are cases where it may be desirable to modify the curative ratio from the optimum to intentionally maximize some particular property of the polyurethane casting at some sacrifice of another property. For example, a cure at high theory - or 100 to 105 percent stoichiometry instead of the more usual 95 percent - will improve flex life of the polymer but will sacrifice some performance in compression set. What is vital is that any modifications of the curative ratio must be done under close control with proper knowledge of what the effect is going to be on other critical physical properties. The other condition that is important to control is the temperature of the prepolymer. This is critical in terms of heat history of the material before it goes into the casting operation as well as temperature during cure and post-cure of the parts.

Processors often use additives to modify the physical properties of urethanes. For example, in low durometer rolls, plasticizers and fillers are used to modify properties. With typical urethane systems, it is very difficult to get below 50 to 55A durometer hardness without the use of a plasticizer. Most low durometer compounds in the 20 to 50A range contain varying amounts of plasticizers to reduce the hardness. Common fillers are silicates, which are often used in printing and coating rolls. Sometimes special fillers - friction-reducing aids such as molybdenum disulfide and fluorocarbons - help to improve wear and friction properties. On occasion, processors add protectants of several kinds, such as UV stabilizers and hydrolysis stabilizers.

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Following are some guidelines that are useful in selecting polyurethanes for demanding applications. Listed are various physical and environmental resistance properties and the types of prepolymers that have the greatest and the least chance of success in applications where these properties are important. This is, of course, only a general guideline. There are many exceptions to these rules, but they can be useful as a starting point in considering materials for a given application.

GUIDELINE SELECTION OF POLYURETHANE FOR USE IN DEMANDING APPLICATIONS

PROPERTY	GREATEST	LEAST
HARDNESS	-	-
TENSILE STRENGTH	ESTER	ETHER
ELONGATION	-	-
MODULUS	-	-
TEAR STRENGTH	ESTER	PPG ETHER
COMPRESSION SET	TDI	MDI
REBOUND	MDI ETHER	TDI ESTER
LOW TEMPERATURE PROPERTIES	MDI ETHER	TDI ESTER
HIGH TEMPERATURE PROPERTIES	TDI	MDI
ABRASION RESISTANCE: - SLIDING -IMPINGEMENT	 ESTER MDI ETHER	 PPG ETHER PPG COST ETHER
HEAT BUILDUP	ETHER	ESTER
HYDROLYSIS RESISTANCE	MDI ETHER	TDI ESTER
OIL RESISTANCE	ESTER	ETHER
HEAT AGING	ESTER	PPG ETHER

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The first property listed, and one that is of perhaps primary interest is hardness. However, since you can obtain all hardnesses with all six basic types of prepolymer systems, this is not a basis for choice among them.

In terms of tensile strengths esters have the edge over ether compounds. However, tensile strength is rarely a key property in urethane applications. All types of polyurethanes can have high elongation. There is really no basis for choice there. The same is true of modulus; all types can have high or low modulus.

GUIDELINE SELECTION OF POLYURETHANE FOR USE IN DEMANDING APPLICATIONS: II		
PROPERTY	**GREATEST**	**LEAST**
LOW DURO FORMULATION (<60A)	TDI ESTER	ETHER
FDA APPROVAL (WET & DRY FOOD)	MDI	TDI
FORMULATION FLEXIBILITY	MDI	TDI
COST	LOW COST TDI ETHER	MDI ETHER

As for low durometer formulations mentioned briefly before, TDI esters are the materials of choice because they can tolerate greater loadings of plasticizers without reduction of physical properties. Ethers generally do not have as high physical properties in low durometer, highly plasticized formulations.

MDI esters are the choice for FDA-approved applications involving dry and wet food contact, particularly for meat or poultry processing. TDI's generally are the least desirable primarily because of the types of diamine curatives used.

MDI's have a greater range of formulation flexibility. To achieve high durometer materials with TDI prepolymers, MBCA or another diamine type curative is necessary; whereas with the MDI's there are several diol curatives that can be used, such as 1,4-butanediol and HQEE. Many mixtures and combinations of these and other diol curatives are possible

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Throughout this list, PPG ethers have appeared in the "least" column quite frequently. While their performance characteristics may not be comparable to the others, very often there are applications where they are desirable. Cost performance is, of course, the reason to use low-cost PPG ethers. They are considerably cheaper than premium grade ethers or esters and are useful in parts that are not highly engineered, that is, in applications where the most outstanding properties of polyurethanes are not fully utilized and therefore low-cost materials can perform adequately.

MDI ethers are listed above as the "least" desirable in terms of cost, which means that they are the most expensive. However, the true cost *in use* really depends upon the particular application because, although the MDI ether prepolymers are only a little more expensive, the curative cost must be factored in. Each case must be calculated on an individual basis: how much does the curative cost, what is the ratio used and how does this contribute to total cost? Sometimes the most expensive material to buy may be the best material for the application because of its cost / performance characteristics. This is a consideration with both premium-grade and low-cost materials.

