

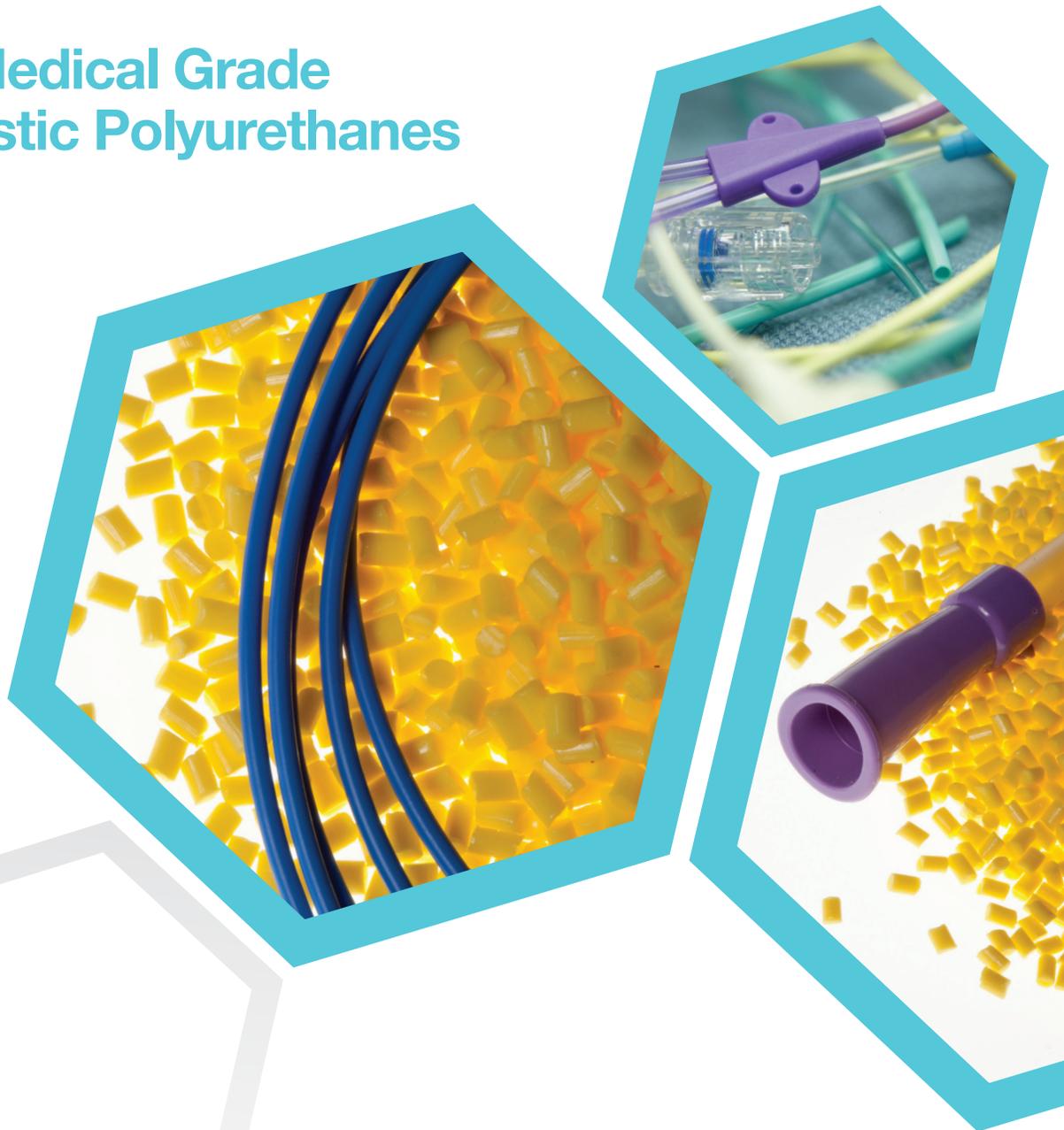


Lubrizol LifeSciences

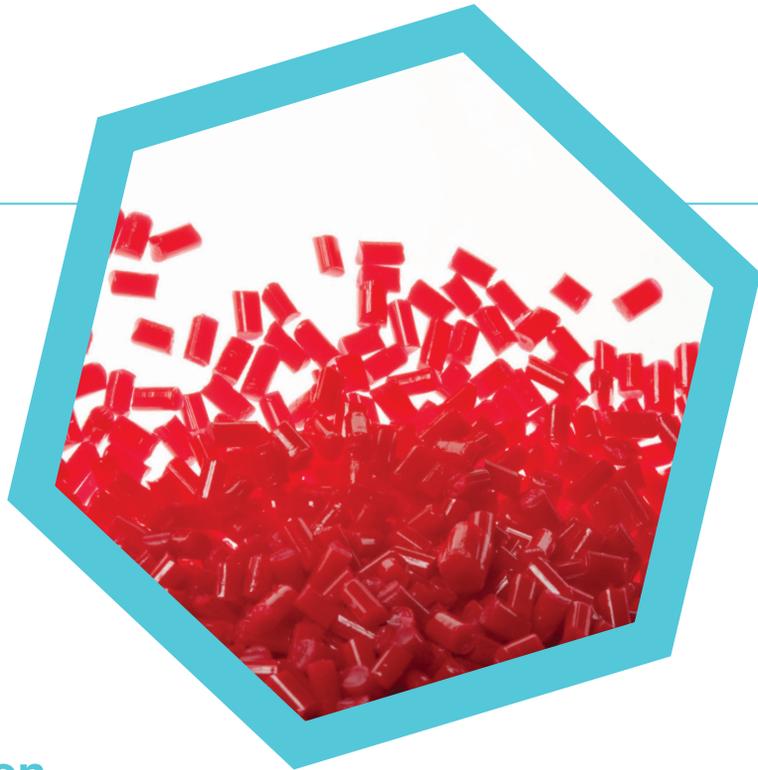
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POLYMER SOLUTIONS

