We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

3,800
Open access books available

116,000
International authors and editors

120M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Polyurethane: An Introduction

Eram Sharmin and Fahmina Zafar

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/51663

1. Introduction

1.1. History of polyurethane

The discovery of polyurethane [PU] dates back to the year 1937 by Otto Bayer and his coworkers at the laboratories of I.G. Farben in Leverkusen, Germany. The initial works focussed on PU products obtained from aliphatic diisocyanate and diamine forming polyurea, till the interesting properties of PU obtained from an aliphatic diisocyanate and glycol, were realized. Polyisocyanates became commercially available in the year 1952, soon after the commercial scale production of PU was witnessed (after World War II) from toluene diisocyanate (TDI) and polyester polyols. In the years that followed (1952-1954), different polyester-polyisocyanate systems were developed by Bayer.

Polyester polyols were gradually replaced by polyether polyols owing to their several advantages such as low cost, ease of handling, and improved hydrolytic stability over the former. Poly(tetramethylene ether) glycol (PTMG), was introduced by DuPont in 1956 by polymerizing tetrahydrofuran, as the first commercially available polyether polyol. Later, in 1957, BASF and Dow Chemical produced polyalkylene glycols. Based on PTMG and 4,4’-diphenylmethane diisocyanate (MDI), and ethylene diamine, a Spandex fibre called Lycra was produced by DuPont. With the decades, PU graduated from flexible PU foams (1960) to rigid PU foams (polyisocyanurate foams-1967) as several blowing agents, polyether polyols, and polymeric isocyanate such as poly methylene diphenyl diisocyanate (PMDI) became available. These PMDI based PU foams showed good thermal resistance and flame retardance.

In 1969, PU Reaction Injection Moulding [PU RIM] technology was introduced which further advanced into Reinforced Reaction Injection Moulding [RRIM] producing high performance PU material that in 1983 yielded the first plastic-body automobile in the United States. In 1990s, due to the rising awareness towards the hazards of using chloro-
The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

4.1. Reaction in the absence of a catalyst

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO...
The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds. The active compound itself acts catalytically in the reaction as follows (Scheme 9).

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to the –NCO group. The reactivity of the –NCO...
Mechanism

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

4.1 Reaction in the absence of a catalyst

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO...
4. Mechanism

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

4.1. Reaction in the absence of a catalyst

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO
4. Mechanism

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

4.1. Reaction in the absence of a catalyst

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO
Scheme 8. Reaction of isocyanate with active hydrogen compound

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

The active compound itself acts catalytically in the reaction as follows (Scheme 9).

Scheme 9. Isocyanate reaction in the absence of a catalyst

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO
The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

The active compound itself acts catalytically in the reaction as follows (Scheme 9).

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO
The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

The active compound itself acts catalytically in the reaction as follows (Scheme 9).

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO...
4. Mechanism

The reaction of an isocyanate with active hydrogen compounds is carried out with or without a catalyst. The self-addition reactions of isocyanates do not usually proceed as readily as reactions with active hydrogen compounds.

4.1. Reaction in the absence of a catalyst

The active compound itself acts catalytically in the reaction as follows (Scheme 9).

As given in Scheme 9, in the reactions proceeding in the absence of a catalyst, the electrophilic carbon of the isocyanate is attacked by the nucleophilic centre of the active hydrogen compound; hydrogen is added to –NCO group. The reactivity of the –NCO
groups is increased due to the presence of the electron withdrawing groups, and decreases by the electron donating groups. While the aromatic isocyanates are more reactive than the aliphatic isocyanates, steric hindrance at –NCO or HXR’ groups reduce the reactivity.

The order of reactivity of active hydrogen compounds with isocyanates in uncatalyzed systems is as follows:

Aliphatic amines > aromatic amines > primary alcohols > water > secondary alcohol > tertiary alcohol > phenol > carboxylic acid > ureas > amides > urethanes.

4.2. Reaction in the presence of a catalyst

The isocyanate reactions of class (a) are also extremely susceptible to catalysis. The various isocyanate reactions are influenced to different extents by different catalysts. Many commercial applications of isocyanates utilize catalysed reactions. Tertiary amines, metal compounds like tin compounds (as mentioned earlier in the chapter) are most widely used catalysts for the reaction (Schemes 10 and 11). The mechanisms are similar to that of the uncatalyzed reaction (Scheme 9).

The tertiary amines and metal salts catalyse the reaction as follows:

![Scheme 10. Tertiary amine catalysed reaction](image-url)
Scheme 11. Metal salts catalysed reaction

The catalytic activity of amines closely parallels to the base strength of the amines except when steric hindrance becomes pronounced. This catalyst is also effective for self-addition reactions while metal salt compounds generally have less influence; tin compounds are particularly poor catalysts in these reactions.

5. Hazards

Although PU are chemically inert in their fully reacted form, the risks of asthmatic symptoms arise on human exposure even in smaller concentrations due to the volatility associated with isocyanates. Isocyanates arise the risk of asthmatic symptoms on human exposure, even in smaller concentrations. On exposure to flames, hazards of ignition are feared. Isocyanates may also be sensitive on our skin. Some isocyanates may also be anticipated as carcinogens. Thus, persons working with isocyanates must be equipped with proper protection devices such as gloves, masks, respirators, goggles, and others, as precautionary measures.

6. Conclusion

PU are thermoplastic and thermoset in nature. The type, position, and structure of both the isocyanate and polyol determine the progress of PU forming reactions as well as their properties and end-use applications. Hydrogen bonding also plays a key role in determining the properties of final PU product. Due to the associated health hazards, complete precautions are necessary while working with isocyanates. PU are available as one-pack or two-pack PU. PU dispersions, waterborne PU, PU Interpenetrating
Networks PU, hybrids and composites are used in various applications such as paints and coatings, adhesives, sealants, foams, absorbents, flame retardants, fuel binders, in automobiles, in biomedical applications (urological stenting practices, carriers of antituberculosis drugs, orthopaedics), extraction of metals, grouting technologies, crashworthiness, treatment of industry wastewater, cast elastomers, and others as also discussed in proceeding chapters.

**Author details**

Eram Sharmin and Fahmina Zafar

*Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia (A Central University), New Delhi, India*

**Acknowledgement**

Dr Fahmina Zafar (Pool Officer) and Dr Eram Sharmin (Pool Officer) acknowledge Council of Scientific and Industrial Research, New Delhi, India for Senior Research Associateships against grant nos. 13(8385-A)/2010-POOL and 13(8464-A)/2011-10 POOL, respectively. They are also thankful to the Head, Department of Chemistry, Jamia Millia Islamia (A Central University), for providing support to carry out the work.

7. References


*Corresponding Author