

Chapter 4

Modern Polyurethanes: Overview of Structure Property Relationship

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The intrinsic features of polyurethanes polymers - such as elasticity, clarity and tunable mechanical properties - are found to be key in industrial and personal care applications. Understanding structure-property relationships in polyurethanes is necessary when designing smart multifunctional materials for specific end-uses.

Polyurethanes have a segmented structure of block copolymers where soft and hard segments form micro domains that may result in two-phase morphology. For example, a change in the molecular weight of the soft segment may affect phase separation that, in turn, dictates a very unique thermodynamic behavior of the polymer affects its mechanical characteristics. The nature of the building blocks and polymer morphology greatly affects film forming properties, stiffness, and polymer behavior under different thermal and physical conditions.

This paper will review effects of the polymer structure on biodegradability and chemical resistance. Physical-chemical characteristics of the polymer to achieve shape memory or self-healing effects will also be discussed.

Introduction

Polyurethanes (PURs) belong to an exciting class of polymers known for their versatile chemistry and unique properties.

Modern PURs can be found in many different end use applications—from soccer balls and Nike shoes to kitchen cabinets, bridges and cars, even cosmetics! Many technologies based on PURs have established themselves as quality standards in the coatings, adhesives and sealants industries. In Personal Care, PURs remain an emerging technology –not as commonly used as in other industries.

In order to design a PUR polymer to deliver performance specific to a targeted end use, one need understand PUR structure property relationships and the changes in behavior this relationship affects.

This article will discuss common building blocks used in the synthesis of polyurethane dispersions, stabilization mechanisms of ionic and non-ionic dispersions and film formation. Many factors in a polymer structure affect its thermodynamic and mechanical properties, chemical resistance and biodegradability. Specifically, the effects of molecular weight, phase separation and crosslinking density on polymer properties will be examined. The discussion will focus on waterborne polyurethane technology since it is most relevant to personal care—not only because of its safety and compliance with industry regulations, but also because of its ability to be tailored to deliver desired performance in various cosmetics.

Discussion

Basic Polyurethane Reactions

Otto Bayer invented PURs in 1937. Three basic reactions lie in the foundation of PUR chemistry:

Urethane bonds are formed when an isocyanate group (NCO) reacts with an alcohol or polyol as shown in Figure 1:

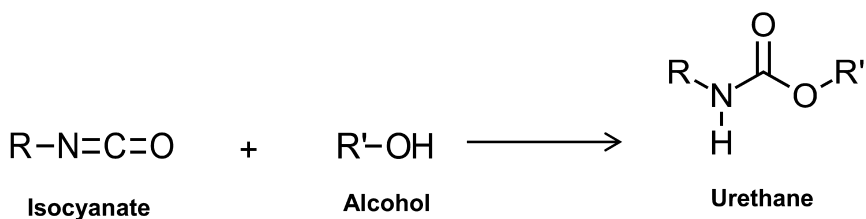


Figure 1. Urethane formation.

Urea bonds are formed when an isocyanate NCO group reacts with an amine as shown in Figure 2:

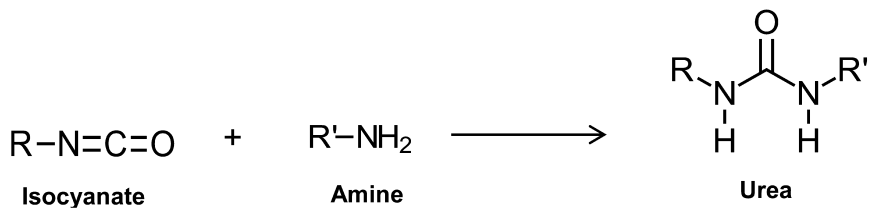


Figure 2. Urea formation.

The third important basic reaction, shown below in Figure 3, is between an isocyanate group and water:

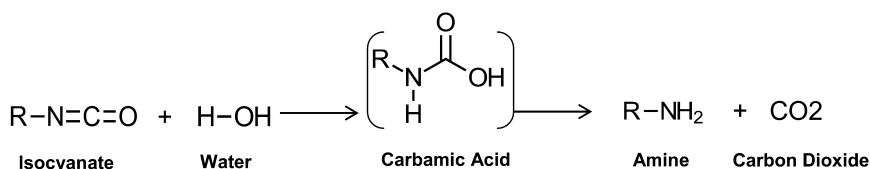


Figure 3. Isocyanate reaction with water.

Water hydrolyzes isocyanate groups to yield amines via unstable carbamic acid and the evolution of carbon dioxide. The co-formed amino groups can react with remaining isocyanate groups to form urea linkages and thus contribute to the extension of the macromolecular chain.

