

# **EMAC 276 Polymer Properties and Design**

**Prof. Lei Zhu**

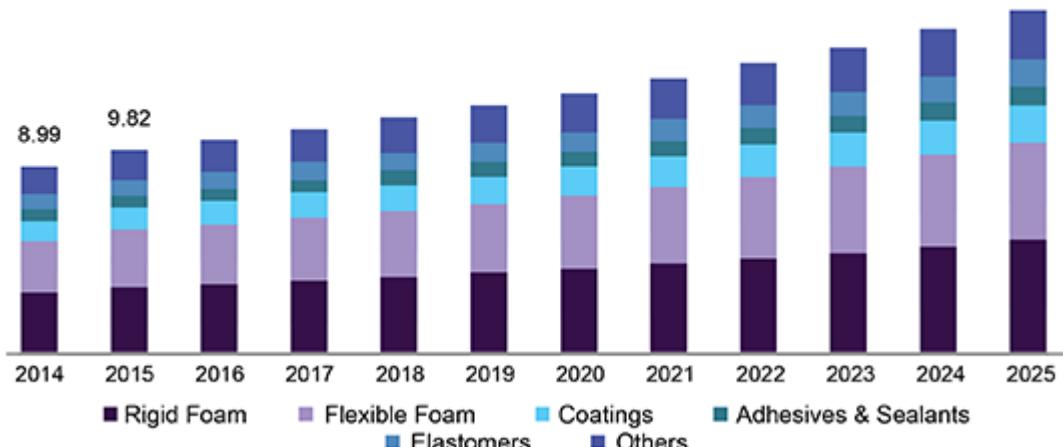
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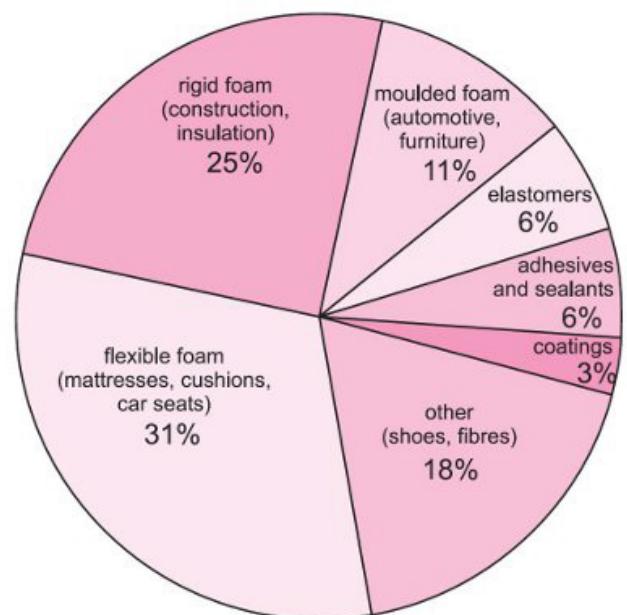
**MWF 10:35-11:25 pm  
Spring 2025**

# Polyurethanes

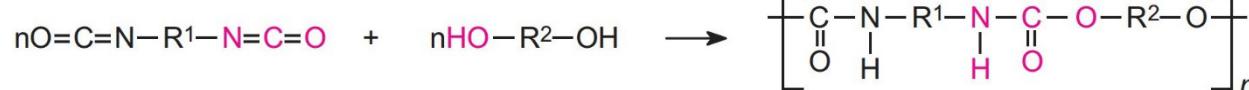
U.S. polyurethane market size, by product, 2014 - 2025 (USD Billion)



Source: [www.grandviewresearch.com](http://www.grandviewresearch.com)



<https://www.essentialchemicalindustry.org/polymers/polyurethane.html>



1937: Dr. Otto Bayer discovered the basic polyurethane chemistry at I.G. Farben:  
<http://www.polyurethanes.org/en/what-is-it/history>

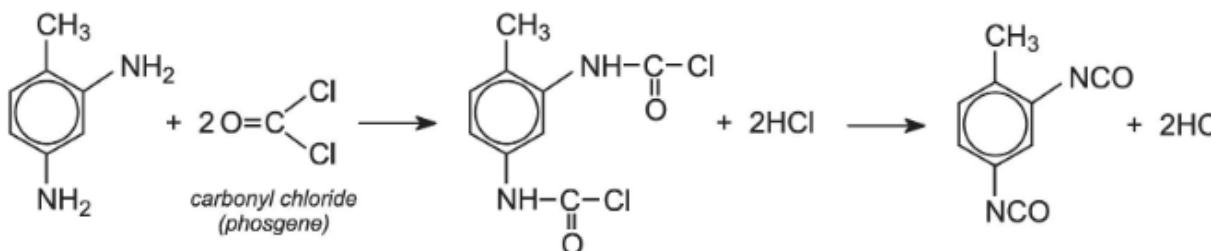


## Do you know some basic PU facts?

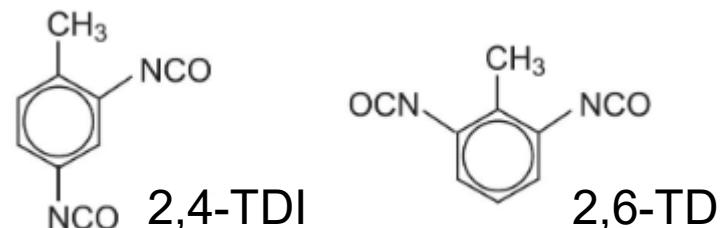
- 1.6 cm-thick PU insulation has the same insulation efficiency as a 1.34 m-thick concrete wall!
- Since 2003, all PU foams have been HCFC-free in EU.
- The first PU surfboard was made in the 1950s.
- Because of the introduction of PUs into refrigerators, models designated A++ today are 60% more efficient than refrigerators 15 years ago.
- In 1973, roller skates were improved and popularized by the introduction of thermoplastic polyurethane (TPU) wheels and, later, TPU boots. Today they are known as Rollerblades.
- The amount of energy used to produce PU insulation for one house is subsequently saved in the space of just one year thanks to the insulation provided.

# Raw Materials

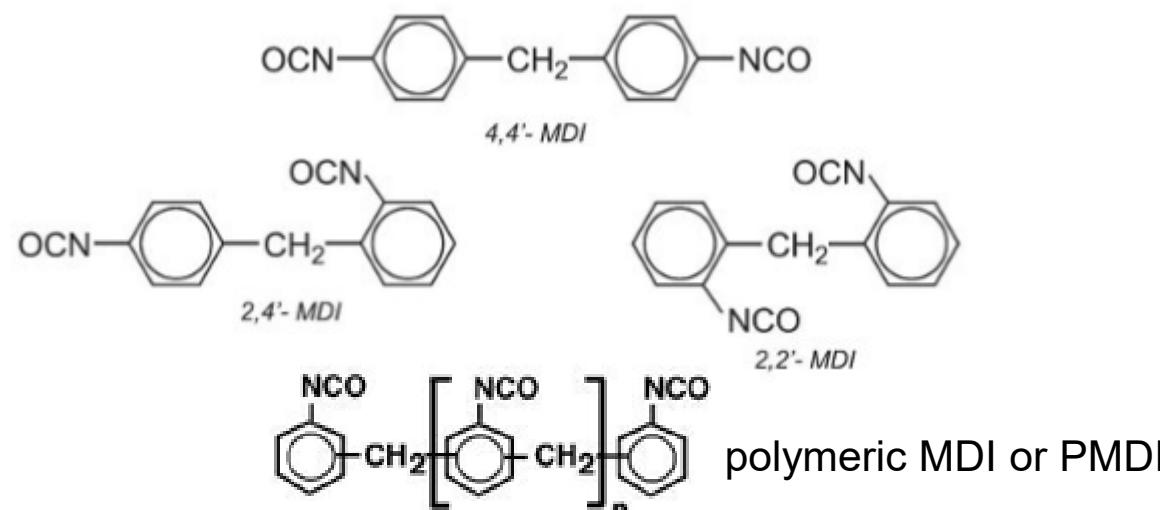
## Isocyanates by phosgenation:



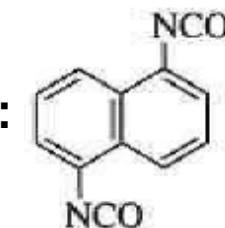
## i) Toluene diisocyanate (TDI):



## ii) Diphenylmethane diisocyanate (MDI):



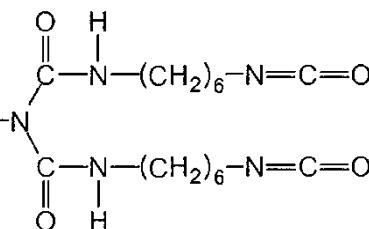
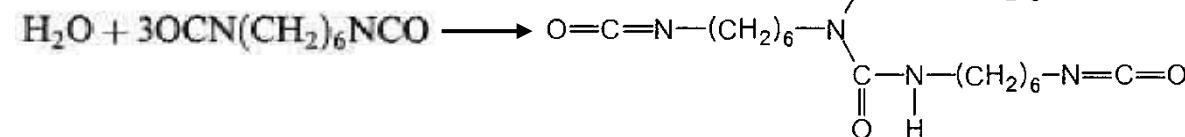
## iii) 1,5-Naphthalene diisocyanate (NDI):



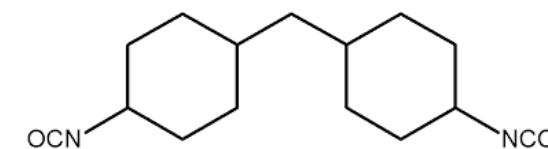
## iv) Hexamethylene diisocyanate (HDI):



To reduce volatility:

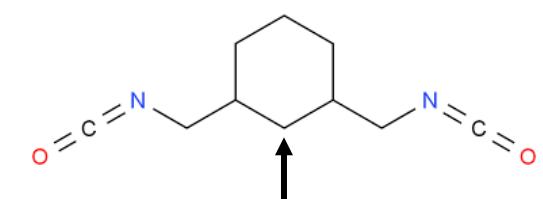
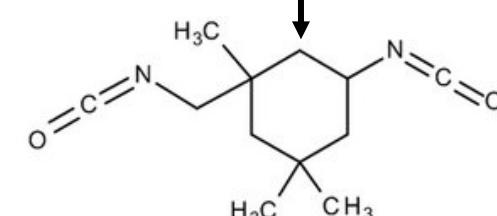


## v) 4,4'-Dicyclohexylmethane diisocyanate ( $\text{H}_{12}\text{MDI}$ ):



better discoloration resistance,  
thermal and hydrolytic stability

## vi) Isophorone diisocyanate (IPDI):



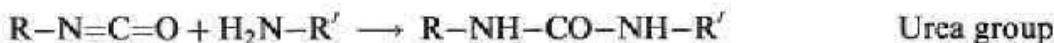
## vii) 1,3-Bis(isocyanatomethyl) cyclohexane ( $\text{H}_6\text{XDI}$ ):

# Various Isocyanate Reactions

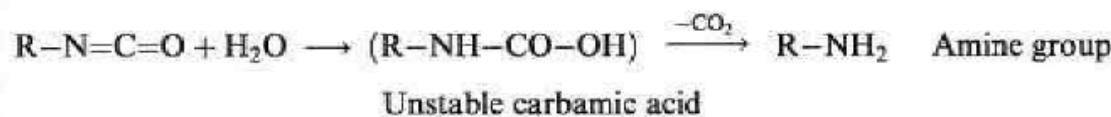
1. With alcohols and phenols ( $R'$  is aliphatic or aromatic):



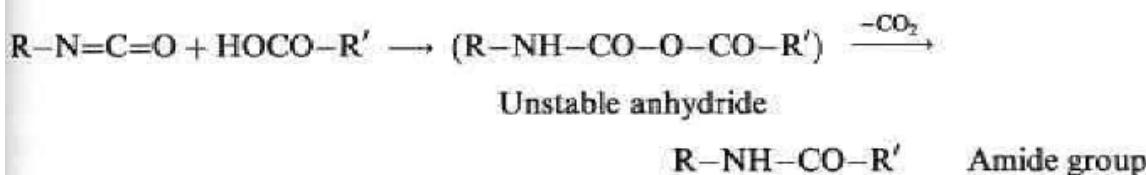
2. With amines:



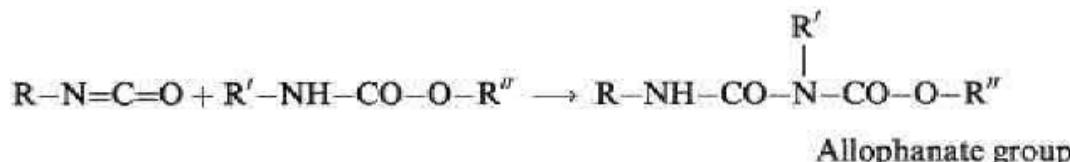
3. With water:



