A Quick Review of Urethane Casting Strategies:
Prepolymers, Quasi-prepolymers, One–shot and Single Component Technologies

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Introduction
Castable thermoset polyurethane elastomers have been processed in the United States since the early 1950’s. First introduced to the big established rubber companies as a new, “atomic age” synthetic rubber that had the potential of obsolescing much of conventional rubber processing equipment such as banburys, mills, kneaders, extruders, boilers and steam distribution systems, etc. In general, the major rubber companies ignored this new, disruptive technology and proceeded with the status quo. As a result, a new set of small, entrepreneurial companies seized upon this technology and took advantages of its many attributes.

Let’s take a moment to review these wonderful attributes.

Easy of processing
Thermoset urethane elastomers are made from low viscosity fluids that range from a few tens to a few thousand centipoises. That means they are easy to mix and pour into a mold. Everyone here knows that a large range of thermoset urethane elastomers can be mixed by hand using a spatula and a plastic bucket. Even today there are several quite successful companies processing urethanes by this hand batch method.

Low entry cost
As stated above, the requirements to enter the castable urethane business is quite modest. It does not require a large space or highly expensive equipment or exotic tooling. A typical urethane shop typically starts up with a few used pizza ovens, a vacuum pump, air compressor, a drill press, scales of various kinds, tin cans, plastic buckets, work tables and few more very common items. Most of this stuff can be (and is) purchased at industrial auctions or industrial supply house such as MSC.
Simple tooling
Producing the vast majority of urethane elastomer parts from thermoset raw materials does not require exotic tooling. They are commonly machined from aluminum or steel ether in house using a few basic machine shop tools (lathes and mills) or down the street at your friendly neighborhood machine shop. Many companies in the business make all kinds of tooling from thermoset cast urethane itself—it’s cheap, quick and easy to make many molds in a short period of time and they are disposable.

Processing
Because thermoset castable urethanes can be cast at atmospheric pressure, no presses are required. This fact greatly simplifies processing- just weigh out the components, mix them, cast into molds, cure at modest temperatures and demold. Done! Many experts in the field have compared it to baking a cake.

Outstanding Physical Properties
Thermoset castable urethane elastomers, as we all know, have outstanding physical properties- tensile strength, tear resistance, low temperature flexibility, excellent oil and water resistance, to name a few. It is these problem solving attributes put into the hands of the few pioneering entrepreneurs that sent them at the head of the class.

Marketing
Thermoset castable elastomers have established an excellent reputation in industry by solving many troublesome problems in such areas as O-rings and gaskets, forklift tires and load wheels, belt scrapers, mineral processing equipment, printing rollers, industrial rollers, skate board and roller skate wheels. The list goes on and on. All this was made possible by a few forward thinking pioneers processing what the so-called experts in the major rubber companies passed off as “interesting but not practical technology”.
Discussion
So far I have given a very brief history of castable thermoset urethanes and described their virtues. The next logical question is how do you process them- what are the options? What are the tradeoffs? As stated in the title of this paper, there are four basic technologies in current use- prepolymer, quasi-prepolymer, one-shot and single component.

Prepolymers
Early on, it was quickly recognized that pure isocyanates liberated a great deal of energy when directly reacted with hydroxyl containing moieties such as glycols and polyols and even much more so with various aromatic primary amines. These reactions are so exothermic that they self-destruct; i.e., no orderly polymer structure could be created. In extreme cases, they would catch fire. A practical way had to found to tame this beast! Synthesizing prepolymer was found to be the answer.

The word prepolymer was coined to give in one word a good description of the process. It stands for pre-reacting the isocyanate with a polyol to decrease the isocyanate content of the isocyanate monomer. Take TDI for instance: it has an isocyanate content of 48% and is packed with potential chemical energy- too much to handle on a practical basis by a processor.

A clever way around this problem is to partially react the TDI with a polyol. In that way some of the chemical energy is used up to form the prepolymer- which still have some available Isocyanate sites to continue the reaction. Take for example the case of TDI and PTMEG-1000 (polytera-methylene glycol) with a molecular weight of 1000 and a functionality of 2.0). If you react one (1) mole of PTMEG-1000 with two (2) moles of TDI you end up with a prepolymer with a molecular weight equal to the sum of all the components (1348) and an NCO content of 6.2%. The beast has been tamed by taking a very small, volatile molecule (TDI) with a
very high NCO content (48%) and creating a much more manageable isocyanate-containing entity (a prepolymer) with a 6.2% NCO content.