Unique Nature of Polyurethanes

Polyurethane polymers are unique and differ from other polymer types mainly because they are segmented copolymers consisting of soft segments formed by a high molecular weight species and hard segments formed by a low molecular weight species. This type of copolymer can have both crystalline and amorphous structures, and thus combines the benefits of both segments and the visco-elastic properties of both phases. The soft segment in polyurethanes contributes high extension and elastic recovery, while the hard segment contributes high modulus and strength to the composite.

The most interesting phenomenon which is responsible for the intrinsic elastic behavior of PURs is the formation of hydrogen bonds between PUR groups. This nature of these bonds is shown in Figure 4.

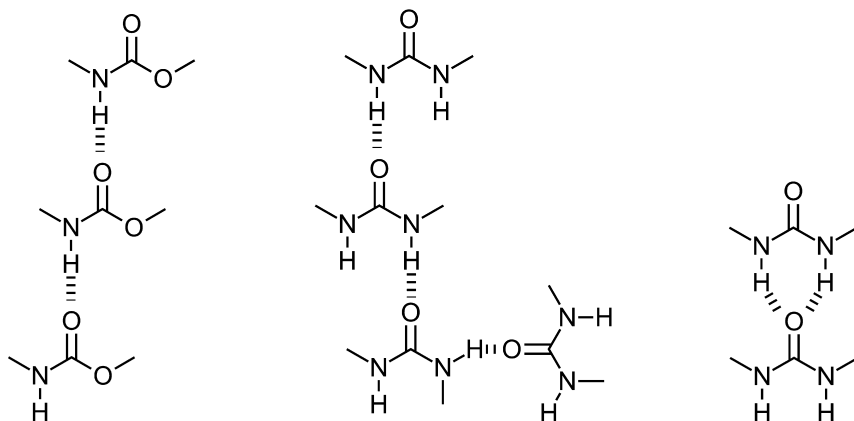


Figure 4. Hydrogen bonding in polyurethanes.

These non-covalent bonds act as crosslinks that break under strain and then easily recover upon release.

EPA regulations and consumer emphasis on green technologies propelled the use of aqueous Polyurethane Dispersions (PUDs) into many industrial and personal care applications in which they replace traditional solvent-borne resins. Simply defined, a PUD is a colloidal system in which a high molecular weight PUR polymer is dispersed in water. Figure 5 schematically depicts the idealized polymer structure and its segmented morphology.

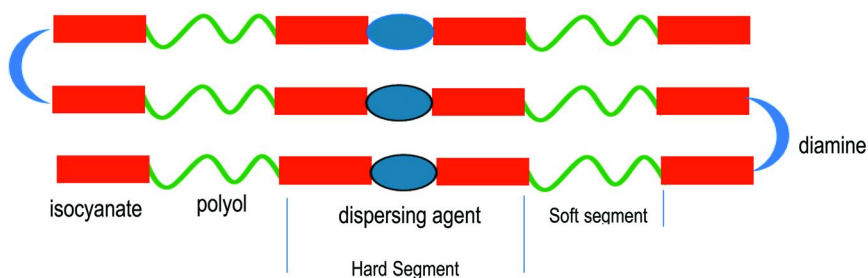


Figure 5. Polymer structure of PUD.

Polyurethane Dispersion: Building Blocks

Diisocyanates (I)

Among the common building blocks that are involved in PUD synthesis, isocyanates, polyols and amines are the three most influential ingredient categories that affect the polymer's properties and performance.

The choice of the isocyanate is one of the most influential factors with respect to the hard segment. Polymer performance will depend greatly on the chemical nature of the isocyanate. In synthesizing PUDs, primarily linear aliphatic and cycloaliphatic diisocyanates and their blends are preferred due to their lower reactivity towards water and light stability.

Schematic structures of aliphatic diisocyanates are shown below in Figure 6.

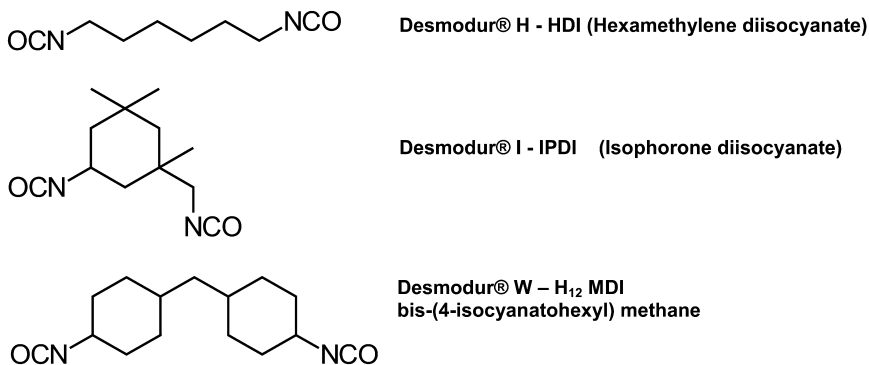


Figure 6. Aliphatic diisocyanates.