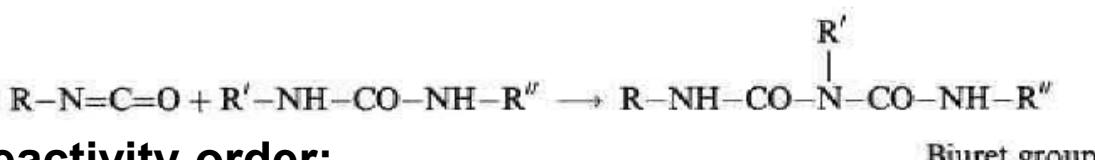
4. With carboxylic acids:



5. With urethanes:



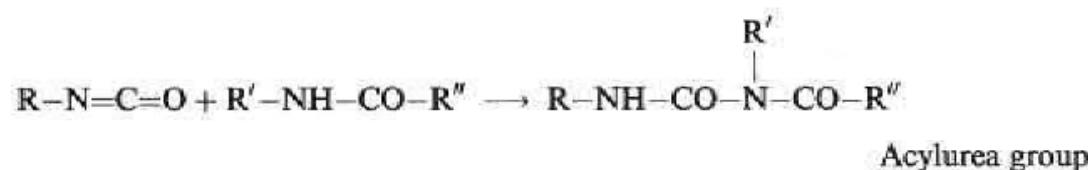
6. With ureas:



**Reactivity order:**

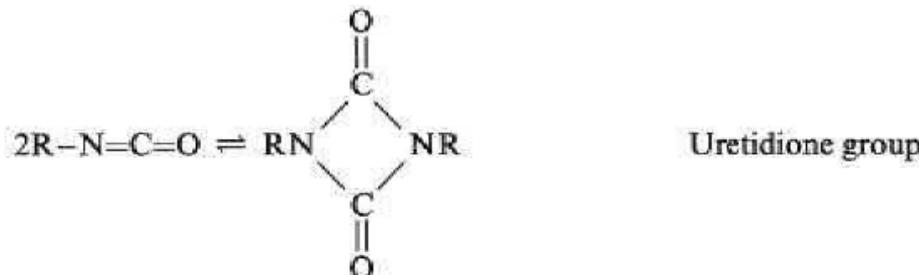
aliphatic amines > aromatic amines > primary alcohols > water >  
secondary alcohols > phenols > acids > ureas > amides > urethanes.

7. With amides:

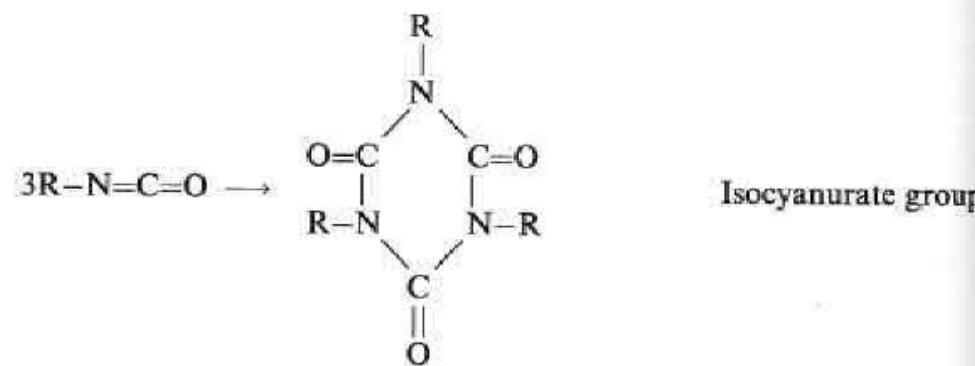


As can be seen, reactions (1–4) lead to linear chains whereas reactions (5–7) result in branched chains.

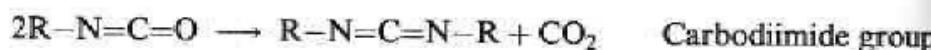
8. Dimerization:



9. Trimerization:



10. Self-condensation:

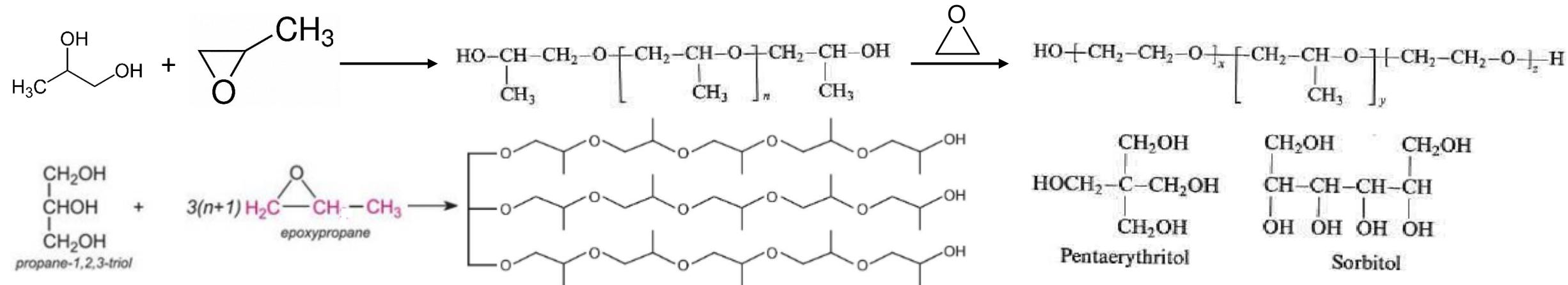


# Polyols

As a general guideline, linear or slightly branched polyols are used for the manufacture of elastomers and flexible foams, whereas moderately and highly branched polyols are used for coatings and rigid foams.

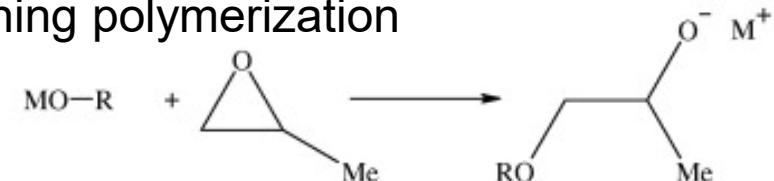
(a) Polyether polyols (PEPs): 90% polyols, better hydrolytic resistance than polyester polyols.

i) Propylene oxide-based (not ethylene oxide-based, which is too hydrophilic)

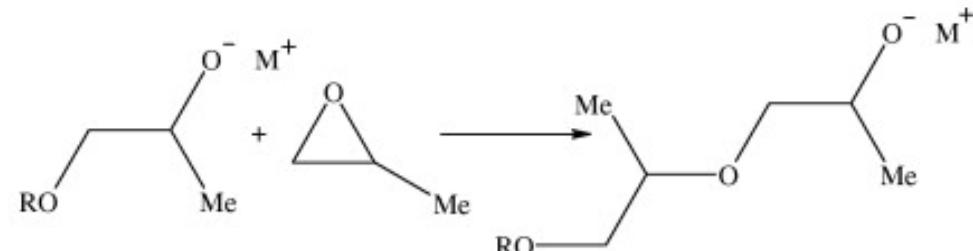


Anionic ring-opening polymerization

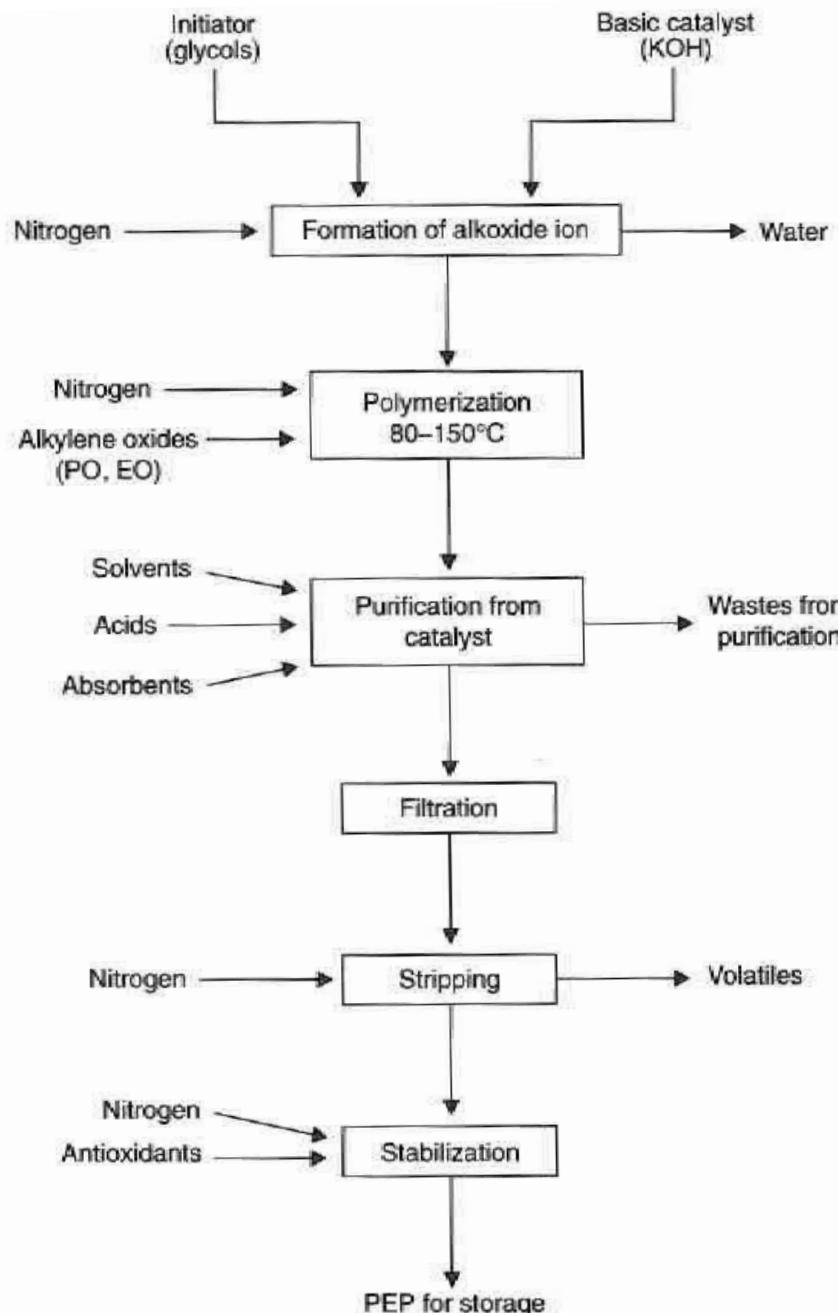
Initiation step:



Propagation step:

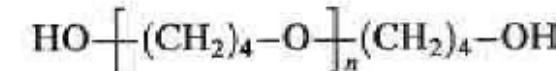


- MW 1000-8000 Da with 2-3 hydroxyl groups for low modulus PUs such as flexible slabs, elastomers (including RIM) and coatings.
- MW 250-1000 Da with 7-8 hydroxyl groups for high modulus highly crosslinked PU such as rigid foams, hard coatings, microcellular or solid plastics
- To better control the isocyanate reactions, the catalyst impurities in PEPs have to be removed, i.e., below 5 ppm.
- Also, proprietary stabilizers should be added to avoid potential oxidation.



# Polyols

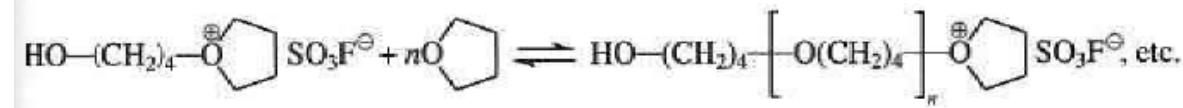
## ii) Poly(tetramethylene oxide) (PTMO)-based PEPs (1955)



Initiation:



Propagation:

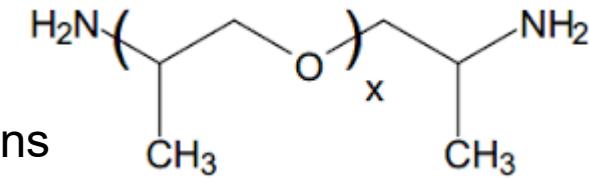


Termination with methanol.

- Used for PU thermoplastic elastomers and fibers (Spandex) because of its low Tg (-84°C) and regular structure for crystallization.
- MW = 600-3000 Da with 2 primary alcohols

## iii) Amine-terminated PEPs

For RIM applications, foam and cast elastomers, epoxy resins



## iv) Filled PEPs for PU foams

Enhance the load bearing characteristics of high resilience flexible PU foams and the strength properties of PU elastomers.

Figure 7.1 Preparation of polyether polyols.

