



# AirMail

TIMELY TECH TIPS AND HOT NEWS FOR OUR GLOBAL POLYURETHANE CAST ELASTOMER CUSTOMERS

## Dealing with **Low Hardness**

Polyurethane elastomers made with Air Products' prepolymers can be formulated to cover a wide range of hardness. Typically, hardnesses range from 10-15 Shore A (durometer), which is softer than a gum eraser, to over 90 shore D, which is much harder than a golf ball.

Sometimes it is difficult to obtain desired hardness, especially low hardness.

Hardness measurements are considered statistically the same if they are  $\pm 3$  points from the average of several measurements. If the hardness is outside this range, then there could be a hardness variation concern.

**1. Potential Causes:**

**1. OVERHEATED PREPOLYMER**  
Using an overheated prepolymer will have the same ultimate effect on the elastomer as if it was processed at an incorrect stoichiometry. You will be able to tell that a prepolymer has become overheated because it will have a lower percent NCO than what is indicated on the prepolymer container.

**2. INCOMPLETE CURE**  
Post-cure is especially critical because it relieves internal stresses and allows proper alignment of the polymer chains.

**3. INCORRECT STOICHIOMETRY**  
With gross errors in stoichiometry, an elastomers' hardness may decrease.

**4. INADEQUATE MIXING**  
Inadequate mixing creates areas in the elastomer that are rich in prepolymer or curative. This leads to incorrect stoichiometry, which in turn results in problems with a parts' physical properties.

**2. Solutions:**

**1. MINIMIZE THE HEAT HISTORY**  
Strictly follow the manufacturer's guidelines for exposure of the prepolymer and curative to heat.

**2. FOLLOW SUPPLIER CURING GUIDELINES**  
Prepolymer suppliers have standard recommendations for the curing of their materials. A typical guideline is to cure the prepolymer for 16 hours at 100°C. However, you must verify this recommendation for each system. Some prepolymer/curative combinations require different conditions.

**3. CALCULATE THE AMOUNT OF CURATIVE PROPERLY**  
Maintaining the correct ratio of curative to prepolymer, which is called stoichiometry, is critical in producing consistent, high-quality elastomers. The typical ratio used to obtain the best combination of properties is 95 percent. This means that 95 percent of the prepolymer isocyanate groups (NCO) are chain extended with the curative, and 5 percent are left to react with other NCO groups to form chemical cross-links.

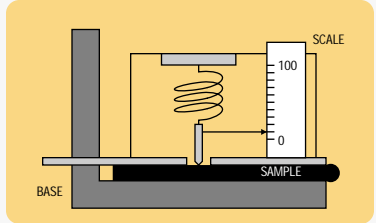
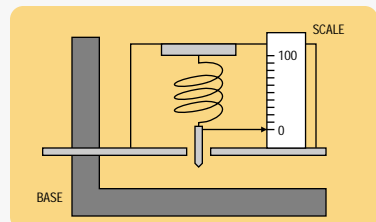
### Why do Elastomers Soften During Storage or Field Use?

Occasionally, the hardness of an elastomer will be acceptable at the time of manufacture, but later, during storage or field use, it will soften considerably.

There are three main causes: Contact with solvents, exposure to excessively high temperatures, and incorrect prepolymer choice. In addition, incorrect stoichiometry can also adversely affect a system and result in softening.

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**Fig. 1 Test Procedure to Measure Hardness (ASTM Method D676):** The hardness of an elastomer is determined with a durometer. This instrument measures resistance to the penetration (without puncturing) of a blunt indenter point pressed onto the elastomer surface against the action of a spring. A pointer moves across a scale to show the resistance to penetration. Scales on the Shore durometer read from 0 to 100, with higher numbers denoting greater hardness. Two scales are commonly used for elastomers: the "A" scale for soft materials, and the "D" scale for materials of higher hardness. These scales do overlap, as Fig. 2 shows.