Isophorone diisocyanate, IPDI, contributes to harder and more chemically resistant materials, while hexamethylene diisocyanate, HDI, imparts great low temperature flexibility and elasticity to the polymer chain. 4,4'-dicyclohexylmethane diisocyanate, H₁₂MDI, makes materials with optical clarity, excellent durability, solvent resistance and toughness. H₁₂MDI also helps to retain gloss longer. Among aliphatic diisocyanates, H₁₂MDI definitely produces the most hydrolytically stable polyurethanes. The polymer morphology of H₁₂MDI systems is also different from that of other diisocyanates, particularly methylene diphenyl diisocyanate (MDI)-based materials. MDI often forms well-defined crystalline hard segments, whereas H₁₂MDI yields smaller amorphous or semi crystalline domains. This difference in morphology results in greater tensile strength and hardness of polymers built with H₁₂MDI (2).

H₁₂MDI is the slowest to react because both of its NCO groups are attached to secondary carbon atoms. HDI is the most reactive among aliphatic diisocyanates because it contains only primary NCO groups. IPDI has the greatest difference in reactivity between primary and secondary NCO groups which helps better control the polymer's molecular weight, and subsequently, its viscosity.

Polyols (I)

Hydroxy-functional polyols often serve as co-reactants for diisocyanates and make up a majority of the resin composition. Both processing and finished properties of the polyurethane will depend to a large extent on the type of polyol

used in the polymer backbone. Low molecular weight diols and triols form hard blocks, while high molecular weight polyesters, polyethers and polycarbonates represent soft blocks. The chemical nature of these polyols will dictate film properties such as glass transition temperature, elasticity, modulus, solvent requirement and solubility. Typical examples of short chain polyols used in the hard segment are: ethylene glycol, 1,4-butanediol, and trimethylol propane. Hard segment content usually controls mechanical properties as well as thermal and hydrolytic stability of the finished polyurethane.

Polyesters (eg. Figure 7) are known to impart greater water resistance and hardness—but are susceptible to hydrolysis. To compensate for this weakness, urea linkages can be introduced into the polymer.

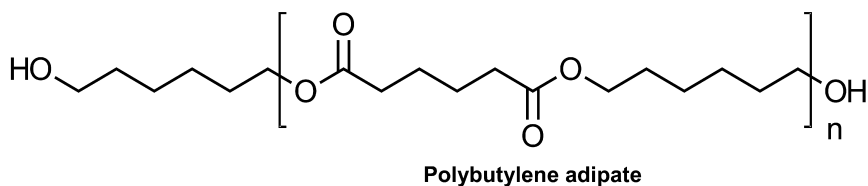
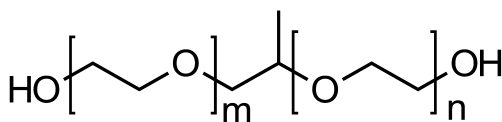
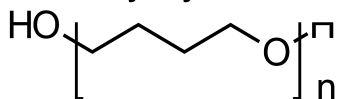


Figure 7. Typical polyester polyol.

Polyethers (eg. shown in Figure 8) are known for their flexibility and lower cost. C4 polyethers also produce materials with excellent hydrolytic stability.



Polyethylene oxide glycol



Polytetramethylene glycol

Figure 8. Typical polyether polyols.

Polycarbonates produce materials with greater hydrolytic stability and solvent resistance (see Figure 9).

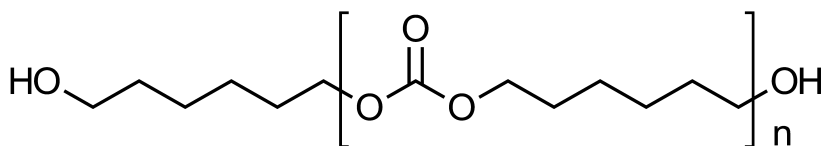


Figure 9. Polycarbonate-based polyol.

The demand for green and sustainable technologies prompted innovation in this category of raw materials. For instance, adipates and some of the glycols can be replaced with succinates and lactides, renewable raw materials sourced from plants. Soybean and castor oils are other plant-derived building blocks that can be incorporated into the polyester or polyether backbone. Such polyols will have an amphiphilic nature and will impart a softening effect on the film. New technology for making polycarbonate from carbon dioxide is emerging as well.

In order to achieve special effects, the use of hydroxyl-functional acrylates, oil-modified alkyd resins, or hydroxyl-functional polybutadienes or fluoroalkyl-containing polyethers is applicable.

To achieve faster biodegradability, polyesters made of lactic or glycolic acids can be used instead of adipates or phthalates.

Dispersing Agents (3)

PUR prepolymers are built as intermediate molecular weight species in the process of synthesizing high molecular weight final polymers. PUR prepolymers are typically very hydrophobic in nature. In order to disperse hydrophobic prepolymers in water, either external or internal emulsifiers are required. Internal emulsifiers (those that can be incorporated into a prepolymer backbone) are usually preferred as they impart superior stability and final dispersion properties compared to external emulsifiers (surfactants). Specifically, polymers with built-in internal emulsifiers have finer particle sizes and reduced water sensitivity. Also, high-shear dispersing processes are not required.