# Polyester Polyols (PESPs)

## Synthesis

### a) Direct polycondensation



### Diols:

- i) linear: ethylene glycol, diethylene glycol, 1,4-butane diol, 1,5-pentanediol and 1,6-hexanediol
- ii) branched: glycerol, trimethylolpropane, pentaerythritol

### Diacids:

Succinic, adipic, azelaic, sebacic or phthalic acid.

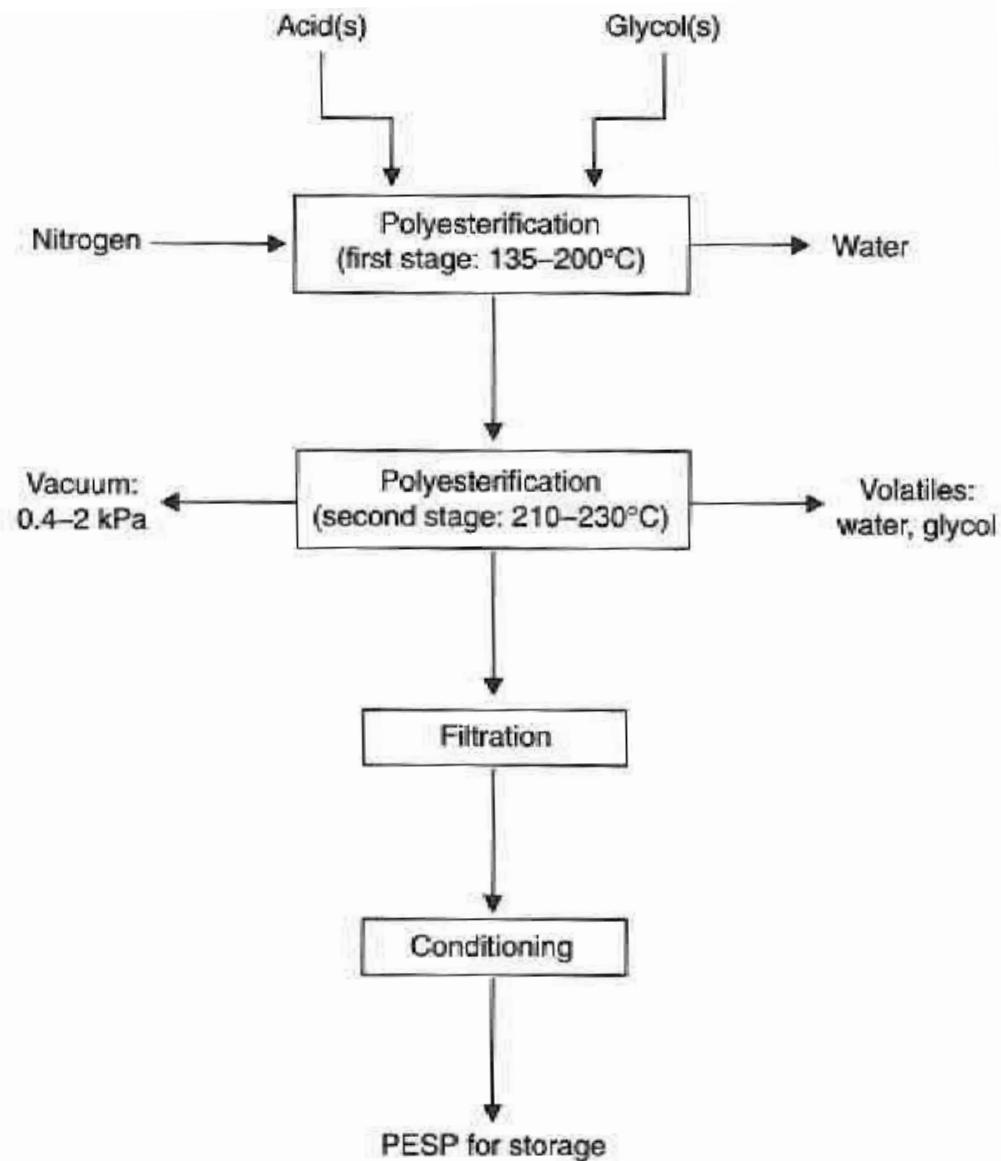
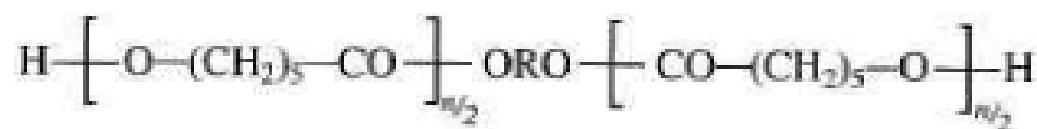
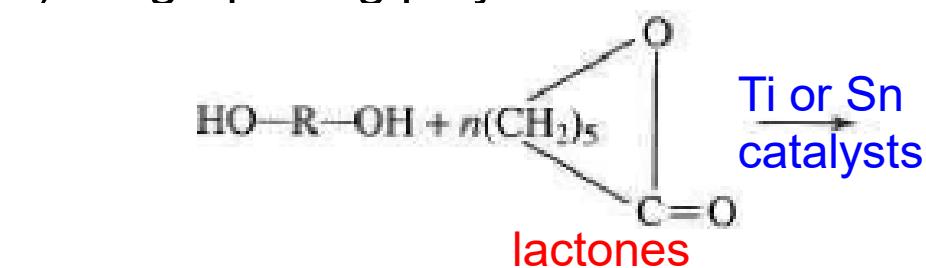


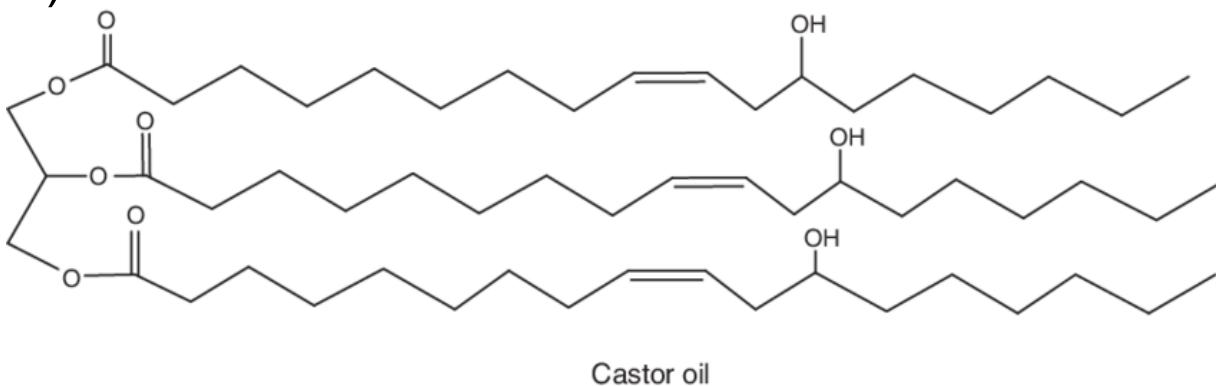
Figure 7.2 Preparation of polyester polyols.

## Polyester Polyols (PESPs)

b) Ring-opening polymerization



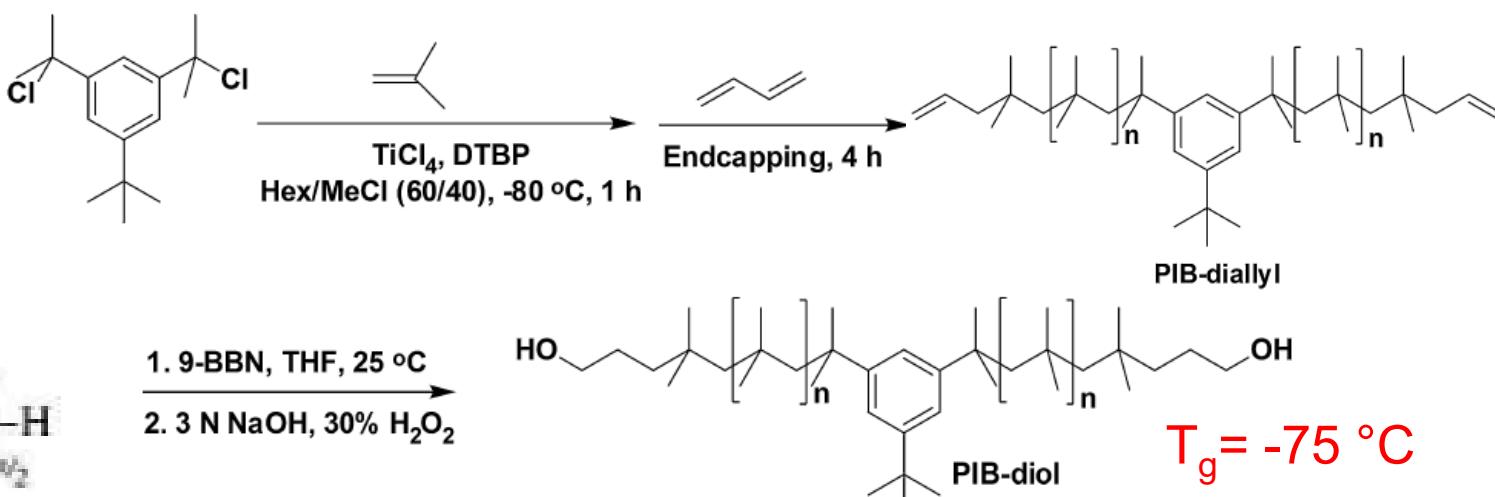
c) Castor oil



### Properties

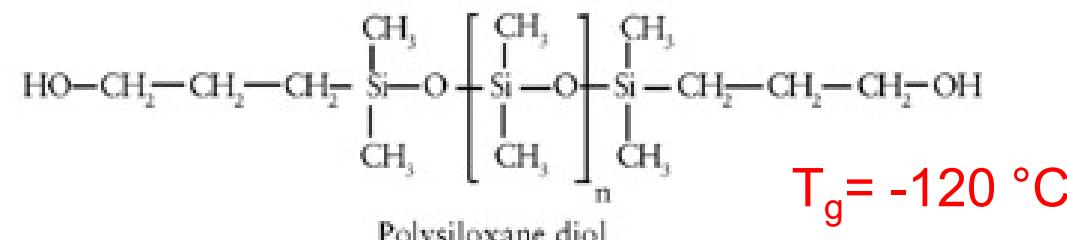
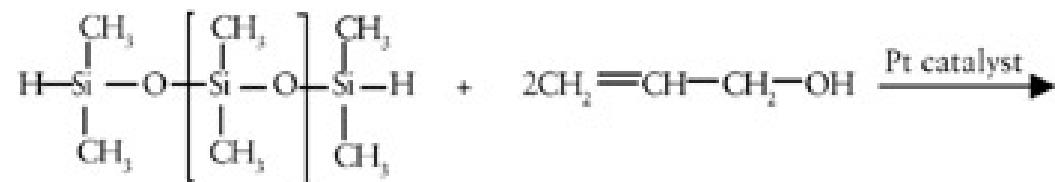
- Low molecular weights (MWs): 2000-4000 g/mol
- Difunctional with diols
- Low glass transition temperatures ( $T_g < -50^\circ\text{C}$ )
- low viscosity for additives

## Polyisobutylene (PIB) Polyols



Hydrolytic/oxidation stability and good gas barrier

## Polysiloxane Polyols



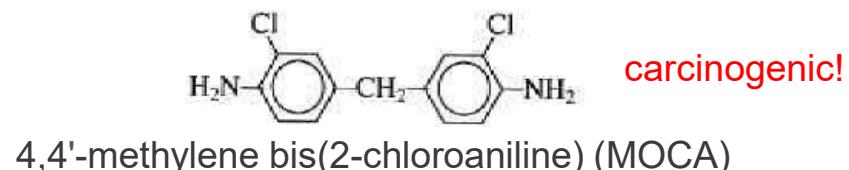
Hydrolytic/oxidation stability and good gas barrier

# Chain Extenders

## Definition:

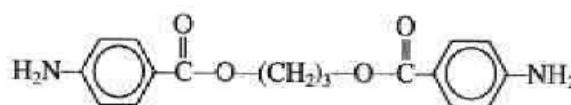
Aromatic diamines and aliphatic or aromatic hydroxyl compounds that form the hard segments for enhancing the mechanical strength of PUs.

Aromatic diamines: very reactive, used with prepolymers for fast reaction such as in RIM.