Drying of Medical Grade Thermoplastic Polyurethanes



Lubrizol



Introduction

Thermoplastic polyurethane (TPU) elastomers are hygroscopic in nature and have a tendency to absorb moisture when exposed to atmospheric humidity. Prior to the processing (i.e. thermal or solvent) of TPUs, the moisture content must be reduced to a minimum to prevent:

- Reduction of the molecular weight
- Change in viscosity
- Loss of mechanical properties
- Defects in the end product
- Rough surfaces
- Poor melt strength
- Pressure fluctuation during processing

IF YOU DON'T DRY IT, DON'T TRY IT

What is a Thermoplastic Polyurethane?

Thermoplastic Polyurethanes are highly versatile elastomers with unique properties that offer both superior performance and processing flexibility. Specifically, a TPU is a block copolymer that consists of alternating sequences of hard and soft segment domains (See Figure 1). TPU's adaptability is due to the presence of both hard and soft segments in its chemical structure. The ratio of hard and soft segments can be manipulated to produce a wide range of durometers. For example, a greater ratio of hard to soft segments will result in a more rigid TPU.

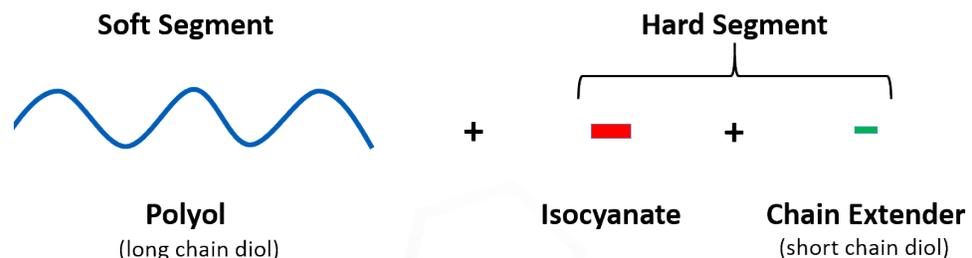


Figure 1. Hard and soft segment diagram of TPUs

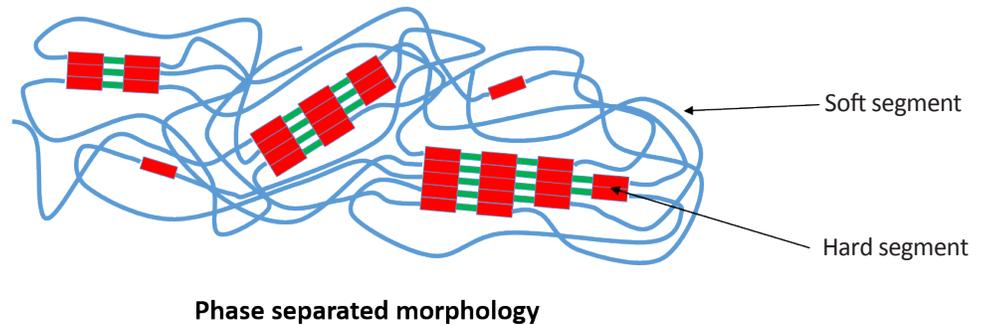


Figure 2. Hard and soft segment phase separated morphology

Hard segments consist of isocyanates and chain extenders, and can be classified as either aliphatic or aromatic depending on the type of isocyanate. Soft segments consist of a reacted polyol. The ratio of hard to soft segments in a given grade of TPU, as well as the type of isocyanate and polyol are responsible for the properties of the resulting TPU.

The Importance of Drying

TPU elastomers are hygroscopic in nature and have a tendency to absorb moisture when exposed to atmospheric humidity. Aromatic polyurethanes undergo a polymerization/depolymerization reaction at an equilibrium rate when processed above 180°C (355°F) to 200°C (392°F). Typical extrusion conditions require temperatures upwards of 180°C (355°F). If water or moisture is present during extrusion, the reaction shown in Figure 3 occurs. This results in breakdown of polymer chains and the release of amines and carbon dioxide. Failure to remove moisture from polyurethanes may also cause polymer rearrangement, molecular weight reduction, and significant loss of physical properties. In addition, excess moisture in TPU resins can cause voids and other defects in extruded and molded parts during the extrusion or molding operation.