TDI prepolymers are made in jacketed chemical reactors, with good agitation, under vacuum. The reactants are gently heated to the point where the reaction becomes exothermic and cooling water is applied to the jacket to control the reaction. As you can imagine, there are many, many different types of backbones and variants within specific backbones to say nothing of a range of molecular weights and functionality for a chemist to play with to meet a wide variety of end use requirements.

It’s worth the time to pause and reflect upon the point that chemical companies that make urethane prepolymers have for over fifty (50) years refined this technology to supply the industry with what is required by the market with respect to processability, physical and chemical properties of the vulcanizate and economics. Once more prepolymers are storage stable for about one year, and can be packaged in 5-gallon pails, 55-gallon drums or totes.

Prepolymers are designed by the manufacturers to be easily and straightforwardly used by their customers, the urethane processor. In summary, just open the drum and process according to directions- much of the painstaking chemistry has been done for the processor.

Summing up, urethane processors take advantage of urethane prepolymer technology to produce a wide variety of parts with highly desirable characteristics. The prepolymer is combined with the prescribed amount of curative or chain extender and poured into a mold. That’s it!
Quasi-prepolymers
A loose definition of quasi is “sort of”. A quasi-prepolymer is not quite a monomeric isocyanate and not quite a full prepolymer. It is in between. It has the characteristics of both and yet some unique properties unto itself. TDI quasi-prepolymers are technically possible to make but are very rarely used in the thermoset castable urethane industry because of obvious health and safety reasons. MDI quasi-prepolymers are overwhelming the ones used in the industry. Typically pure MDI monomer is partially reacted with a glycol or polyol to reduce the NCO content of pure MDI from about 44% down to a range of 12 to 25%. MDI quasi-prepolymers contain both free monomeric MDI and MDI prepolymer. This mixture solves a lot of problems- pure MDI’s tendency to dimerize. Quasi-prepolymers are liquid at room temperature and much easier to formulate as well as easier to mix without separation. Pure MDI tends to be hydrophobic, common glycol chain extenders tend to be hydrophilic and, as such, requires high shear mixing to consistently produce high quality parts. Most MDI quasi-prepolymers are stable for several months at room temperature, making life a little easier for the processor. MDI quasi-prepolymers can be either purchased from a number of reputable suppliers or made in house.

There are two basic reasons for making quasi-prepolymers in house: cost savings and proprietary formulations. Any time you purchase something simple that you can do yourself you are wasting money. The reason is the possibility of making your own propriety quasi-prepolymer with the possibilities of using lower cost raw materials or novel glycol structures such as MP-diol, 1,3-triethylene glycol, 2,2’-thiodiethanol, CHDM (1,4-cyclohexanedimethanol), to name a few. The combinations and permutations are almost endless.

Since the MDI-polyol reaction is mildly exothermic, very simple equipment is required to make MDI quasi-prepolymers. A typical reactor is a heated, agitated tank capable of withstanding a full vacuum and pressure up to 30 psig. Many companies have modified
120 gallon compressed air tanks, readily available at industrial supply stores, such as MSC, to do this job. The modification process is really very simple: cut a hole in the top and weld a flange designed to accept an agitator; drill a few more small holes near the top to accept vacuum/pressure lines and a thermal couple, add a bottom valve and nipple that will be used to add the MDI and polyol or glycol and remove the product, then add some bottom and side heaters, wrap some insulation around it and you have a quasi-prepolymer reactor. No cooling system is required. Don’t forget to weld on some legs!

Quasi-prepolymers based thermoset cast urethane systems have another great advantage. The technology enables the use of much cheaper, liquid at room temperature polyols that can be formulated into systems that can be processed at or just above room temperature and require no post curing at elevated temperatures if properly catalyzed. Because these systems can be processed at or near room temperature, a skilled formulator can sneak in a reasonable amount of MOCA or E-300 into the “B” side of a formulation to enhance specific physical properties such as tensile and tear strengths and still have enough gel time pour most parts.

Another great feature of quasi-prepolymer based thermoset cast urethane systems is the ability to formulate them so the “A” to “B” ratio are simple whole number integers such as 1:1, 1:2, 3:2, etc. This makes it vastly simpler to process either by hand batching or machine dispensing. Unlike prepolymers which have ratios of “A” to “B” typically 9 or 10 to 1, any small deviation for true ratio in quasi-prepolymer systems is not catastrophic. Not so with MDI prepolymers!