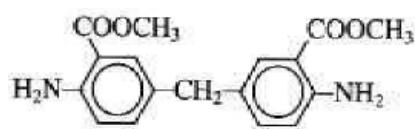


To replace MOCA:

CAYTUR 21  
4,4'-Diaminodiphenylmethane complex with NaCl



POLACURE 740M  
Trimethyleneglycol-bis(4-aminobenzoate)



POLACURE 1000  
4,4'-Methylene-bis(2-carbomethoxyaniline)

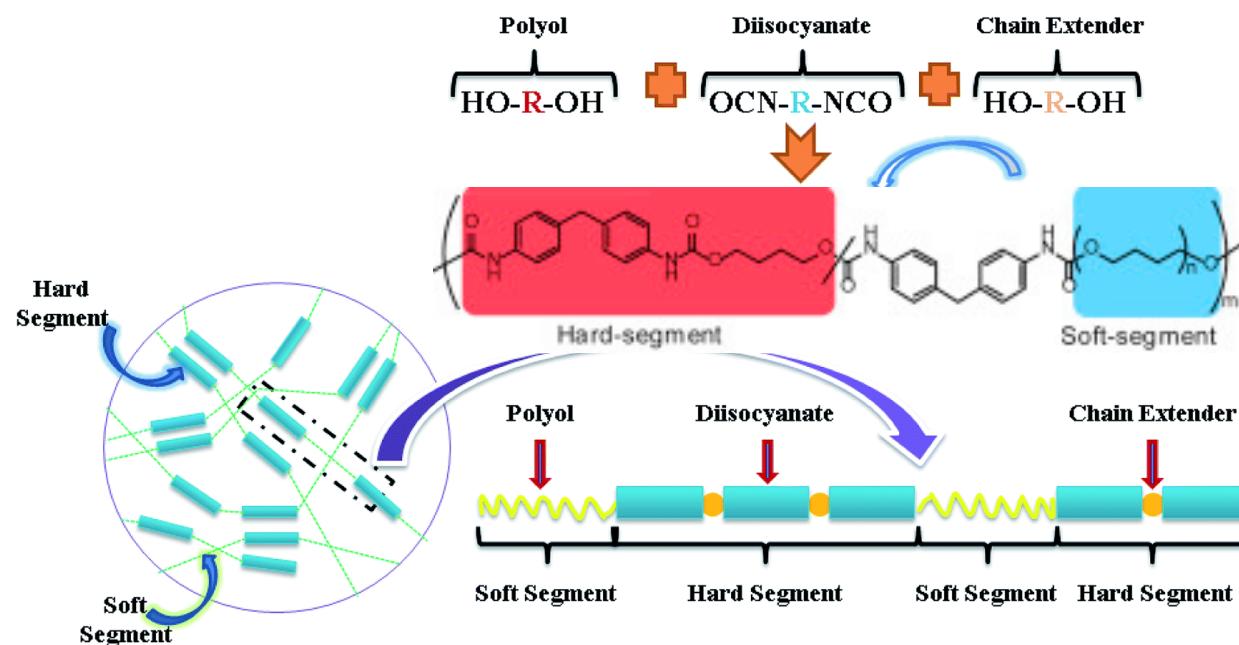


Table 7.1 Influence of glycol and amine chain extenders on PU properties

Glycols	Property	Amines
	Reactivity of the system	→*
	Tensile strength	→
	Modulus	→
	Hardness	→
	Abrasion resistance	→
	Compression set	→
←	Resilience	→

\*low → high

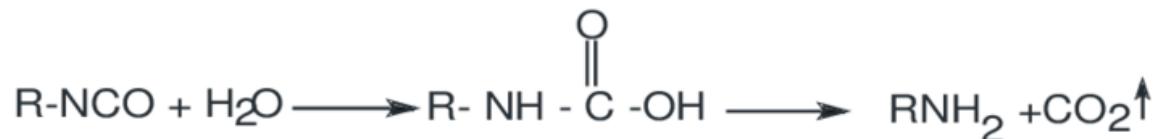
# Chain Extenders

## Aliphatic or aromatic diols

Chain extender/cross-linker	Structure	Mol wt g/mol	Equiv. wt g/eq	OH/NH number
Water		18	9	6233
Ethylene glycol		62	31	1808
1,2-Propylene glycol		76	38	1475
1,3-Propylene glycol		76	38	1475
Diethylene glycol		106	54	1057
Neopentyl glycol		104	52	1078
Butanediol		90	45	1244
Hexanediol		118	59	951
Cyclohexane dimethanol		144	72	779

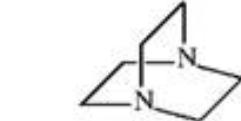
Chain extender/cross-linker	Structure	Mol wt g/mol	Equiv. wt g/eq	OH/NH number
Hydroquinone bis(2-hydroxyethyl)ether		198	99	567
Resorcinol bis(2-hydroxyethyl)ether		198	99	567
Bisphenol A bis(2-hydroxyethyl)ether		316	158	355
Bisphenol A bis(2,3-dihydroxypropyl)ether		376	94	597
4,4'-Methylenebis(2-chloroaniline) (MOCA)		267	133.5	420
Glycine		92	31	1828

Water reacts with isocyanates for foams:

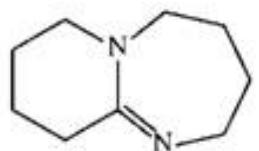
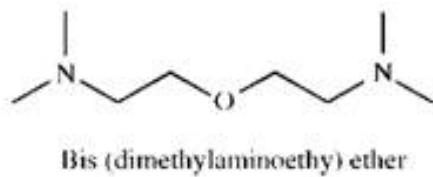


# Catalysts for Accelerated Kinetics

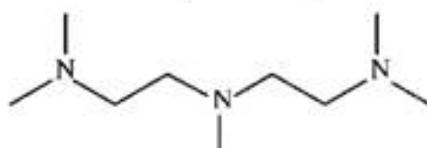
## Tertiary amines and organometallics



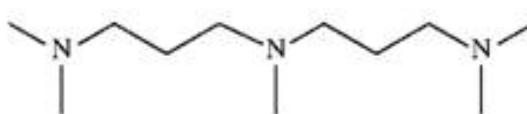
Triethylene diamine (TEDA)

1,8-diazabicyclo (5.4.0)  
undec-7-ene (DBU)

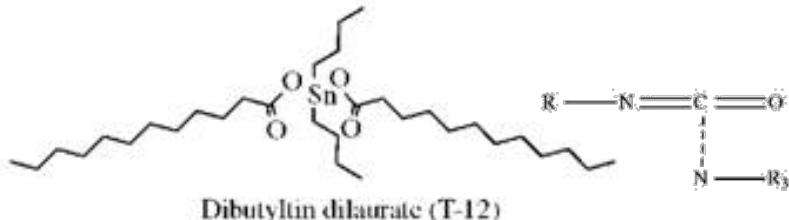
Bis (dimethylaminoethoxy) ether



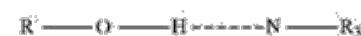
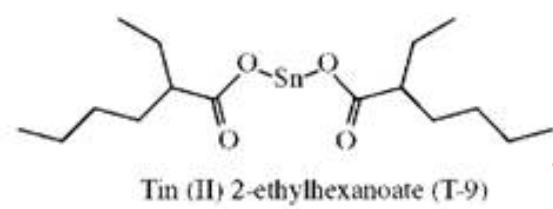
Pentamethyl diethylenetriamine



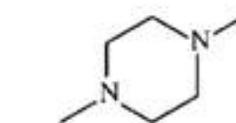
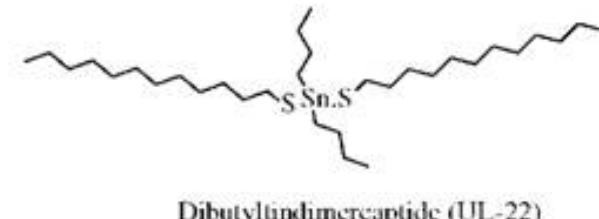
Pentamethyldipropylbenzyltriamine



Trade names in parenthesis



To enhance electrophilic character of -NCO



Dimethylpiperazine

## Postulated mechanisms

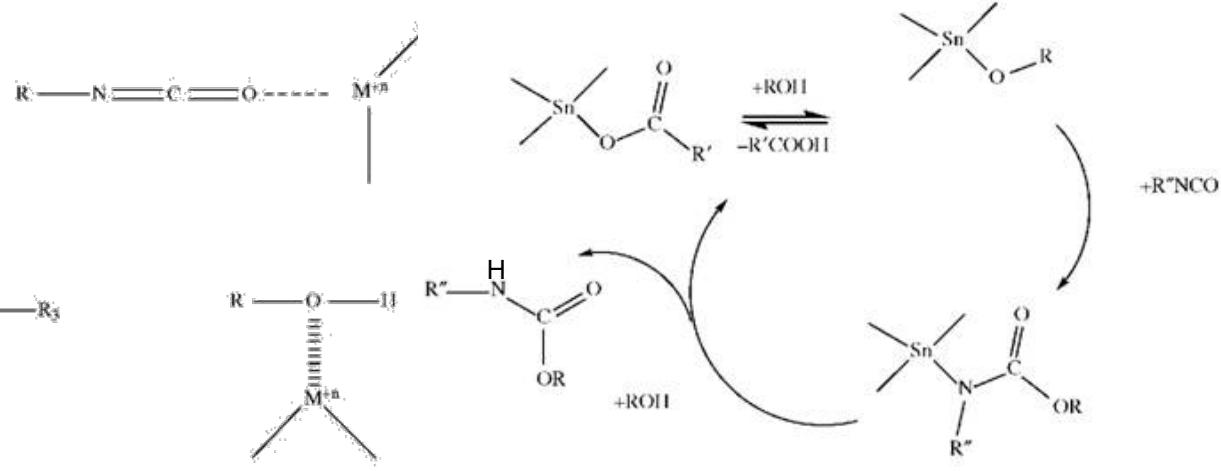
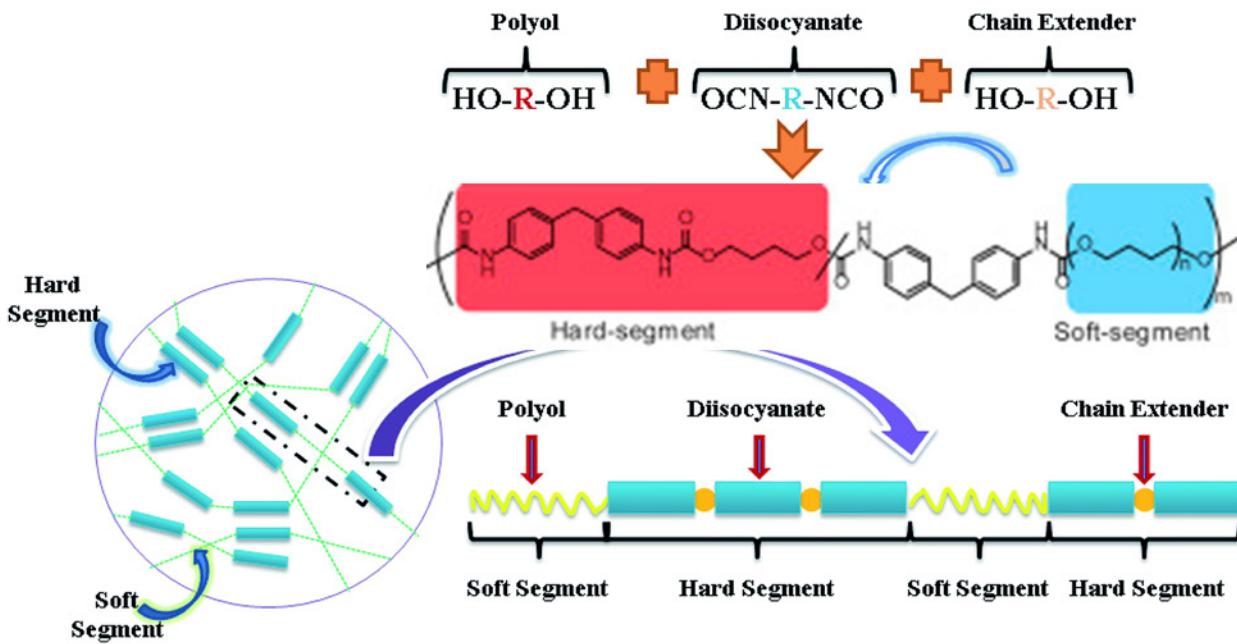


Table 7.2 Effect of various catalysts on isocyanate reactions [32]

	Relative rates of isocyanate reaction with			
	n-Butanol (a)	Water (b)	Diphenylurea (c)	a:b:c
None	1.0	1.1	2.2	0.45: 0.5:1
Triethylamine	86	47	4	21.5:11.7:1
Tetramethyl-1,3-butanediamine	260	100	12	21.6: 8.3:1
Triethylenediamine	1200	380	90	13.3: 4.2:1
Tributyltin acetate	80 000	14 000	8000	10.0: 1.7:1
Dibutyltin diacetate	600 000	100 000	12 000	50.0: 8.3:1

# Cast Polyurethane Elastomers

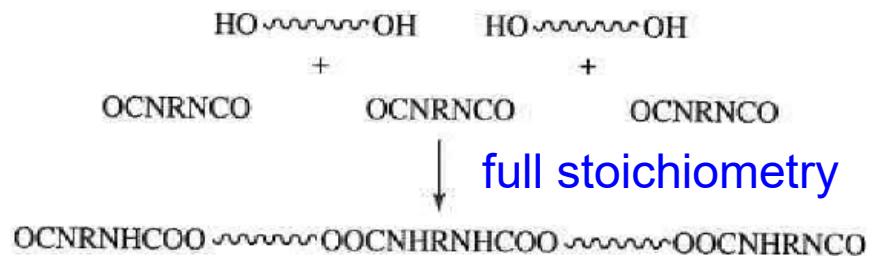


## Structure-property relationships

- Soft segments  
Blocks of isocyanate + high MW polyol.
- Hard segments  
Blocks of isocyanate + chain extender.
- Multiblocks – microphase separation
- Crosslinked – **from >2 functional groups**

## PU cast elastomers

- Linear or branched polyether/polyester polyols are used in thermoset PU elastomers with MWs of 2000-6000 Da.
- Isocyanates are pure, crude or polymer MDI as well as TDI mixtures.
- Chain extenders consist of both amine and glycol types (ethylene glycol, diethylene glycol, 1,4-butanediol).
- Full prepolymer method (**high viscosity**)



- Quasi prepolymer method (**low viscosity**)  
Part of polyols reacted with the full amount of isocyanate to form isocyanate-capped polymers + free isocyanates. Then, the rest polyols are added to complete the reaction.