Internal emulsifiers contain either ionic or non-ionic hydrophilic groups. Hence, prepolymers modified with ionic groups or with hydrophilic polyether will become self-dispersing. Among ionic emulsifiers, anionic types, such as salts of sulphonic or carboxylic acids, are typically used.

Schematic structures of internal emulsifiers are shown below in Figure 10.

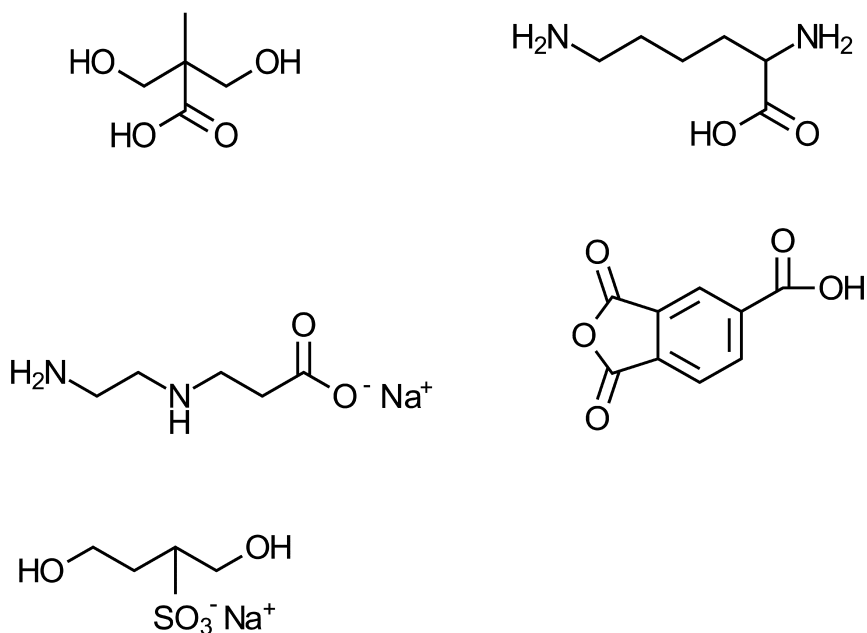


Figure 10. Internal emulsifiers.

Salts of tertiary amines will render polymers cationic. These types of PUDs are almost exclusively used in paper and leather applications.

Non-ionic emulsifiers are almost exclusively represented by polyethylene oxide polyethers similar that shown in Figure 11 below.

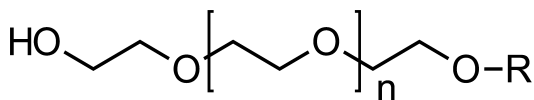


Figure 11. Non-ionic emulsifier.

The ionic dispersion is stabilized by the formation of electrical double layers between the ionic centers and their counter ions which migrate into the continuous water phase (3). The interference of electrical double layers from different particles results in particle repulsion. This stabilization mechanism is known as ionic repulsion and is illustrated in Figure 12. Ionic dispersions are sensitive towards electrolytes and freezing. However they are stable at high temperatures ($>70^{\circ}\text{C}$), have an exceptionally long shelf life, and are somewhat stable under strong shear forces.

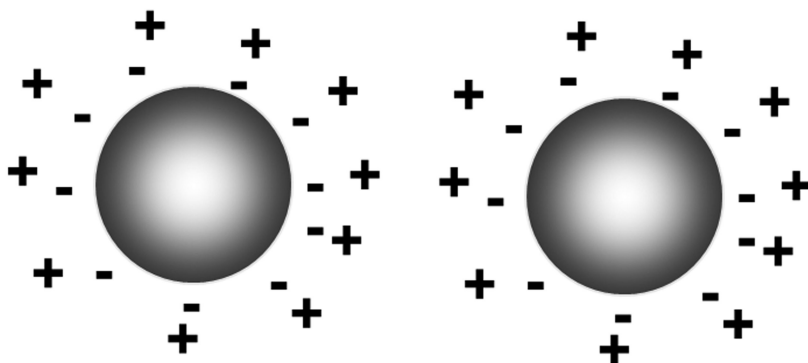


Figure 12. Ionic stabilization.