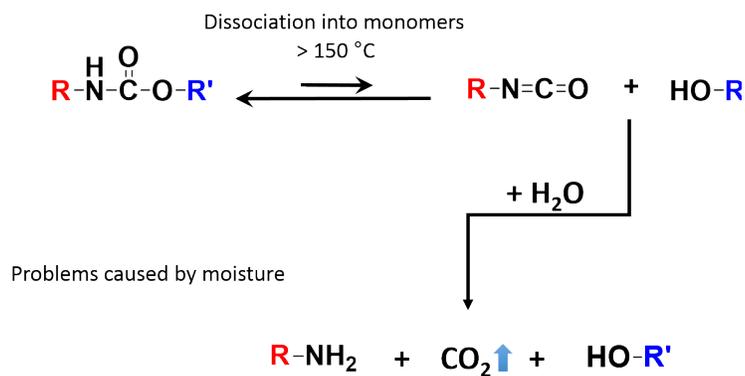


Figure 3. Result of moisture in TPU processing

Impact of Moisture During Extrusion

When looking at the impact of moisture, compare extruder pressure to that of the resin temperature in the extruder. Figure 4 shows the normal process of pressure decrease as temperature increases during single screw extrusion. The plot also demonstrates that when moisture content is outside of recommended maximum amount (0.02% to 0.05% by weight) for the resin, the pressure drops rapidly. Pressure instability, or drifting of an otherwise stable process, can be an indication of excess moisture in the resin.

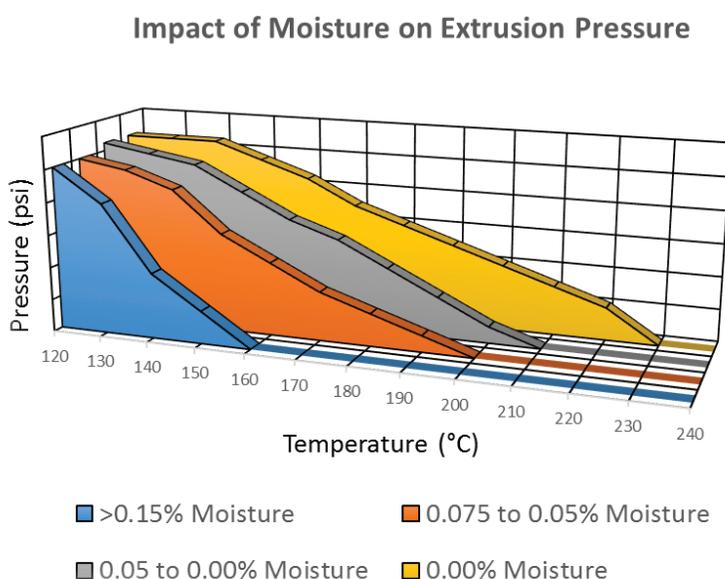


Figure 4. Impact of moisture on processability

In the case of aromatic TPUs with excess moisture, irreversible depolymerization starts at 150°C (302°F) as illustrated in Figure 5. When looking at Figure 5, you will also find time dependence and the degradation impact of moisture. At 180°C (356°F) the degradation rate becomes a concern in the presence of moisture, as typical single screw extrusion and molding residence times are long enough to significantly and irreversibly degrade the resin. Because processing temperatures for most aromatic TPUs are above 180°C (355°F), the material must be thoroughly dried. It is important to note that temperatures in excess of 250°C-300°C (482°F - 572°F) can cause thermal degradation in aromatic TPUs, regardless of moisture content.

By comparison, aliphatic TPUs undergo a polymerization/depolymerization reaction around 200°C (392°F) to 220°C (428°F). In some cases this is above the processing temperature, and moisture in the resin does not typically cause irreversible depolymerization. However, moisture in aliphatic TPU can cause processing instabilities, which may affect melt viscosity and create melt defects (bubbles, splay, etc). The typical thermal degradation temperature for aliphatic TPUs is 270°C (518°F), regardless of moisture content.

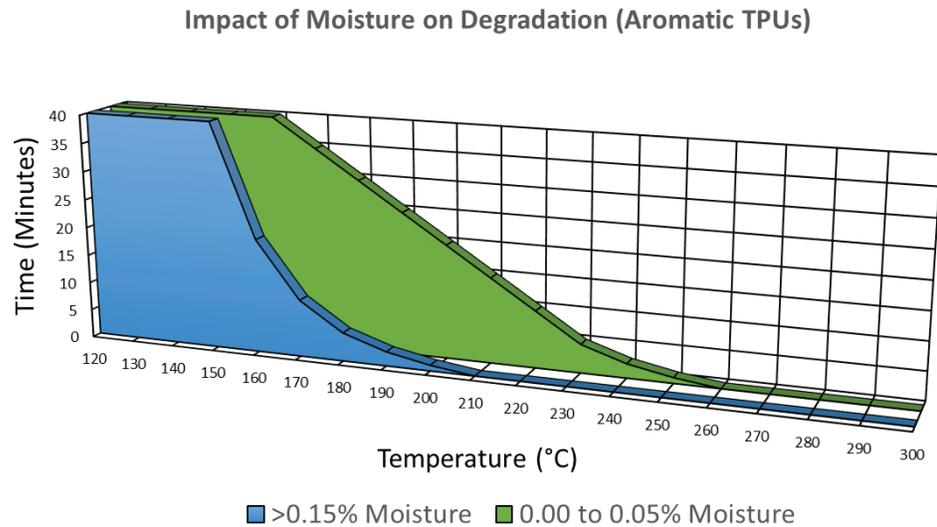


Figure 5. Impact of moisture on degradation time (aromatic TPUs)

Drying Methods and Equipment

When exposed to ambient air, TPU resin can absorb up to 3% water by weight. To properly dry TPU resin, four essential parameters must be considered:

- Temperature
- Dew point
- Time
- Airflow

Drying temperature is crucial, as water molecules can form intermolecular bonds with hygroscopic materials such as TPU. Should this happen, heat is required to break the intermolecular bonds. While higher temperatures dry the resin more quickly, excessive heat may result in oxidation, premature yellowing, and/or thermal degradation.