# Full vs. Quasi Prepolymer Method

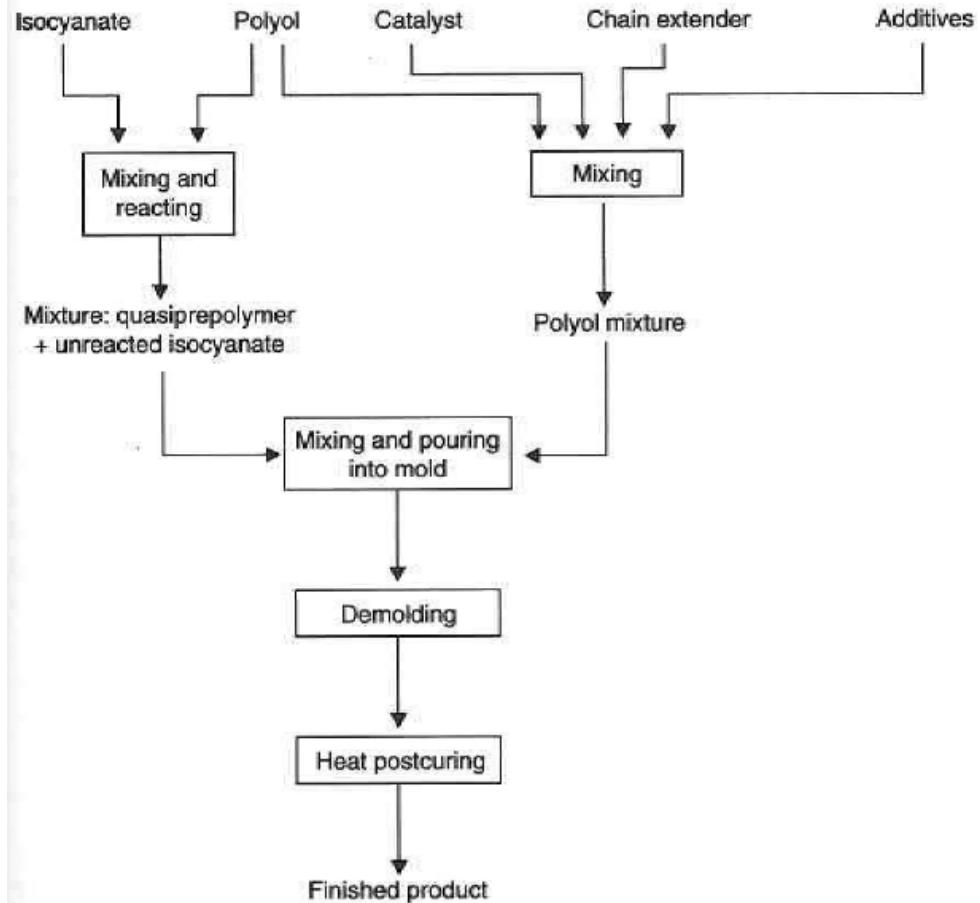
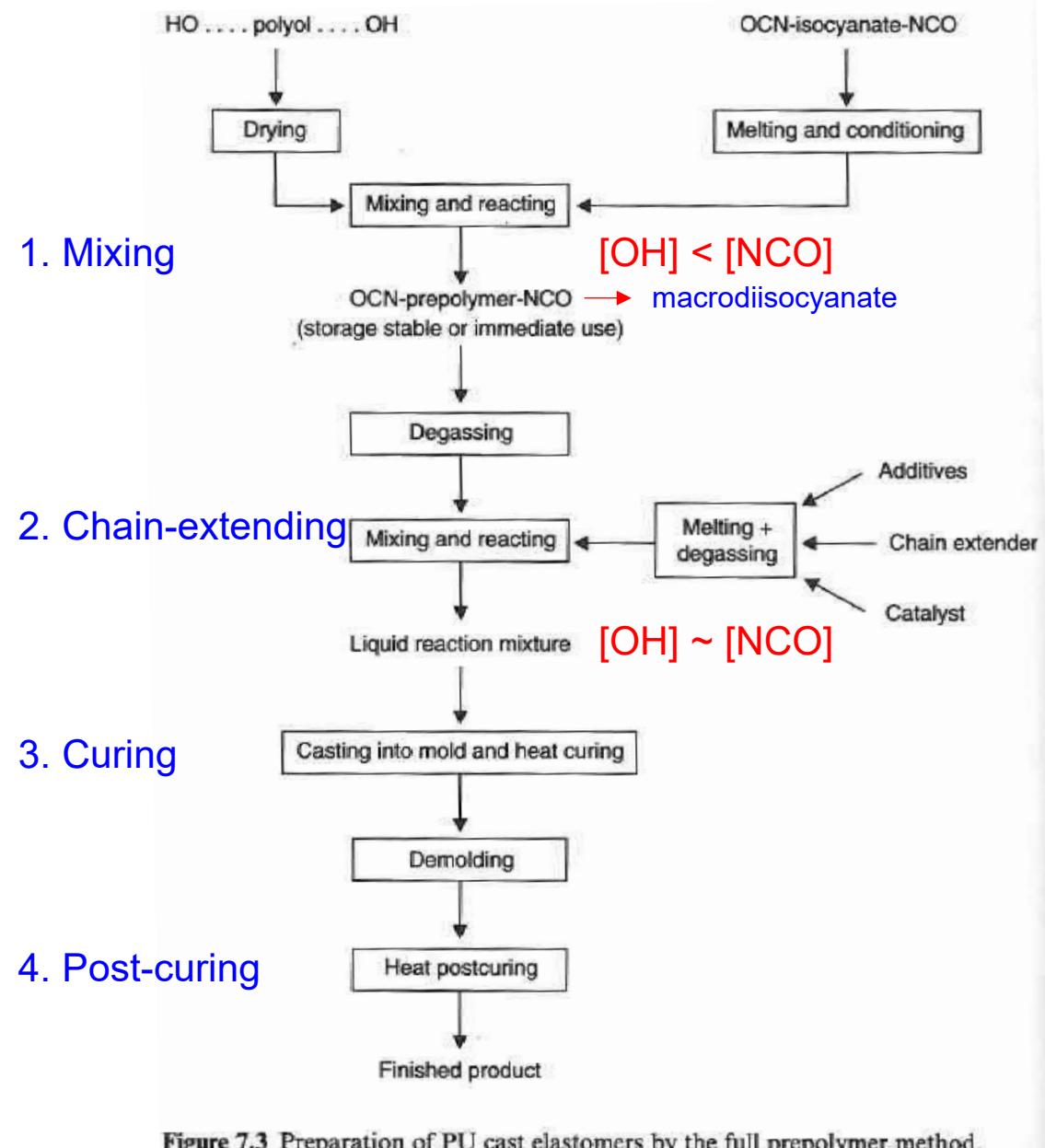


Figure 7.4 Preparation of PU cast elastomers by the quasi prepolymer method.

Isocyanate index =  $[NCO]/[all\ OH] \times 100\%$   
 Crosslinking density is controlled by the isocyanate index.

## One shot method

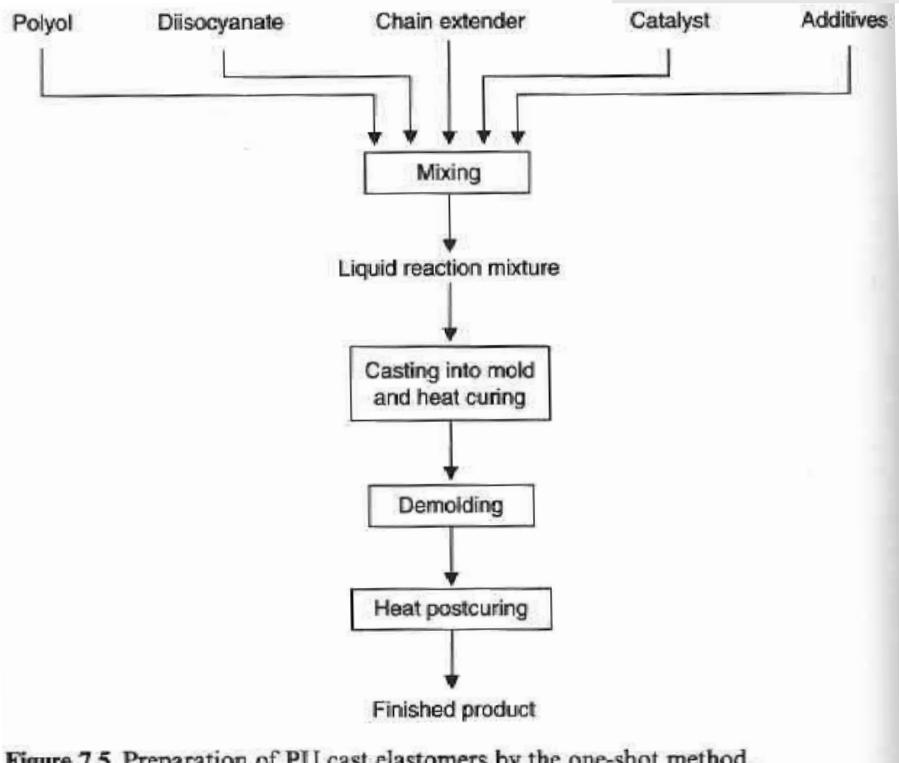


Figure 7.5 Preparation of PU cast elastomers by the one-shot method.

Table 7.3 A typical formulation and reaction conditions for casting polyurethane elastomers

	Parts by weight	
Prepolymer (PTMG/TDI), 4.2% NCO	100	100
MOCA	12.5	-
1,4-Butanediol	-	4.0
Trimethylolpropane	-	0.3

	Conditions	
Prepolymer temperature (°C)	100	100
Extender temperature (°C)	115	100
Pot life (min)	12	45
Demolding time at 100°C (min)	30–45	90
Postcuring at 100°C (h)	16	20

# Properties and Applications

Table 7.4 Effect of the amount of chain extender on some PU properties [35]

Hard segment (%)	Hardness (Shore A/D)	Flexural modulus (MPa)
25	82A	4.3
50	60D	484
75	78D	1382

Table 7.5 Some properties of PU cast elastomer based on a 6000 MW polyether triol chain

Property	Value
Density	1.10 g/cm <sup>3</sup>
Tensile strength	24 MPa
Elongation	275%
Modulus 100%	13.7 MPa
Hardness (Shore A)	95

## Properties

- A broad range of properties can be obtained by selecting appropriate formulations and reaction conditions.
- Among the most outstanding properties are high abrasion resistance, tear strength and tensile strength, and excellent resistance to aliphatic hydrocarbon fuels, oils, oxygen and ozone.
- They are also good electrical and thermal insulators.
- They may be formulated from hard (50 Shore D) to very soft (10 Shore A) (controlled by the amount of hard segments).
- Major shortcomings are low resistance to steam, aromatic and chlorinated solvents and strong acids and bases.
- The maximum service temperature is 120°C.

## Applications

<https://www.youtube.com/watch?v=ANEMJuMSnj0>

- For cast PU elastomers: printing and industrial rollers, pipes and impellers for mining and quarrying industries, flexible tooling molds, recreational surfaces (in multisports halls, tennis courts and children's playgrounds), solid industrial tires for fork and lift trucks, skateboard and roller skate wheels, soft cast elastomer (tire filling material for heavy vehicles), sealing gaskets and oil field equipment, diaphragms and a variety of other mechanical applications.