The stabilizing mechanism of non-ionic dispersions (illustrated in Figure 13) can be explained in terms of entropic or steric repulsion. When the particles approach closely, the freedom of motion of hydrophilic chains in the water phase becomes restricted, leading to a reduction of entropy. Non-ionic dispersions show greater stability to low temperatures, pH changes and strong shear, but are sensitive to degradation at high temperature

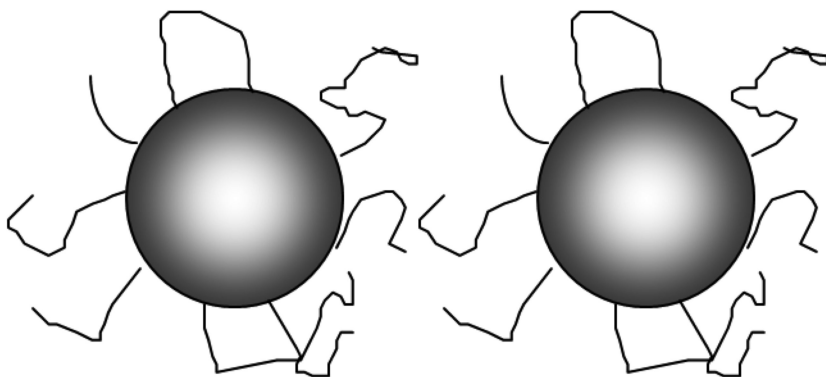


Figure 13. Non-ionic or Steric stabilization.

Greater hydrophilic modification of the polymer yields smaller particle sizes in the dispersion. However, in this case the viscosity of the dispersion tends to increase, leading to lower solids content. Ultimately, the amount of internal emulsifier in the prepolymer backbone has to be balanced to obtain a stable dispersion with the highest possible solids content.

Both stabilization types can be combined to achieve desirable synergistic effects:

- Lower overall hydrophilicity
- Tolerance to pH changes and towards electrolytes
- Freeze/thaw stability
- Fine particle size

Amines

In the synthesis of PUDs, water soluble amines are used as chain extenders to build up molecular weight in the final stages of the reaction. The preferred reaction is between amines and isocyanates compared to amines with water, thus making it possible to conduct reactions between amine and NCO groups in the presence of water. Typically, aliphatic linear and cyclic di- and tri-functional amines are used, depending on the desired properties of the final polymer. Urea linkages are formed as a result of the reaction between amines and diisocyanates. These usually improve the hydrolysis resistance, thermal stability and mechanical strength of the polymer.

Film Formation

In the PUD, polymer particles remain discrete as they are dispersed in water. Film formation occurs when the water evaporates and particles coalesce to form a continuous smooth matrix. Figure 14 shows stages of the film formation process from the starting point of applying raw material on the substrate to the dry-to-touch film (2).

Polyurethane Dispersion (PUD)

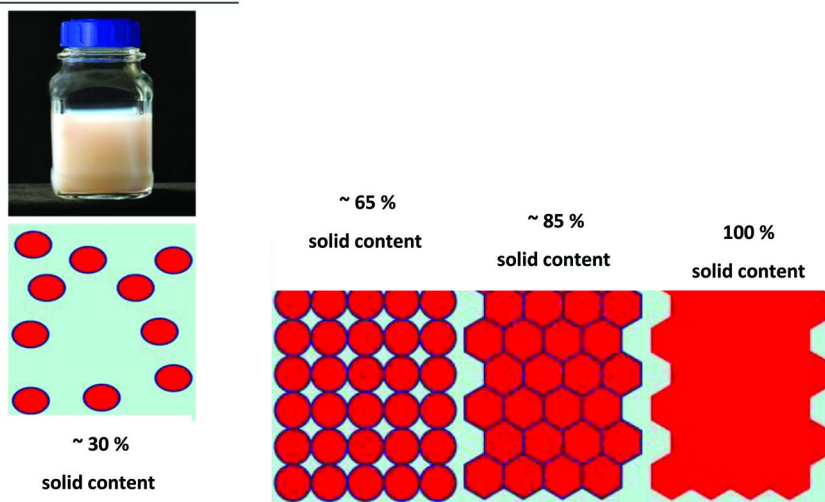


Figure 14. Film formation in PUDs.

Hence, film formation is a physical process driven by several factors:

- Glass transition temperature of the polymer
- Minimum film formation temperature
- Humidity
- Coalescent solvent or plasticizer

The lower the glass transition temperature of the polymer, the easier it becomes to form a film. The more flexible the polymer, the lower minimum film formation temperature it will have. Brittle or very cross-linked polymers will require the help of a plasticizer or coalescent solvent to form a film at room temperature. Particle size will also influence film formation; a wide particle size distribution will lead to better packing and less water sensitivity of the film after water evaporates.

Morphology of the Polymer

Knowledge of a polymer's morphology is essential for understanding structure/properties relationships. This knowledge allows one to vary the morphology in a controlled manner in order to achieve the desired properties in a material.