In addition to heat, the dew point of air in the drying equipment determines the degree of resin dryness that can be reached. Dew point is the temperature to which air would need to be cooled in order to reach 100% relative humidity (i.e. to form dew droplets). Low dew point air creates low vapor pressure around the pellet, which allows moisture to be drawn to the outside of the pellet. Prolonged hot air drying with “moist” air (i.e. dew point too high) will result in inadequate drying. Thus, a low dew point is required for achieving adequate drying of the resin. Lubrizol recommends a drying air dew point of -40°C (-40°F) for all medical grade TPU resins.

Because TPU resin does not dry immediately, sufficient time is needed for complete drying. Drying time can vary based on the temperature and dew point of the drying air. Specific drying times depend on resin composition and initial moisture content.

Sufficient airflow in the dryer is critical to effectively heat the resin to the specified temperature. Airflow must be adequate to maintain the temperature needed to dry the specific volume of resin during residence time in the dryer.

Dryer Technology

Principle of Desiccant Dryers

A desiccant dryer system operates as a closed loop system where heated “dry” air is circulated over a thermoplastic resin, which releases absorbed moisture into the passing air. This “wet” air subsequently passes through a desiccant molecular sieve material. The desiccant material is able to absorb moisture from the circulating air making it “dry” again. There are two forms of desiccant systems; a desiccant bed system (see Figure 6) or a desiccant wheel system (see Figure 7).

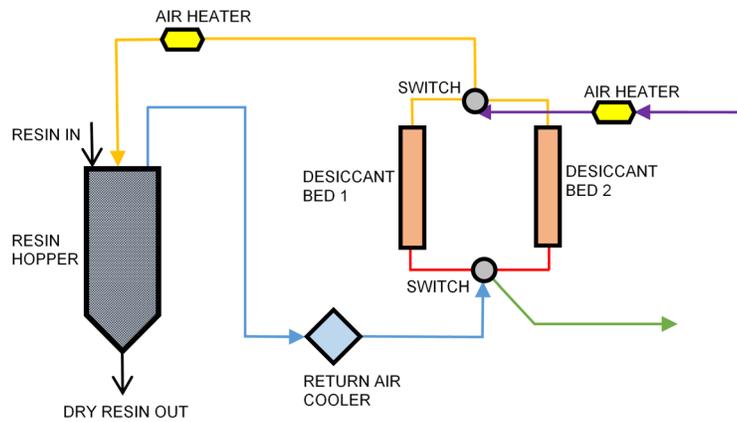


Figure 6. Schematic diagram of a two desiccant bed dryer.

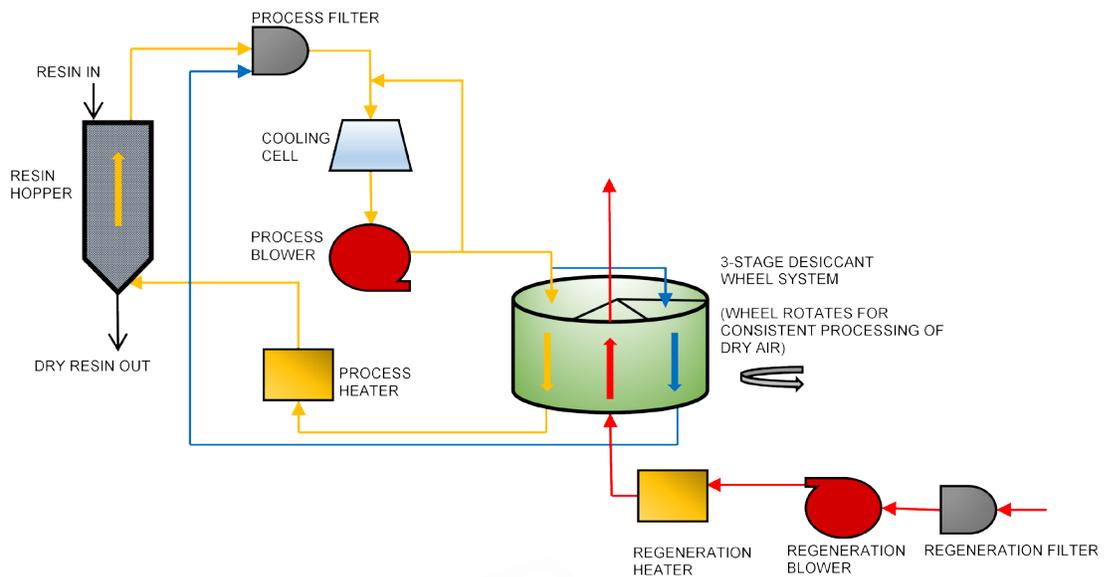


Figure 7. Schematic of desiccant wheel dryer.