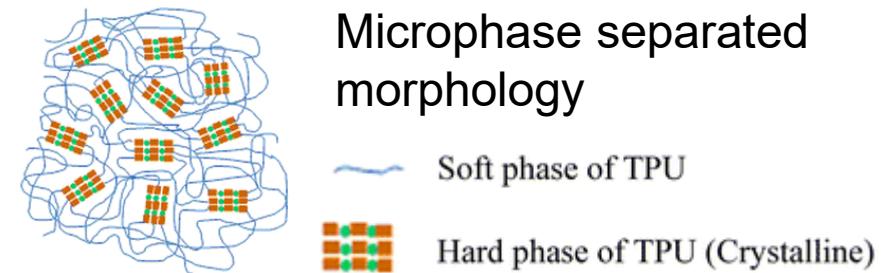
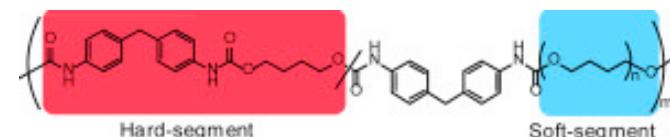
# Thermoplastic Polyurethane Elastomers (TPUs)

- TPUs represent ~10% of the total of TPEs.
- TPUs have become the second most important class of urethane elastomers.
- They are linear block copolymers processed on conventional plastic processing equipment by any standard method used for thermoplastics such as injection and compression molding, extrusion, calendering and film blow molding.

<https://www.youtube.com/watch?v=LGv3JtnMbLM>

## Synthesis

- Isocyanates: MDI for general applications and  $H_{12}MDI$  for color-stable coatings. **2 functional groups**.
- Diol polyols: poly(butylene adipate) glycols, PCL glycols and PTMO glycols. **2 functional groups**.
- 1,4-Butanediol is the choice of chain extender.
- Full prepolymer, quasi prepolymer or one-shot techniques are all applied in the manufacture of TPUs.
- Even can be synthesized by extruder with intensive mixing.
- Isocyanate ratio =100% for linear blocks:



**Table 7.6** Some properties of TPUs based on polycaprolactone polyester

Hardness	80 Shore A	55 Shore D
Tensile strength (MPa)	52	43
Elongation (%)	490	350
Modulus 100% (MPa)	6	20

## Properties and Applications

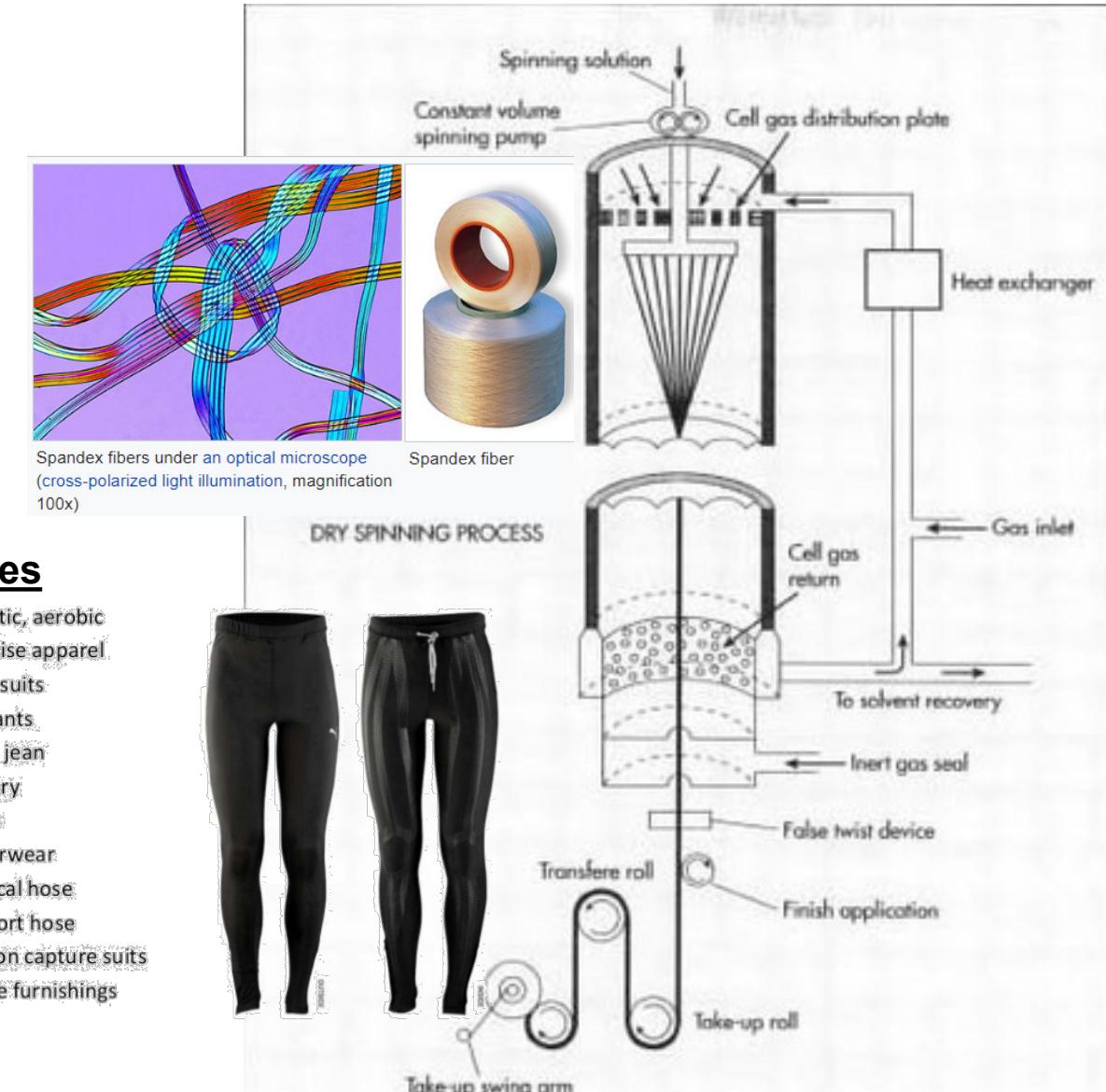
- The hard segments control the hardness, modulus and tear strength while the soft segments provide flexibility, low temperature properties and solvent, oil and hydrolysis resistances.
- Mechanical strength is temperature sensitive (<120°C).
- The most important applications are wire and cable jacketing, sheet and film, household gadgets, gears, various backing pads in abrasive applications, components for mining and drilling machinery and for agricultural equipment, medical devices, rolls and diaphragms. TPUs are used not only as elastomers, but also for the preparation of adhesives, coatings and films.

# Polyurethane Fibers (Spandex)

- TPE fibers with >85% TPUs (Lycra® invented in 1958 by chemist Joseph Shivers at DuPont)
- Softness, high modulus, elongation and instant recovery when the stress is released, excellent resistance to oxidation, body oils and dry-cleaning solvents and good dyeability.
- Spandex fibers have surpassed the properties of any elastomeric fibers known and they have replaced natural rubber fibers in many applications.

## Synthesis

- Long chain polyols are polyethers such as PTMG or linear polyesters that are reacted with TDI and/or MDI to form the prepolymer.
- For chain extension, aliphatic amines (ethylene diamine), aromatic amines (*m*-phenylenediamine or hydrazine) are usually used. Spandex fibers are prepared by either solution or reaction spinning.
- Crosslinks are produced through biuret and allophanate structures at elevated temperatures during the curing of fibers.



Watch a YouTube video in class

# Millable PU Rubbers

## Synthesis

- Vulcanizable PU gums are used in small volume.
- Processed on conventional rubber roll mills.
- Before vulcanization they are linear PUs.
- Storage-stable prepolymers w/ hydroxyl terminal groups (isocyanate index <100) from linear polyols such as poly(ethyleneglycol adipate) or PTMG and MDI or TDI. **They contain unsaturated side chains.**
- In the next step, these prepolymers are roll-milled with the other ingredients.
- Crosslinked by one of the three ways, namely, sulfur, peroxides or block isocyanates.

## Properties

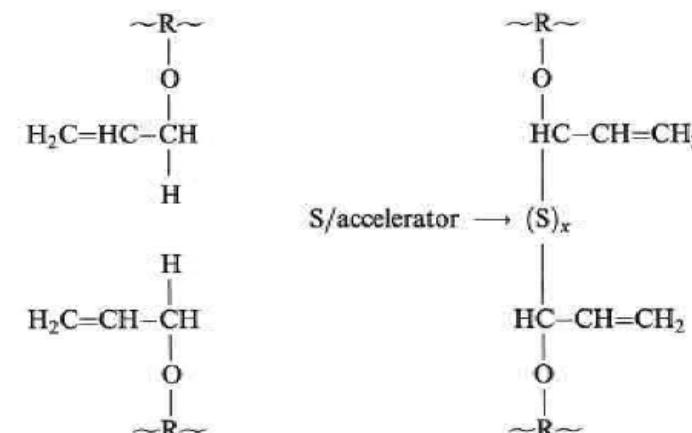
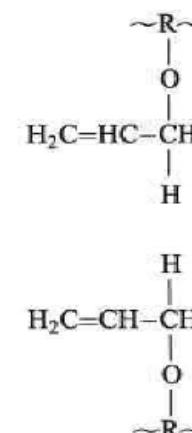
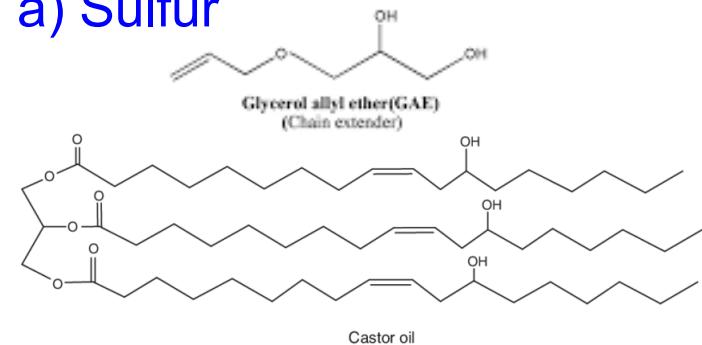
- The polymer of choice for demanding applications requiring superior abrasion resistance and mechanical strength as well as oil and ozone resistance.

## Applications

- Shoe insoles
- Rollers and belting
- Military and aerospace
- Medical applications
- Industrial tires

## Vulcanization methods:

### a) Sulfur



### b) Peroxides

dicumyl peroxide

TSE Millathane® Millable Polyurethane Rubber

<https://www.youtube.com/watch?v=pgjgoV6JRWw&feature=youtu.be>



1 – Insole to absorb impacts

# PU Foam Intro

## Characteristics

- The most versatile foams, from very soft to very rigid
- Different foams are made by different raw materials, different equipment and different processing

## Flexible foams

- In flexible foams, the chains are long and the crosslinks are farther apart, permitting more movement.

## Rigid foams

- In rigid foams, the crosslinks are close together, containing a tight network and restricting movement.

## Two ways for making flexible foams:

### **Hot molding**

- For TDI and less reactive secondary hydroxyls
- Molding temp: 80-120°C, molding time: 20-30 min

### **Cold-molding for high resilience (HR) foams**

- For more reactive MDI/PMDI and primary hydroxyls
- Molding temp: 30-50°C, molding time: 4-20 min
- Grafted with acrylonitrile-styrene copolymers to increase the load bearing capacity

# Flexible Foams

## Water is used with two purposes:

- i) To release CO<sub>2</sub> for foaming
- ii) As chain extender and finally lead to biuret crosslinked structure
- iii) Can be used together with other blowing agents, such as fluorocarbons and CH<sub>2</sub>Cl<sub>2</sub>

## Blowing index, I<sub>B</sub> per 100 pts. polyol:

$$I_B = [H_2O] + [CCl_3F]/10 + [CH_2Cl_2]/9$$

## Catalysts

- At least one catalyst.
- For less reactive PEPs with secondary hydroxyls, synergistic catalysts must be used w/ a proper ratio:  
Tertiary amine: favor –NCO/H<sub>2</sub>O reaction and CO<sub>2</sub>↑  
Tin catalyst: formation of urethane bond and gelation  
A balanced ratio helps bubble-blown w/ proper gelation

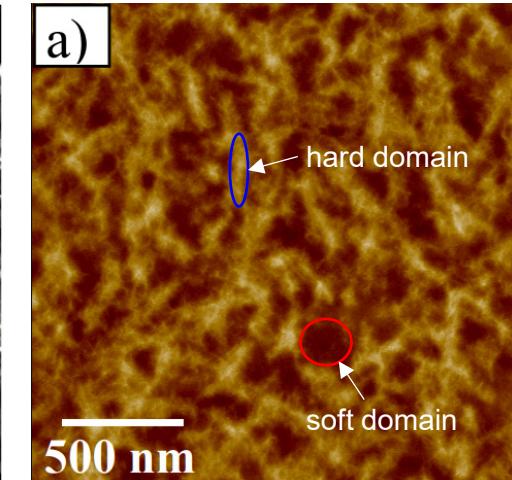
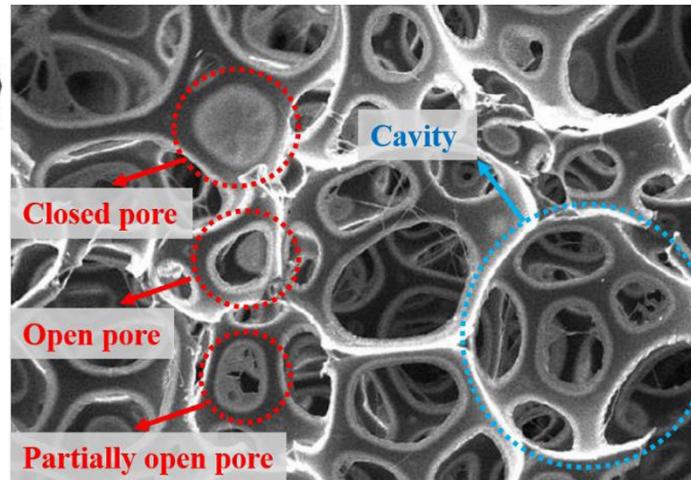
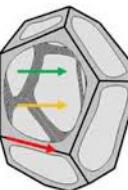
## Surface active agents (i.e., surfactants)

- Silicone block copolymers, usually around 1% level

# Flexible PU Foams

**Table 7.7 A formulation of a flexible polyurethane foam**

	<i>Parts by weight</i>
Polyether triol (PPO MW 3000)	100
80/20 TDI, 110 index	41
Water	3
Triethylenediamine	0.3
Stannous octoate	0.15
Silicone block copolymer	1.0



*Polym. Adv. Technol.* 2018, 29, 852-859; *J. Macromol. Sci. Part B: Phys.* 2003, 42, 6, 1125-1139.