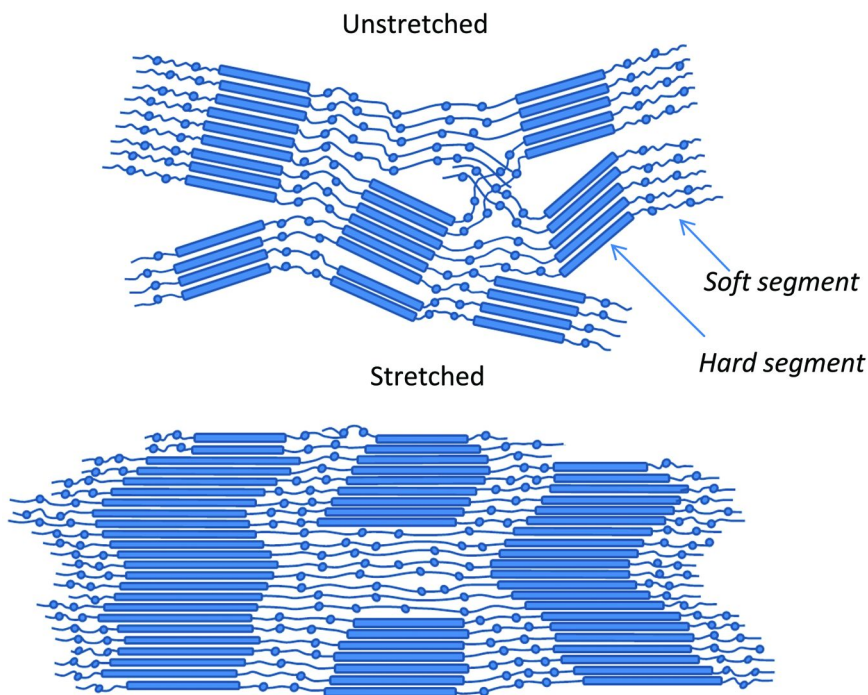


Figure 15. Molecular reinforcement due to orientation.

PURs are famous for their toughness, meaning a unique combination of strength and flexibility. This unique PUR feature can be explained from a polymer morphology standpoint. The polymer macromolecular structure in stretched and unstretched modes helps to explain this phenomenon. Molecular reinforcement is taking place in the stretched mode (as illustrated in Figure 15) (1).

In the unstretched form, there is phase separation between Soft and Hard Segments. As the polymer is strained, both domains become oriented in the direction of strain, causing more intense molecular interactions, which leads to molecular reinforcement.

In Figures 16 and 17, DMA graphs show a classic case—as strain increases, the point of “densification”(molecular reinforcement) is reached, whereupon stress sharply rises. This explains why PURs maintain high strength at high elongation. Moreover, the stress/strain relationship will depend greatly on the polymer composition. The influence of the structure of the soft segment on tensile strength and elongation is related to intermolecular association and crystallization during stretching. Effects of the soft segment are pronounced mainly in polymers with a continuous soft segment phase, e.g., those with soft segment content above 50%.

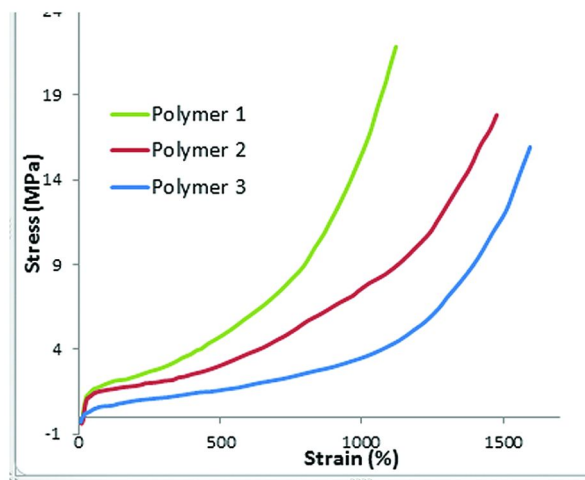


Figure 16. Stress/Strain behavior.

The graph on Figure 16 illustrates that the level of strain where the ‘densification’ phenomenon occurs depends on both Hard Segment length and content. For PURs with higher Hard Segment content, the strength increase occurs at lower strain (see example of waterborne PUR polymer Polymer 3 in Figure 16).

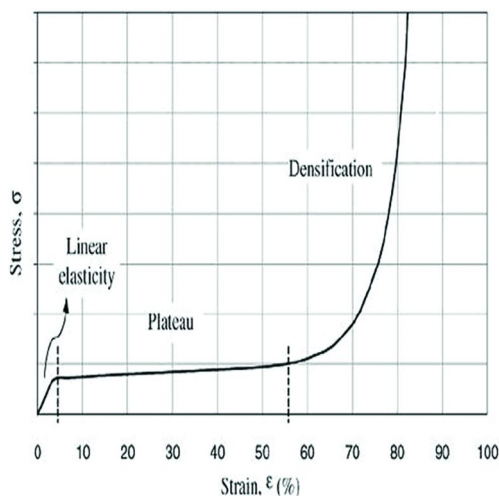


Figure 17. Densification phenomenon.