During operation of a desiccant bed dryer, the desiccant bed becomes saturated with moisture that has been removed from the resin. After a period of time, it becomes fully saturated and is no longer able to reduce moisture in the passing air. To further dry the material, the saturated desiccant bed first needs to release its absorbed moisture. The process of drying a desiccant bed is called “regeneration.” This process is explained in detail in the “regeneration” section below.

In the desiccant wheel dryer, the desiccant wheel is constantly rotating, allowing the unit to go through its drying, cooling and regeneration process constantly. Because the desiccant wheel unit is constantly running, it is more efficient and has a lower power consumption rate. Unlike the desiccant bed system, this system does not have to shut off part of the unit to regenerate the desiccant.

Regeneration

The process of drying a moisture saturated desiccant bed is achieved by passing heated ambient air over the desiccant. Elevated temperature (>200 °C [392°F]) causes the desiccant bed to release absorbed moisture.

For desiccant bed type dryers, while the saturated desiccant bed is regenerating, another dry desiccant bed is switched into the closed loop and is able to continue drying the material.

For desiccant bed dryers, once the bed is sufficiently dry, it is cooled and can be switched back into the closed loop when the alternate bed becomes saturated with moisture.

For desiccant wheel dryers, air that has been filtered and heated above 200°C (392°F) is passed through the regeneration section, removing moisture absorbed by the desiccant wheel.

If the dryer has only one desiccant bed, the material will not dry during the regeneration of the moisture saturated bed. To overcome this time loss, dual or quad bed desiccant dryers have been developed. Lubrizol prefers multiple desiccant bed or desiccant wheel type dryers for TPUs, as a continuous flow of dry air with a low dew point is required for complete drying. Single desiccant beds tend to produce a larger fluctuation in moisture content in the air, which is not ideal for drying Lubrizol TPUs.

The Efficiency of a Desiccant Bed

If the dryer has been in use continuously for longer than two years, or an equivalent period intermittently, some degradation of the molecular sieve in the desiccant beds may have taken place. The dryer may no longer be able to reach the specified dew point. The best way to establish if there has been a serious deterioration of moisture absorption capacity is to calibrate the dryer on a regular basis with an external calibrated dew point meter.

Return Air Cooling

Desiccant beds have better moisture absorption capacity when they remain at a low temperature, as more moisture condenses at a lower temperature (see Figure 8). A return air cooler is sometimes placed between the material hopper and the desiccant bed to reduce the temperature of returning hot air. The presence of a return air cooler is recommended for drying Lubrizol TPUs.

In desiccant wheel dryers, the drying, regeneration and cooling zones are located around the wheel. The section of the desiccant wheel in the cooling zone will decrease in temperature and will increase its ability to absorb moisture from the drying air. As the wheel rotates continuously, the desiccant will consistently go through drying, regeneration and cooling zones.

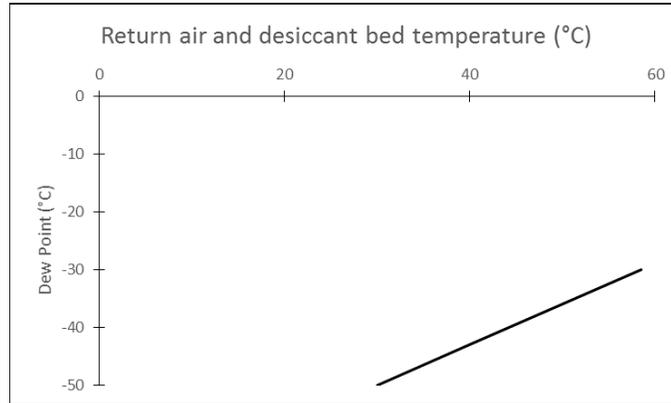


Figure 8. Dependency of dry air dew point on return air and desiccant bed temperature

Principle of Compressed Air Membrane Dryers

Another method of drying thermoplastic resin is a compressed air membrane dryer. A compressed air membrane dryer uses specialty membrane filaments that pull water molecules out of saturated air. Water is then pulled through the membrane to vents outside the membrane casing. The newly dehumidified air is then heated and circulated into the resin hopper. Air is then recirculated through the unit to remove moisture from the resin (see Figure 9).

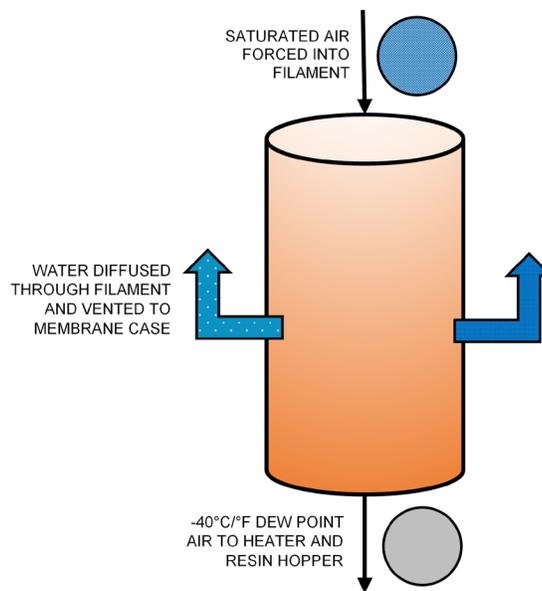


Figure 9. Diagram of membrane in compressed air/membrane dryer.