The creation of quasi-prepolymers also reduces the hydrophobic/hydrophilic compatibility problems of many prepolymer systems, making it much easier to get repeatable results under mild mixing conditions. The simple ratios, low processing
temperature requirements and component compatibility features makes dispensing machine design and operation very simple and easy.

In many cases, no complicated dynamic mixing head is required—static mixers do the job just fine. Many companies have designed and built their own dispensing machines in-house using only maintenance personnel. Quasi-prepolymer technology makes much easier to transition from a hand batch shop to a machine pour operation.

One-shot
I am going to use a rather strict and somewhat arbitrary definition of one-shot casting technology. One-shot technology, as I define it, is the utilization of only monomeric components on both the “A” and “B” sides. Thus, for the “A” or isocyanate side, an MDI would be utilized. The MDI could be pure 4,4’-MDI, blends of 4,4’ and 2,4’-MDI or so-called crude or polymeric MDI with a functionality up to 2.3.

On the “B” or polyol side, each polyol and glycol is kept separate. All components are blended together at once and poured into a mold. The advantage of this technology is that the chemical components of a castable thermoset cast elastomer systems can purchased individually at the lowest possible price. The processor does not have to pay for the services of someone to make a prepolymer or quasi-prepolymer or for that matter, establish in house quasi-prepolymer capability. Of course handling 4,4’-MDI does require attention to its storage—generally in refrigerated reefers.

The sky is the limit with respect to the possibilities of compounding exactly what the end use or customer demands with respect to physical/chemical properties and or cost.
Once more, one-shot technology is amenable to machine processing, albeit using quite sophisticated, expensive equipment. Each component is injected into the mix head under precise temperature and ratio control and mixed vigorously. This is called “compounding in the head”. Of course this requires sophisticated pouring machine equipment with reliable, precision flow meters, and feedback loops controlled by a computer. In summary, one-shot technology allows, with just the inventory of a half-dozen or so chemical components, the processor to formulate a vast array of proprietary, thermoset, castable urethane elastomers to meet many market demands and still maximize profits!

**Single Component (Shoot and Scoot)**

Single component liquid castable thermoset urethane elastomers are hard to classify. There are two basic but different systems reported in the literature. One system uses MDI prepolymer that are coupled with a blocked curative or chain extender so that it is inert at room temperature. That extender is methylene dianiline (MDA) blocked with sodium chloride. This allows the prepolymer and it’s blocked (inert) curative to be combined in a single, stable package by the manufacturer.

All the processor has to do is open the drum, pour out what is required of the pre-degassed material, fill the mold and place it in an oven to cure. As the material heats up, the sodium chloride disassociates from the MDA moiety. The free MDA is now able to react with the MDI prepolymer and the system cures. The residual sodium chloride is left in the cured elastomer but has almost no measurable effect on physical or chemical properties. Another variation of this blocked isocyanate principle use oximes, pyrazoles, caprolactams and other chemicals as the blocking agents. In this case the blocking agent is used in larger amounts and still remains in the system. It functions as a plasticizer and somewhat degrades properties. This technology is limited to certain
durometers and dimensions. A typical end use is in certain print rollers.

Another completely different approach to the single component urethane elastomer concept involves the use of di-beta hydroxyethylether of hydroquinone (HQEE) in a solid, almost nano-size dispersed particles. The system consist of a liquid MDI adduct, HQEE solid micro particles dispersed in a polyol with a heat activated catalyst (zinc stearate). This system is stable for several hours (it slowly reacts at room temperature) but quickly cures when heated to the point where the HQEE melts and becomes active. When placed in a 150C mold, a part cures very quickly and can be demolded in approximately two minutes. This technology is the basis for liquid injection molding (LIM), first cousin of reaction injection molding (RIM). For a more complete description of this system, see US patent 4,119,594.

Epilogue
So there you have it-four basic ways to process liquid castable, thermoset polyurethane elastomers. They range from fully prepared single component (shoot and scoot) systems where all the processor has to do is pour the material into a mold and place it in an oven to multi-component one shot systems processed in sophisticated, computer controlled dispensing machines. Each method has its advantages and disadvantages as well as limitations to durometers and other physical properties. These four basic methods of processing liquid castable, thermoset polyurethane elastomers have something to offer anyone in or contemplating entering the business.