SPECIFIC APPLICATIONS		
APPLICATION	POLYURETHANE TYPE	BASIS OF CHOICE
ROLLER SKATE WHEELS	MDI ETHERS	HIGH RESILIENCE
PRINTING ROLLS	TDI ESTER	SOLVENT RESISTANCE,GOOD PHYSICAL PROPERTIES AT LOW DUROMETER
OIL PIPELINE PIGS	TDI ESTER	OIL,ABRASION RESISTANCE
GRAIN HANDLING APPARATUS	MDI ESTERS	TEAR RESISTANCE, LOW RESISTANCE
FORK LIFT TIRES	TDI ETHER	LOW HEAT BUILDUP
HAMMERS	TDI ESTERS	TEAR RESISTANCE, LOW RESILIENCE
SANDBLAST CURTAINS	MDI ETHER	HIGH RESILIENCE - IMPINGEMENT ABRASION RESISTANCE
LAUNDRY EQUIPMENT	MDI ETHER	HYDROLYSIS RESISTANCE
PAPER MILL ROLLS	TDI	HYDROLYSIS RESISTANCE, DYNAMICS, HARDNESS STABILITY
MEAT PROCESSING EQUIPMENT	MDI ESTER*	FDA WET FOOD APPROVAL

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*SPECIAL GRADES

There are some specific applications where one type has advantages that are so outstanding as to make it dominate all other types of polyurethanes.

High quality roller skate wheels are practically all MDI ethers, mainly because of their high resilience. High resilience gives good speed performance and a smooth ride.

TDI esters are the materials of choice for printing rolls because of their high solvent resistance and good physical properties in low durometer formulations.

For oil pipeline pigs it is important that they have high abrasion resistance in addition to high oil resistance to prevent their being worn down by going through miles of pipe. Because of this, TDI esters have been the choice since they combine oil resistance with high sliding abrasion resistance.

On the other hand, for grain handling apparatus, (sheet goods, buckets and the like) MDI esters have been the materials of choice. The ester component provides high resistance against abrasive grain and the MDI component produces compositions that are FDA-approved for contact with dry food.

As for forklift truck tires, TDI ethers have taken over a major segment of this market because of their low heat buildup and the high load bearing ability of these materials compared to others.

For hammers, TDI esters are the materials of choice because of the combination of high tear resistance with low resilience. Tear resistance is necessary to prevent deterioration of the face of the hammer, and low resilience causes the energy of the hammer to transfer into the object being struck rather than allowing it to bounce back at the worker.

Sandblast curtains require high resilience and abrasion resistance in an impingement mode. MDI ethers, because of their high resilience, allow the particles to bounce back without transferring much kinetic energy in the form of heat to the sandblast curtain.

MDI ethers are materials of choice for laundry equipment, such as agitators or pulsators for washing machines, because of their outstanding hydrolysis resistance. However, TDI ethers are preferable for paper mill rolls, because of their combination of hydrolysis resistance and hardness stability. In paper processing applications, it is important that the hardness and dynamic properties of the roll remain consistent over a range of operating temperatures so that performance of the roll remains constant.

MDI esters are preferred for meat processing equipment because FDA wet food approval is required for this application. These special ester formulations combine the properties of abrasion resistance and fat and oil resistance with FDA approval.

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SELECTION AND PRODUCTION

To evaluate an application that may be appropriate for polyurethane, The following basic steps are recommended:

SELECTING A POLYURETHANE FOR A NEW APPLICATION

- Decide which properties are of key importance – physical properties and environmental resistance
- Select Polymer/Curative Systems which are likely candidates
- Consult your suppliers for recommendations and further information
- Consider engineering design changes
- Review your plant capabilities
- Run whatever preliminary tests are available
- Make prototype units of one or more candidate systems
- Field test in actual service, make comparisons, get approval from customers
- Gear up for production

First, look at the application carefully and decide which properties are of key importance both in terms of the physical properties and the environmental resistance necessary in the urethane. Select a few candidate polymer and curative systems that should offer appropriate performance. Once you've done this, go to urethane suppliers for their recommendations and for further information. They will certainly be willing to help you and will welcome discussion of new applications. The suppliers may also help with suggestions of material or test data that is not available in their published literature. Bear in mind that you are using a material with different properties than rubbers, metals or plastics. Make sure that the part is designed to take maximum advantage of these properties

Next, review your plant capabilities. Make sure the compounds you have chosen are ones that can be run in your plant either under its present setup or, barring that, consider what sort of investment you might have to make for processing of the proposed material. Depending on the potential market for the application, new investment may be justified.

Then run whatever preliminary tests are available. If it is a new application, for example, where the part must come in contact with an unusual chemical solution, make sure that the urethane you select can tolerate this. Again, consult with your supplier; they will usually be willing to help you with tests of this type.

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At this point, if everything continues to look good, make prototype units of one or more candidate materials. Make sure that your prototypes are well identified so they don't get misplaced in the field and, importantly, so that you can properly track their service history. Get the parts out in actual service, make comparisons of the performance of these test units against whatever is currently being used. If it's a brand new application where nothing like it has ever been done before, test the parts against whatever criteria you and your customer have in mind.

Finally, make sure that you and your customer agree on the test results and that he approves of the part based on the prototype evaluation.
Once you have reached this point you are ready to gear for production and for a successful and profitable business venture.

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