Dew Point Meters and Calibration

The specification of a dryer will give an indication of the lowest possible dew point it can reach. If the dew point is approximately -40°C (-40°F), the dryer is most likely able to dry Lubrizol TPUs.

Dew point on desiccant dryers is measured using a dew point meter. Dew point meters must be calibrated often, especially when used continuously.

It is important to note that measured dew point readings appear to become lower with time, but as the desiccant gets older, its efficiency decreases and the true dew point rises (see Figure 10).

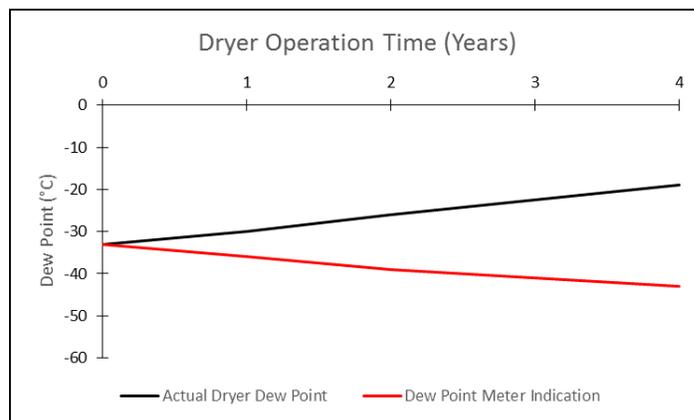


Figure 10. Example of the discrepancy between actual and measured dew point of dryer.

To ensure accuracy from a permanently connected dew point meter, disconnect it from the dryer and expose the sensor to ambient air for a few hours each month. This prevents the sensor from drying out, which causes inaccuracy. Refer to manufacturer recommendations for further details.

Location of the Dew Point Meter is Important

An internal or external dew point meter should be used to measure samples from the air inlet to the drying hopper in order to provide the best indication of equipment performance. A dew point meter will help detect any malfunction of the drying system prior to processing. All drying systems should be pre-dried by running the system one full cycle prior to loading. This way, the system will achieve the necessary operating temperature. Pre-drying ensures the dew point of the air in the drying hopper is -40°C (-40°F) before Lubrizol TPU resins are placed into the hopper.

Specifying a Dryer

Specification of a dryer for Lubrizol TPUs should take into account the overall drying capacity needed (lbs or kg per hour), as well as temperatures and drying times required by the specific TPU grade. The following sections of this guide give recommendations for drying specific Lubrizol medical grade TPU resins.

To obtain additional guidance on dryer specifications, contact a drying equipment supplier. See a partial list of drying equipment suppliers shown below in Table 1.

Table 1. Partial list of dryer suppliers

Company	Location
Conair	Cranberry Township, PA
Novatec	Baltimore, MD
Labotek	Frederikssund, Denmark
Harmo	Nagano, Japan
Motan Colortronic	Überlingen, Germany
Una-Dyn Inc.	Woodbridge, VA
Wittmann	Torrington, CT

Note: This list is given for convenience and is not intended to be complete or a recommendation of suppliers