The molecular weight of the polymer will also play a role in determining final properties and the end-use of the polymer. The degree of chain extension, chain termination, and the isocyanate- to-hydroxyl ratio are the key factors affecting molecular weight. The greater the extent of the reaction between isocyanates and hydroxyl groups, the higher the molecular weight of the polymer becomes, as it is shown on Figure 19. Mechanical properties, viscosity and adhesion will greatly depend on the optimal molecular weight determined for each specific application. As shown in Figure 18 below, the tensile strength of the polymer increases significantly with increasing molecular weight, while elongation is reduced.

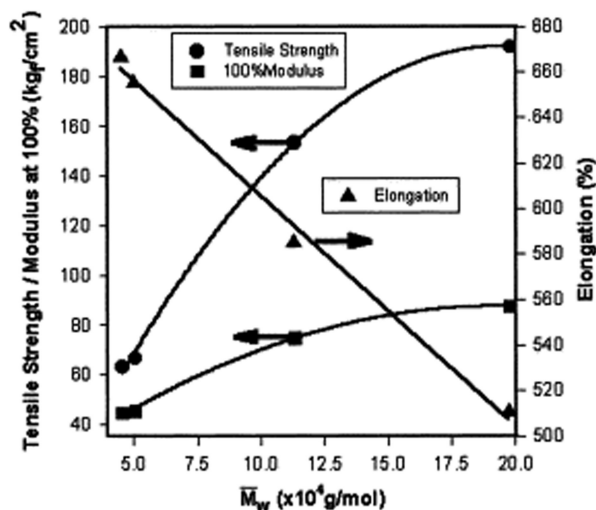


Figure 18. Tensile Strength vs. Mol. Wgt.

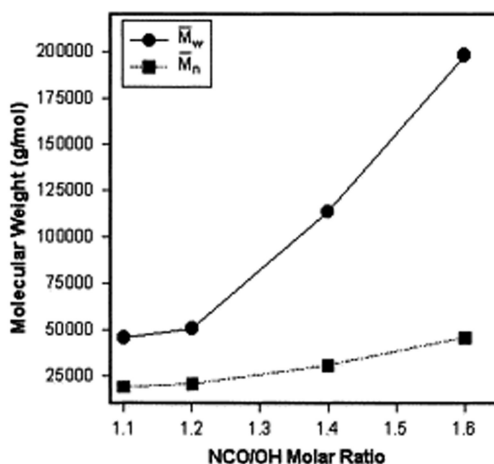


Figure 19. Effect of Index on Mol. Wgt.

Effects of Crosslinking

A polymer's hardness, chemical resistance and abrasion resistance can be increased via chemical or physical crosslinking. Chemical crosslinking is achieved via the addition of another reagent that will polymerize within the existing polymer and form IPN (interpenetrating network) structures as shown in Figure 20. If the polymer has free functional groups, OH or COOH, another reagent (aziridines, blocked isocyanates, carbodiimides, waterborne polyisocyanates and melamine formaldehydes) can react with these groups to create additional crosslinking. Equivalent weights of these functional groups affect the crosslinking density.

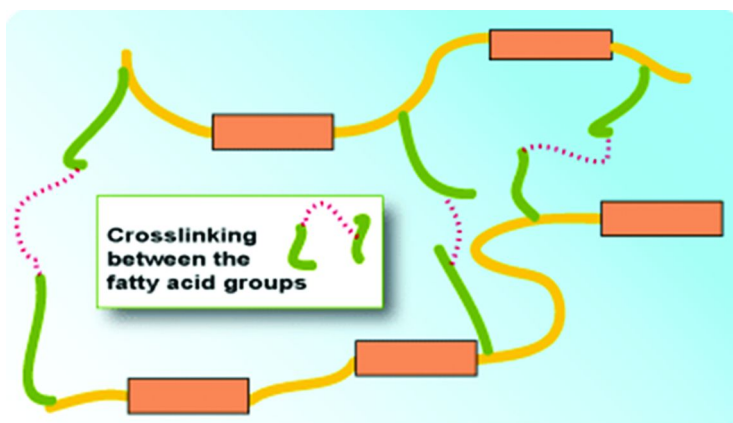


Figure 20. Chemical crosslinking.

Breathability (water vapor permeation) and moisture resistance (no film swelling occurs upon exposure to water) can be obtained with the introduction of side chains containing polyethyleneoxide ether subsequently crosslinked with one of the above listed reagents. The resulting polymer will demonstrate breathability with high moisture resistance (4).

Physical crosslinking is obtained when non-covalent bonds are formed between polymer chains and through phase separation.

Effects of Phase Separation

What drives phase separation versus phase mixing?

One of the factors that drive phase separation is thermodynamic incompatibilities between Soft Segments and Hard Segments—for instance, between aliphatic Soft Segments and aromatic Hard Segments or between soft and hard segments with wide differences in polarity. From a kinetic point of view, phase separation can be driven by increased mobility of either the Hard or Soft Segment. This explains the effect of annealing on segmented PURs. Increased mobility during annealing allows the polymer to rearrange into a thermodynamically more favorable arrangement (5).