## One-shot synthesis with two types:

- i) The circulating type w/ high pressure RIM mixing.
- ii) Non-circulating type w/ low pressure mixing

Both types need precise control of pressures, temperatures and flow rates and automatic flow control.

## Disadvantage of one-shot synthesis:

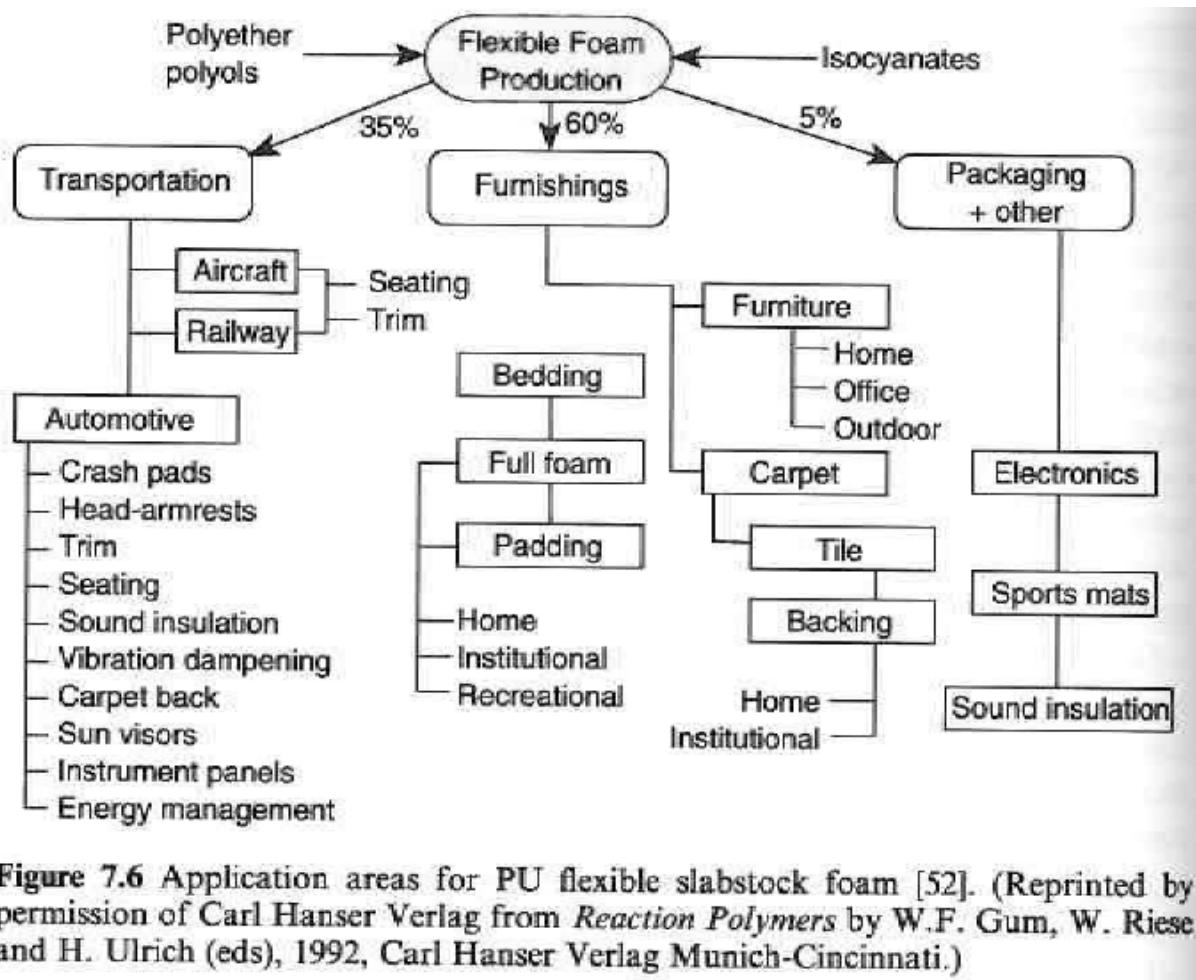
Need to flush the head with solvents after each shot.

The reactive liquid mixture is poured continuously onto a conveyer system yielding foam slabstocks. After 5-10 minutes, the foam can be cut and handled. The slabstocks are then heat cured for 24 hours and then cut into different sized products and shapes.

# Properties

- i) (left) Open cellular structure of flexible PU foam. The bubbles change from spherical to polygonal as they grow.
- ii) (right) Microphase separation by tapping-mode atomic force microscopy (AFM) with phase contrast: Bright domains have a high modulus (hard segments); dark domains have a low modulus (soft segments).
- iii) In addition to physical crosslinking by the hard segment, slight chemical crosslinking also exist due to branched polyols and some biuret/allophanate links.
- iv) The final mechanical properties of a flexible foam depend both on the macroscopic cell geometry and on the microphase morphology of the polymer contained within the structural elements of the foam. Low hysteresis is needed for cushions.

# Flexible PU Foam Applications



- i) Flexible PU foams are manufactured with densities in the range of 0.016-0.048 g/cm<sup>3</sup>, semiflexible foams 0.096-0.192 g/cm<sup>3</sup>, high resilience (HR) foams 0.028-0.048 g/cm<sup>3</sup>.
- ii) Based on the broad range of load bearing capacities and resiliencies, the largest volume of foam is used for cushioning applications for furniture, automobiles, aircraft, bedding and carpet underlay.
- iii) Polyether based foams are preferred as they have a higher resilience than polyester-based foams.
- iv) Flexible foams based on polyesters perform better for textile applications as laminates for cold weather clothing; they are particularly resistant to dry cleaning solvents.
- v) Packaging for military hardware, electronic parts and delicate products, acoustic and thermal insulations and safety equipment.
- vi) Filters for oils, chemicals and various air pollution control devices.

<https://www.youtube.com/watch?v=u9Sj1KmmzQI&t=97s>

# Rigid PU and Polyisocyanurate Foams with Closed Pores

**Major Application:** Building thermal insulation

## Raw Materials:

i) **Isocyanates:** crude PMDI or mixture with TDI and MDI, isocyanate index ~250 for rigid PU or 450-500 for isocyanurate.

## ii) Polyols:

- a) PEspPs from PET scraps with better flammability rating
- b) PEPs with high functionality (up to 8) and low MW. Better compatibility with Freon-type of blowing agents.
- c) Halogen- or phosphor-containing polyols for flame-retardancy.

iii) **Silicone block copolymers** as surfactants to control the size, shape, and distribution of bubbles.

iv) **Catalysts:** Mostly tertiary amines and rarely metallic salts.

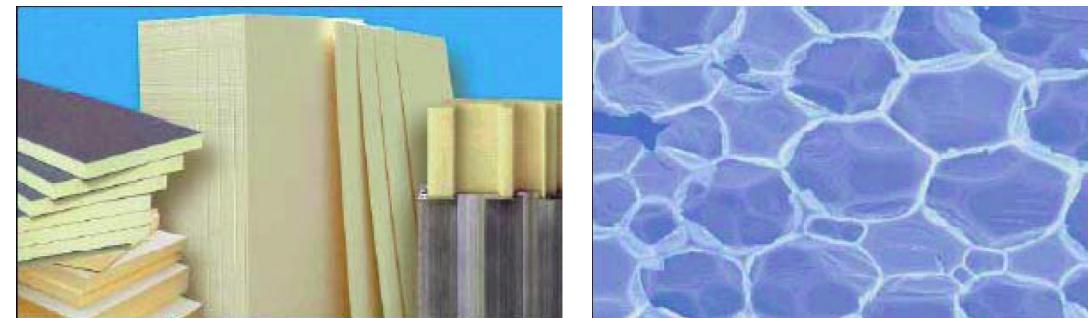
v) **Blowing agents:** To keep low thermal conductivity (K), Freon-type is preferred because of their low K.

- air, 0.024;
- carbon dioxide, 0.014;
- fluorocarbons, 0.008–0.010.

vi) Water leads to  $\text{CO}_2 \uparrow$  and polyurea for better mechanical strength of the rigid foam.

**Table 7.8** A common formulation for thermal insulation PU rigid foam

	<i>Parts by weight</i>
Polyether polyol	100
Glycerol	10
PMDI	stoichiometric + 5%
CFC-11	50
Triethylenediamine	0.5
Silicone block copolymer	1.0



**Table 7.9** Some properties of polyurethane–polyisocyanurate foams

<i>Property</i>	<i>Value</i>
Density	0.024–0.096 g/cm <sup>3</sup>
Initial <i>K</i> -factor	0.019 W/m · K
Equilibrium <i>K</i> -factor	0.024 W/m · K
Service temperature	–185 to 150°C (compared to –40 to 95°C for rigid PU foam)
Compression strength	0.14–0.28 MPa
Shear strength	0.10–0.24 MPa

vii) **Polyisocyanurate and cyclotrimerization** lead to stronger foam and high crosslinking density, together with good flame retardancy and very good hydrolytic stability.

# Rigid PU and Polyisocyanurate Foams

## Manufacturing Methods:

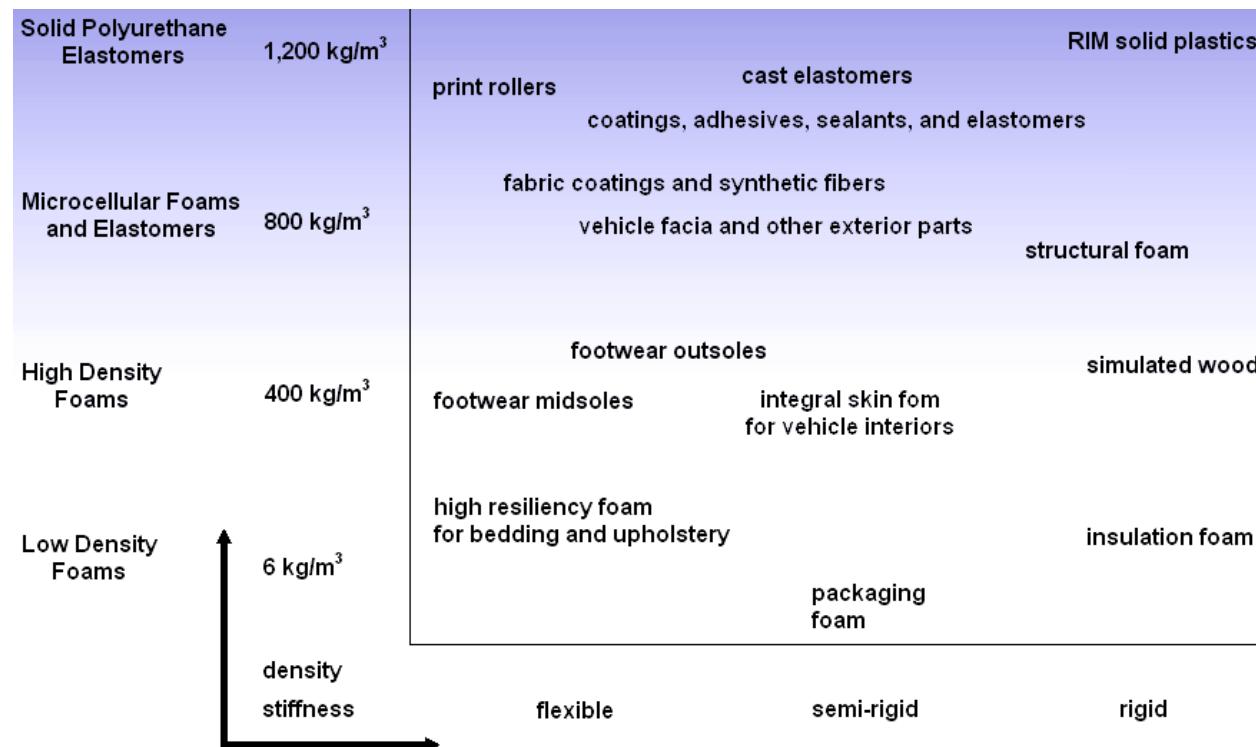
- i) Either in plant or by portable equipment and pour-in-place methods.
- ii) One-shot, prepolymer and quasi prepolymer techniques
- iii) Continuous slabbing (pouring into large blocks onto a moving conveyor), other processing alternatives include pouring-in-place, spraying, frothing and laminating.