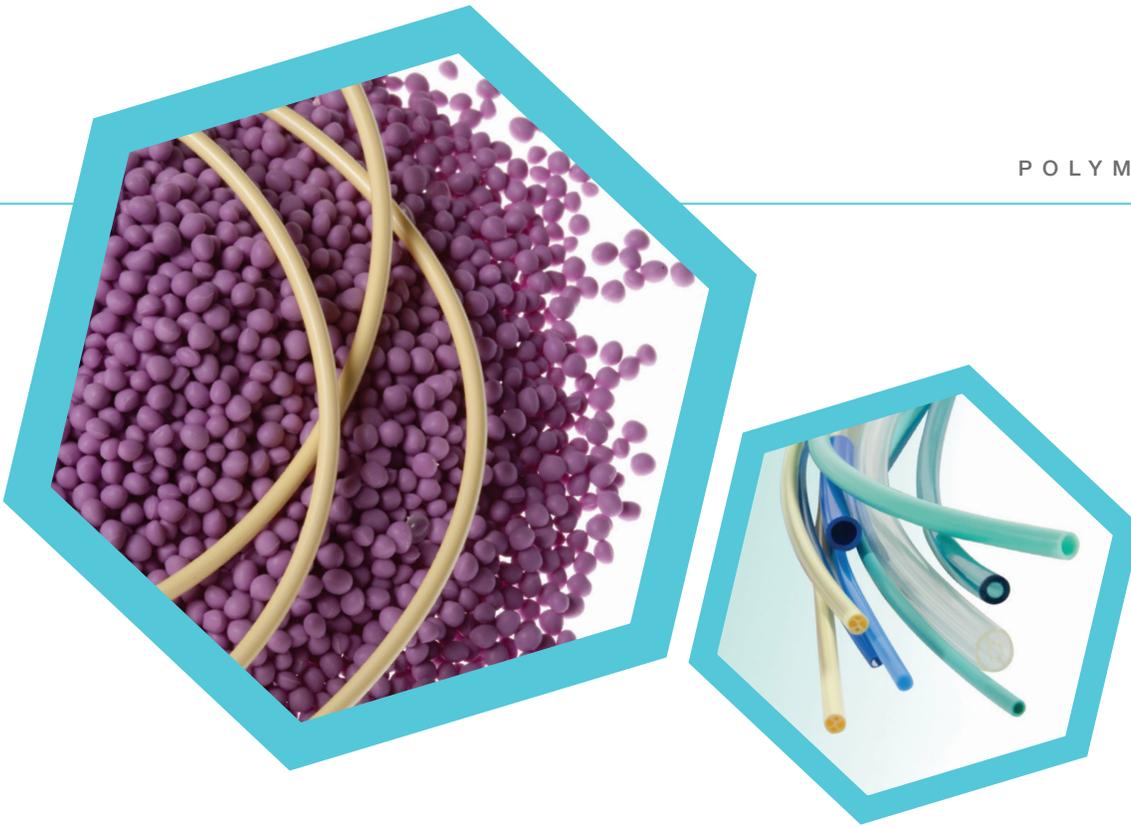
Moisture Analyzer Equipment

To determine and control the moisture of TPU resin, measuring the moisture content is recommended. Simple gravimetric weight loss moisture analyzers can be used. Moisture analyzers should be specified to allow for moisture determination to as low as 0.001 percent water. Table 2 shows a partial list of moisture analyzer manufacturers. Lubrizol typically recommends 145°C (293°F) for 10 minutes to obtain a moisture reading depending on the instrument used and the specific TPU to be tested.

Table 2. Partial list of moisture analyzer suppliers

Company	Location
A&D Engineering	San Jose, CA
Arizona Instruments	Chandler, AZ
Brabender Instruments	South Hackensack, NJ
Mettler Toledo	Columbus, OH
OHAUS	Parsippany, NJ
Radwag	North Miami Beach, FL
Sartorius	Bohemia, NY
Scientific Industries	Bohemia, NY
Shimadzu Scientific Instruments, Inc.	Columbia, MD

Note: This list is given for convenience and is not intended to be complete or a recommendation of suppliers



Drying Requirements for TPUs

To achieve optimal chemical and mechanical properties, TPUs are recommended to be dried to a moisture content (by weight) of:

- Less than 0.02% for AROMATIC TPUs
- Less than 0.05% for ALIPHATIC TPUs

The amount of moisture that can be tolerated in processing depends on process temperature, residence time of the molten polymer, and chemistry of the TPU being processed. Higher temperatures, longer residence times, and higher durometer resins impose more stringent drying requirements to prevent moisture related defects.

Once dry, it is critical to retain low resin moisture levels during processing. Ambient air humidity will have a significant impact on how quickly TPU resins re-absorb moisture when exposed to the environment. Keeping resin dry during processing can be achieved by mounting the dryer hopper to the equipment feed hopper. Alternatively, a small shot hopper can be used if it is fed by a closed loop dry air conveyor from a larger dryer hopper.

Effect of Moisture on Extruded and Molded Parts

Failure to remove moisture from Lubrizol TPUs prior to melt processing may cause polymer rearrangement, molecular weight reduction, and significant loss of physical properties as shown in Table 3. The excess moisture in TPU resin can cause voids and other defects in extruded and molded parts during processing. Although voids may not always be apparent during extrusion or molding of resins with high moisture content, degradation of the material and reduced physical properties are extremely likely.

Table 3. Typical effect of resin moisture on 80 Shore A aromatic TPU during melt processing

% Moisture	0.01%	0.08%	0.20%
Durometer (Hardness)	82	80	81
100% Modulus (psi)	850	830	810
300% Modulus (psi)	1780	1550	1330
Ultimate Tensile Strength (psi)	7180	3750	1810
Ultimate Elongation (%)	580	630	570
Tensile Set (%)	20	80	100
Die C Tear (pli)	580	550	410
Compression Set (%)	30	45	50

During injection molding, incomplete fill (short shot), splash or splay marks, and flashing and nozzle drool are all examples of potential issues that may occur with high moisture content during processing. During extrusion, high moisture content in the resin can result in process instability, bubbles, and rough surface. Depending on the moisture level and processing conditions, these visual cues may or may not be present.

Physical degradation of material and its physical properties can still occur in the absence of visual indications of moisture. Verification of moisture level using a moisture analyzer prior to processing is important to ensure resin is dry prior to processing.

Drying Aromatic TPUs

Pellethane®, Tecothane™ and Aromatic Carbothane™ are aromatic TPU products. To achieve optimal chemical and mechanical properties, processors should dry Pellethane®, Tecothane™ and Aromatic Carbothane™ TPUs to a moisture content of **less than 0.02 weight percent**.

Desiccant or compressed air type dehumidifying dryers are best suited for drying Pellethane®, Tecothane™ and Aromatic Carbothane™ products. A dew point of -40°C (-40°F) or lower is recommended. An air inlet temperature (at the hopper) between 82°C and 104°C (180°F and 220°F) is recommended for drying where hopper capacity is sufficient in size. Typical drying time to reach a 0.02% moisture level for resin taken from a sealed bag will normally be two to four hours. However, specific drying times depend on resin composition, moisture content, and drying temperature.