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## Dealing with Low Hardness

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### Question: Cold Hardening

**QUESTION:** How could a 50A hardness part we produced change to 80A in the field over the winter?

**ANSWER:** This cold hardening may be the result of soft segment crystallization, which frequently occurs with soft parts under 70A hardness. The backbone of these systems is generally a high-molecular-weight polyester polyol. The polyester in this material sometimes forms concentrated regions that can solidify or crystallize, which increases the overall hardness of the elastomer.

A quick way to determine if this is the cause of the increased hardness is to place the hardened elastomer into a 212°F (100°C) oven for several hours. After cooling the part to room temperature, if the hardness returns to its original, lower value, then the problem is soft segment crystallization. Unfortunately, the hardness of the part will increase again, so this is not a permanent fix the part should not be put back into service.

The best way to minimize cold hardening is to use Versathane™ QM prepolymers. With this type of mixed backbone prepolymer, the crystallinity of the elastomer is disrupted enough to reduce the chance of soft segment crystallization. Versathane QM prepolymers also have the advantage of shorter meltdown times versus standard polyester prepolymers. ▲

### Why do Elastomers Soften During Storage or Field Use?

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**CONTACT WITH SOLVENTS:** Continued contact with most petrochemical-based solvents can cause many polyether-based elastomers to soften significantly. Water, which is also a solvent, can have a softening effect on most polyester elastomers after sustained contact. To avoid these problems, we recommend designing the application area so that elastomers do not come in contact with any solvents.

**EXPOSURES TO EXCESSIVELY HIGH TEMPERATURES:** Continued exposure to elevated temperatures can cause the urethane bonds within an elastomer to break down, leading to part softening. To minimize overall heat exposure, elastomers should be insulated from the heat source. In addition, the temperature level should be monitored.

**INCORRECT PREPOLYMER CHOICE:** Polyether and polyester-based elastomers react very differently to solvents. It is important to use the most appropriate prepolymer backbone for the application. Generally, polyether prepolymers should be chosen for use with aqueous environments, and polyesters for use with most organic solvents. It has been documented that polyester-based elastomers can soften considerably when stored at elevated temperatures under high humidity. ▲

Polyurethane Elastomers	Hardness Scales			Conventional Plastics & Rubbers
	DUROMETER A	DUROMETER D	ROCKWELL R	
			150 —	— Phenolics
			140 —	
			130 —	
			120 —	— Acrylics
			110 —	— Polycarbonate
			100 —	— Nylon
Papermaking rolls —	80 —	70 —	90 —	— Polystyrene
Metal-forming wiper dies —	70 —	60 —	70 —	— Polypropylene
			50 —	
Nonspark hammers —	95 —	50 —	50 —	
Solid truck tires —	90 —	40 —		
Metal-forming die pads —	80 —	30 —		
Idler rolls —	70 —			
Abrasive-handling pads —	60 —			
Silk screen wiper blades —	50 —			— Auto tire treads
Door seals —	40 —			— Inner tubes
Can tester pads —	30 —			
Printing rolls —	20 —			— Rubber bands

**Fig. 2 Hardness:** Polyurethane elastomers made with Air Products' prepolymers can be formulated to cover a wide range of hardness. This table shows the spectrum of hardness values possible and a few examples from the correspondingly wide range of applications.

Many processors will use an average percent NCO for determining the amount of curative to use with a prepolymer. However, with some prepolymers, this can amount to a stoichiometry error as great as 5 percent. That affects properties significantly, depending on the target stoichiometry.

Each drum of prepolymer has a specific percent NCO. Be sure to calculate the amount of curative to be used with the prepolymer in each drum:

$$(\% \text{ NCO}) \times (\text{stoichiometry}) \times (\text{curative equivalent weight}) \times (\text{amount of prepolymer}) = 42.02$$

#### 4. MIXING OF ALL COMPONENTS WELL

Use a pigment to help highlight areas of insufficient mixing. ▲

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