## Applications:

- Home and building insulation
  - for walls, roofs, and structural components,
  - for refrigerated trucks, trailers and railway cars,
  - for refrigerators/freezers (household/commercial/industrial),
  - for insulation of storage tanks and pipes,
  - for insulation in automobiles, aircraft and ships.
- Flotation and large compartments, small boats, in oil industry.
- Simulated wood: Less expanded, high density structural and decorative foams are used for doors, windows and other accessories, and in furniture manufacture. Different wood grains may be captured perfectly on the foam surface.

Watch a video in class:

How the rigid foams are made for building insulation blocks.



# PUs by Reaction Injection Molding (RIM)

## What is RIM?

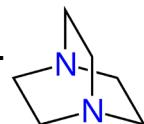
This video gives a really good introduction:

[https://www.youtube.com/watch?time\\_continue=262&v=TWEfbGH-Ewc&feature=emb\\_logo](https://www.youtube.com/watch?time_continue=262&v=TWEfbGH-Ewc&feature=emb_logo)

The RIM process consists of a precise and individual metering of all liquid components and their thorough and extremely rapid mixing. The highly reactive liquid mixture is injected into molds where the reactions take place, and the polymer is formed and shaped into the final products at a high production rate.

## Components (similar to other PU formulations)

- Polyols: PEPs end-capped with primary hydroxyls or amines. MW: 2000-6000 Da.
- Chain extenders: glycol and amine, e.g., 2,4/2,6-diethyltoluene diamine, 80/20 isomer mixture (DETDA).
- Catalysts: Usually RIM is so fast (0.8-1.2 sec), no catalysts are needed. If needed, they are dibutyltin dilaurate and tertiary amines, especially DABCO (1,4-diazabicyclo[2.2.2]octane).



## Operation

- i) Continuous circulation to keep constant temperature.
- ii) Intensive mixing by high pressure impingement: 0.3-4 cm<sup>3</sup> chamber, self-cleaning, gelation time between 1-2 sec.

**Table 7.11** Typical conditions for reaction injection molding [69]. (Reproduced by permission of Taylor & Francis, Inc. from *Principles of Polymer Systems* by F. Rodriguez, 2nd edn, 1982, pp. 354. All rights reserved)

Formulation	Parts by weight
Resin stream:	
Polyols	150
Dibutyltin dilaurate (catalyst)	0.045
Amine (cocatalyst)	0.6
Isocyanate stream:	
Polyfunctional isocyanate	96
Blowing agent (Freon type)	3
Methylene chloride	1
Processing parameter	Condition
Resin temperature	54°C
Isocyanate temperature	21°C
Mold temperature	57 ± 3°C
Resin pressure	120 atm
Isocyanate pressure	100 atm
Throughput	1.1 kg/s
Demolding time	1–2 min
Postcure	1 hour at 120°C

**Internal Mold Release (IMR):** Zinc stearate solubilized in the polymerizing mixture to reduce mold preparation time.

# Reinforced RIM (RRIM)

Milled glass up to 40-50%, treated with aminosilane adhesion promoter, fibrous calcium silicate mineral or treated mica are used as fillers in reinforced RIM (RRIM) to provide a high flexural modulus and low thermal expansion coefficient, especially in thin parts. These find particular usage in automobile parts.

**Table 7.12** Some properties of PU/urea RIM for automotive applications [68]

Property	Unfilled	15.8% Glass filled
Density (g/cm <sup>3</sup> )	1.02	1.07
Hard segment content (%)	41.1	30.9
Flexural modulus (MPa)		
-29°C	849	618/392*
22°C	405	360/194*
70°C	304	260/137*
Tensile strength (MPa)	26.7	15.2
Elongation (%)	195	125/180*
Coefficient of thermal expansion ×10 <sup>-6</sup> /°C (from 66°C to 121°C)	170	51/145*

\* parallel/perpendicular

# Foam RIM

For microcellular or foamed parts, the reaction mixture is injected into the mold without filling it completely. Filling the mold is completed by the expansion of the material, which can vary from 5-10% expansion for microcellular elastomers to 60-75% expansion for structural foam systems.

Surfactants (polyoxyalkylene-polysiloxane copolymers) are used to facilitate the formation of a fine cell structure.

The same variations for the manufacture of cast elastomers and foams are used in RIM processes:

- true one-shot system: all components are individually and simultaneously introduced into the mixer;
- two-component system: isocyanate - component A, and all other ingredients - component B;
- quasi prepolymer system: the isocyanate is reacted with a part of polyol to give the quasi prepolymer (component A); the remaining polyol is premixed with all other ingredients and constitutes component B.

## Applications

- Automobile: RIM/RRIM PU, polyurea, PU/urea and PU/isocyanurate elastomers and foams have found numerous applications in the automotive industry for the production of exterior large size components such as front and rear bumpers, instrument housings, head rests, steering wheels, pneumatic tires for tractors and other parts.
- Shoe soles: RIM microcellular elastomers or flexible and semiflexible foams for shoe soles.
- Rigid foams are used in the furniture and building industries.

# PU Coatings, Adhesives and Sealants

PUs are largely used for coatings, adhesives and sealants owing to their outstanding properties such as **abrasion resistance, toughness, flexibility, tear strength, adhesive properties** and **solvent resistance**.

Chemistry of PU coatings, adhesives and sealants is similar to that for other PU materials:

- Aromatic TDI, MDI or PMDI are the isocyanates for non-light exposed applications.
- Aliphatic and cycloaliphatic isocyanates are chosen for applications w/ weatherability and appearance.
- Polyethers, polyesters, acrylic polyols, glycols and amines are used as prepolymers and chain extenders.
- Most are thermoset PUs, whereas some applications use thermoplastic PUs.
- Catalysts, fillers, pigments, plasticizers, other additives, and even solvents are used in the formulation.

To meet pollution and safety regulations, PU water dispersions are also used for coatings and adhesives, thus avoiding the use of organic solvents.

Both one-component and two-component PUs are available:

The **one-component** system actually consists of several components mixed and stored together and can be **cured by oxygen in air, moisture or heat**. They are based on soluble PU with high MW.

The **two-component** systems are stored as two separate components that contain ingredients terminated in active groups, and they are mixed just before the application (short pot life) and then cured. Two-component systems are used **in more demanding applications** for physical characteristics.

# PU Coatings

## One-component PU coatings

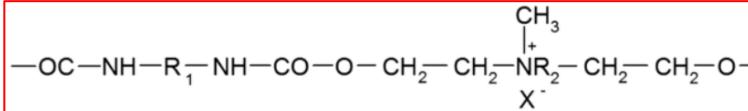
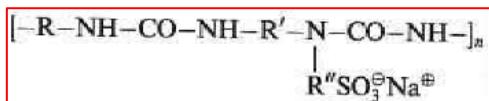
- Uralkyds: urethane-modified alkyds, can be cured by oxygen in air, used for wood finishes and enamels.
- Moisture cured coatings based on NCO-terminated prepolymers are limited to thin films and in places with relative humidity of 40-75%. Major markets are for concrete and wood seamless floors.
- These coatings are also available as water dispersions.

## Two-component PU coatings

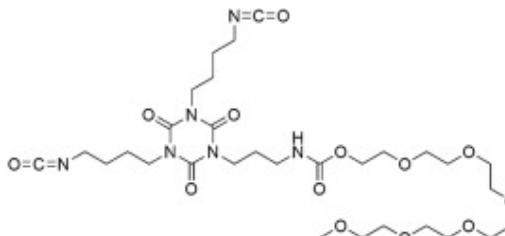
- The most important types of PU coatings.
- They need meter-mix equipment. PU coatings are largely used for aircraft, heavy machinery, buses, trucks, and maintenance coatings.

## Water dispersions

- PU ionomers: can be directly dispersed in water.



- PEG-protected isocyanate blocks (e.g., Bayhydur®)



Bayhydur 3100

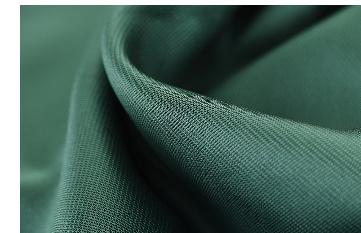
## Typical Applications



building/construction



furniture



water-resistant textile



scratch-resistant coating/films



conformal PU coating  
water-resistant



rust-preventive PU coating

## Advantages over other coatings

- For floors, it is better than epoxy coating, which tends to crack and flake. PU floor coating will not.
- For metals, it can prevent rusting. However, it won't stop it for already rusted irons.
- Adhere strongly to the substrate due to its polar nature.
- Tough, flexible, and scratch-resistant
- Water-resistant (but not ice-phobic for wind blades)

<https://www.youtube.com/watch?v=oD2Cio0m3TM>

# PU Adhesives

- Strong adhesion due to the polar nature of the compounds in the formulation. Furthermore, the isocyanates present in PU compositions may react with any active hydrogen present in the adherent or with the thin films of water often present on the surfaces of materials such as ceramics, glass and metals. PU adhesives are very useful when elastomeric bonds are required on flexible substrates such as rubber or plastic.
- Two-component adhesives result in more flexible and softer elastomers. One of the components is an NCO-terminated prepolymer and the other is a polyol or polyamine. They are extensively used in the automotive industry, to laminate panels for construction, foam to textiles, or plastic films together for food packaging. Hybrid adhesives have been prepared from PU-epoxy or PU-acrylics.
- Aqueous PU latex adhesives are growing in importance in order to avoid the use of large amounts of volatile organic solvents in open systems.

## What is a Polyurethane Adhesive???



Learn about the applications, advantages, disadvantages, cure times and much, much more

### Advantages

- Stick on most surfaces, whether porous or not: metals, wood, rubbers, leather, tile, glass, most plastics, concrete, brick, etc.
- Short working time of ~20 min and hours to full strength.
- Cure by moisture and waterproof afterwards.
- No need to mix and directly use for 1-component adhesives.
- Available in different viscosities.
- Hot melt adhesives use high MW PU with solvents. After solvent evaporation, apply heat to glue. Used in shoe industry. Sometimes use reactive hot melt adhesive for two components.
- By far the best glue for cryogenic environment, no embrittlement
- Good outdoor durability due to UV resistance.

### Disadvantages

- Not as strong as epoxy adhesives.
- Cannot glue PE, PP, and PTFE.
- The glued parts need to be tightly fit; otherwise not strong.
- Cannot cure well under very dry condition.
- Become weak above 80-100 °C.
- Tends to foam and squeeze out, especially when moisture is high in the air.
- Although nontoxic when fully cured, intermediates are toxic.
- Limited shelf life. When opened, will go bad quickly due to exposure to moisture.
- Quite sticky and difficult to get off hand (need gloves).

# PU Sealants

**Sealants** are materials introduced into joints in order to prevent the transmission of water, vapor, and air, and to absorb the expansion and contraction of the joint. Silicone and PU are two major sealants.

- They contain 30-50% PU resins, together with fillers, pigments, plasticizers and other additives.
- They can be formulated as one-component moisture cured systems or as two-component fast curing systems.
- PU sealants exhibit low modulus, low hardness (10-50 Shore A), excellent adhesion, 100% elasticity (high joint movement capability), high abrasion resistance, low temperature flexibility and low moisture transmission.

## Applications

- Modern high-rise construction for insulated glass windows
- Sealing windshields and clay sewer pipes
- Highway and airport sealants and different marine applications



## Difference between PU and silicone sealants

Sealants	PU	Silicone
UV resistance	Not good, need additives	Good
Lifespan	5 years	20 years
Cost	Less expensive	More expensive
Versatility	Less	More
Wood sealing	Good adhesion	Poor adhesion