Figure 11 shows a typical drying curve for Pellethane® TPU.

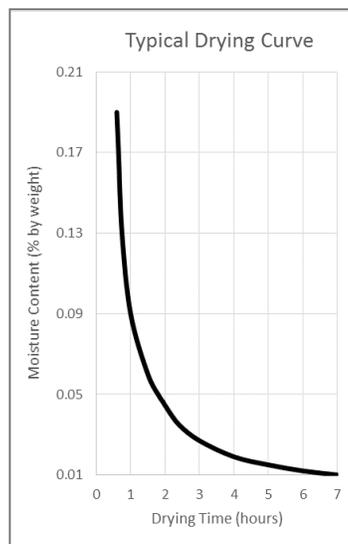


Figure 11. Typical drying curve for Pellethane® TPU

Table 4 shows the recommended inlet air temperatures (at the hopper) for various Pellethane® TPU:

Table 4. Recommended inlet air temperatures for Pellethane®

Shore hardness	Inlet air temperature	
	$^{\circ}\text{F}$	$^{\circ}\text{C}$
80A	180 - 200	82 - 93
90A	190 - 220	88 - 104
55D	190 - 220	88 - 104
65D	210 - 230	99 - 110
75D	210 - 230	99 - 110

If Pellethane®, Tecothane™ and Aromatic Carbothane™ TPU will dry for an extended period of time, (i.e. overnight), decrease dryer temperature to 65°C (150°F), then increase the temperature to the recommended level two to three hours before processing. Use the upper temperature range only when the moisture content of the resin is greater than 0.10 percent or when hopper residence time is less than 90 minutes.

For further drying and processing information, refer to the material technical data sheets (TDS).

Drying Isoplast® and Tecoplast™

Ideal processing of Isoplast® is only possible at a moisture level below 0.02 weight percent (preferable below 0.01 weight percent). Isoplast® that is put into drying hoppers directly from the sealed shipping containers should typically dry in four to six hours under optimal drying conditions (see dryer requirements). If the seals on the containers have been broken, or if the resin has been exposed to the atmosphere for any reason, the necessary drying time can increase to 10 to 12 hours.

If Isoplast® resin has been stored in an open container for greater than 14 days, it is recommended to discard the material due to the difficult removal of deeply absorbed moisture in the pellet.

Not every dryer is capable of adequately reducing the moisture level in Isoplast®, as it releases moisture in the material rather slowly. However, desiccant dryers are suitable for drying Isoplast® provided they can produce:

- an air flow of minimum 2.5 m³/hr/kg (40 ft³/hr/lb) of material
- a drying temperature between 85°C (185°F) and 138°C (280°F), dependent on the Isoplast® grade
- a continuous dry air flow with a dew point of -40°C (-40°F)

In addition, the hopper must be designed to ensure plug flow so that all pellets have a similar residence time.

Each Isoplast® resin has a specific drying temperature range which must be controlled very carefully. The resin itself must be at the temperature indicated. A substantial amount of heat can be lost between the dryer control unit and the dryer hopper. If the dryer hopper is not insulated, more heat will be lost, especially along the outer shell. To avoid heat loss, the hopper must be insulated and the thermocouple should be located at the inlet of the drying hopper.

When drying, it is important to keep the air returning to the desiccant unit below 55°C (130°F). If the air returning from the dryer hopper to the desiccant unit is above 55°C (130°F), the unit cannot remove moisture from the air. Drying becomes progressively less efficient if the return air is hotter than 55°C (130°F).

When return air is above 65°C (150°F), no drying will take place. Most dryer manufacturers can supply an after-cooler for drying units that will cool the return air below the 55°C (130°F) maximum allowable temperature. As the required drying temperature increases, the need for an after cooler also increases.

Once dry, it is critical to retain low resin moisture levels during processing. The ambient air dew point will have a significant impact on how fast Isoplast® resins pick up moisture when exposed to the environment. During the summer, when ambient temperatures and humidity are both at their peak, Isoplast® resins that have been properly dried can pick up enough moisture to cause splay (bubbles and streaking) in as little as 15 minutes.

Retaining low resin moisture levels during processing can be accomplished by mounting the dryer hopper directly on the in feed of processing equipment. Alternatively, a small shot hopper can be used if fed by a closed loop, dry air conveying system from the large dryer hopper.

Similar to Isoplast[®], Tecoplast[™] drying requires a dew point of -40°C (-40°F) at 93°C (200° F) for at least four to six hours prior to thermal processing. For further drying and processing information for Tecoplast[™], refer to the technical data sheet (TDS).

Drying of Aliphatic TPUs

Aliphatic TPUs such as Tecophilic[™] and Tecoflex[™], must be dried with a dew point of -40°C (-40°F) minimum at 65°C (150°F) for at least two hours. Aliphatic Carbothanes[™] require the same parameters with at least four hours of drying prior to processing. Aliphatic TPUs should be dried to a moisture content of **less than 0.05 weight percent** to attain ideal chemical and mechanical properties. For further drying and processing information of Tecophilic[™], Tecoflex[™] and Aliphatic Carbothane[™] TPUs, refer to their technical data sheets (TDS).

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