The molecular weight of the Soft Segment is another factor affecting phase separation—the greater the distance between anchoring sites connecting Hard Segment to Soft Segment, the more mobile the Hard Segment, allowing for easier phase separation.

As hardness increases with Hard Segment content, the extent of phase mixing increases—the Hard Segment becomes dispersed in the Soft Segment domain, thereby hindering Soft Segment mobility. This increases the Soft Segment glass transition temperature, T_g . However if the Hard Segment is relatively crystallizable, increased Hard Segment content will increase its crystallizability and thus increase phase separation. These changes in phase separation affect not only the hardness of the polyurethane, but also its low-temperature properties.

Cross-linking will decrease phase separation since the crosslinks hinder mobility and therefore impede phase separation. Varying crosslink density, however, allows one to control, among other things, the modulus, softening behavior, clarity and chemical resistance of a material. Figure 21 shows the effect on crosslink density on storage modulus.

Choice of chain extender can also influence phase separation. Studies have been done that show certain chain extenders allow for more or less hydrogen bonding in the hard segment. Increased hydrogen bonding increases physical crosslinking which in turn affects crystallizability and stress-strain behavior.

Annealing drives phase separation since both Hard Segment and Soft Segment domains regain their mobility at higher temperatures allowing them to realign and even crystallize. Crystallization results in a greater degree of phase separation. The length of hard segment domains determines the limits of hard segment crystallization, determining, in turn, the melting point, and ultimate thermal stability. Introducing asymmetrical structures like 2,4 and 2,6 isomers of TDI, will break up crystallinity and favor increased phase mixing.

Polymers with phase-separated structures form hazy films. Very transparent and glossy films are typically obtained with amorphous polymers.

E-module measurement

Schematic plot of storage modulus curves

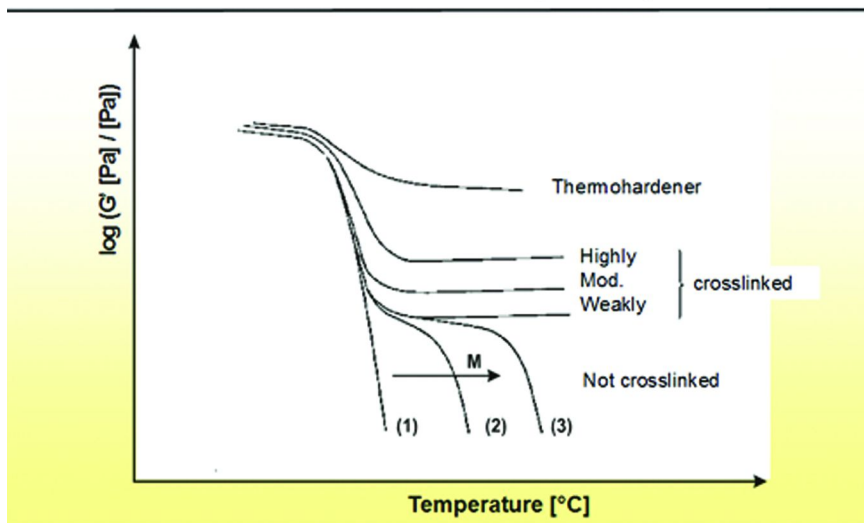


Figure 21. Schematic plot of storage modulus curves showing the effects of crosslink density. (Reproduced from Bayer MaterialScience TPU Tech Center Website.)

Conclusion

Waterborne polyurethanes are a versatile class of environmentally friendly polymers that can be designed with a wide range of properties suitable for high performance applications. They often offer a unique balance of flexibility, hardness, mechanical strength and durability combined with excellent sensorial attributes and appearance. In cosmetics, these film-forming polymers contribute to excellent water and rub off resistance, controlled delivery of actives, and long-lasting wear without sacrificing aesthetics and sensorial properties. Films made of linear polyurethanes are distinctively soft and silky to touch, having smooth transparent surfaces. In skin care applications, such polymers enhance the efficacy of active ingredients such as sunscreen filters, anti-inflammatory aids and salicylic acid, helping to achieve mild and efficacious products with excellent aesthetics. In hair care applications, waterborne polyurethanes make a difference in obtaining long lasting humidity resistance, dynamic durable styles and healthy appearances. Moreover, these polymers are generally safe and of high quality, friendly to human skin biology.

Suggested Additional Reading

1. Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC Press LLC: Boca Raton, FL, 1999; pp 4-31-4-32, 4-36, 14-1-14-3.
2. Meier-Westhues, U. *Polyurethanes: Coatings, Adhesives and Sealants*; Vincentz Network: Hannover, Germany, 2007; pp 67-68.

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