Polyurethane and Related Foams

Chemistry and Technology

Kaneyoshi Ashida

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Taylor & Francis
Taylor & Francis Group
Boca Raton London New York

CRC is an imprint of the Taylor & Francis Group,
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CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-10: 1-58716-159-1 (Hardcover)
International Standard Book Number-13: 978-1-58716-159-9 (Hardcover)

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Library of Congress Cataloging-in-Publication Data

Ashida, K. (Kaneyoshi)
Polyurethane and related foams : chemistry and technology / Kaneyoshi Ashida.
p. cm.
Includes bibliographical references and index.
ISBN 1-58716-159-1 (acid-free paper)
1. Plastic foams. 2. Polyurethanes. I. Title.

TP1183.F6A74 2006
668.4'93--dc22 2006040589

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Dedication

To the late Dr. Toshio Hoshino, Professor, Tokyo Institute of Technology, who led me to a pioneering research field, and to the late Dr. Kurt C. Frisch, Professor, University of Detroit Mercy and director of the Polymer Institute of the same university, who encouraged my research activities.

Preface

Polyurethane foams debuted over 60 years ago. At the present time these types of foams make up the largest segment in the thermosetting foam industry.

This book describes polyurethane (PUR) and urethane linkage-modified polyisocyanurate (PIR) foams. A characteristic of these foams lies in the versatility of their physical properties, such as flexibility, viscoelasticity, semi-flexibility, rigidness, and heat and flame-resistance at a wide variety of foam densities. This versatility is derived from molecular design by the choice of raw materials and foaming reactions.

For example, polyurethane foams are prepared by the reaction of polyols with polyisocyanates in the presence of blowing agents. The molecular weight and the functionality of polyols affect the resulting foam properties. Polyisocyanates act as the jointing agent of polyols. Therefore, urethane and related foams are recognized as building block polymers.

Blowing agents are the key materials for polyisocyanate-based foams. Due to the ozone depletion problems in the stratosphere, physical blowing agents have gone through a revolutionary change. Chlorofluorocarbons, (CFCs), and hydrochlorofluorocarbons (HCFCs) have been phased out. The next generation of blowing agents includes hydrofluorocarbons (HFC), C_5-hydrocarbons, water, and liquid carbon dioxide. This book highlights this next generation of blowing agents.

This book is intended to be informative to people in research and development, production, processing, testing, marketing, sales, and foam applicators, as well as professors, students, and others.

Acknowledgments

My warmest acknowledgments to Mr. Hideyo Sugimura, my son-in-law and director of Vision-Ease-Lens, Inc. for his assistance. I also wish to thank all the collaborators and assistants in research and development work, and Mrs. Yoko Ashida, my wife, for her support in writing this book.

About the Author

Kaneyoshi Ashida joined the University of Detroit Mercy in 1981 as senior research professor and laboratory director of the Polymer Institute. He retired from the Institute in 1998.

He graduated from the Tokyo Institute of Technology in 1943 and received his doctorate from the same university in 1957.

He worked as director of the Urethanes Research Department of the Yokohama Research Complex, Mitsubishi Chemical Ind. Co. Ltd. Before he joined Mitsubishi Chemical Industries Ltd., his research and development was carried out at Hodogaya Chemical Industries and Nisshinbo Industries, Inc.

Dr. Ashida's research activities were in polyurethane foams for 41 years while simultaneously working on polyisocyanurate foams in parallel, for 32 years. He is the inventor of 120 patents, author of close to 80 papers, and author or coeditor of 21 books.

Dr. Ashida received the Gold Medal and Certificate of Merit from the German Plastic Industry, Plastic Foam Division in 1985 as the first pioneer of polyisocyanurate foams. He is known worldwide as the father of polyisocyanurate foams. He served as chairman of the Far East Safety Committee of the International Isocyanate Institute for six years.

Contents

chapter one

Introduction

Polymeric materials consisting of solid phase and gas phase are called plastic foams, foamed plastics, cellular plastics, or polymeric foams and are classified into two categories: thermoplastic foams and thermosetting foams.

Polyurethanes, also referred to as urethanes, are characterized by the urethane linkage: $-NH-C(=O)-O-$. The linkage is formed by the reaction of organic isocyanate groups with hydroxyl groups as shown by the model reaction in Equation 1.1, although other groups, such as ether, ester, biuret, allophanate, amide, and others may be present in the polymer molecule.

$$R-NCO + R'-OH = R-NH-C(=O)-O-R' \qquad (1.1)$$

Polyurethanes are sometimes referred to as PUR, and polyurethane foams are referred to as PUR foams.

Polyurethane and other isocyanate-based polymeric foams are prepared by the reaction of addition, condensation, and/or cyclotrimerization. The literature regarding isocyanate reactions and resulting foams is listed following Table 1.1. It covers all kinds of polyisocyanate-based foams that appear in the literature.

The history of technological developments in isocyanate-based foams is described in Chapter 2, which is an overview of about 60 years of history. Chapter 3, "Fundamentals," covers isocyanate chemistry, raw materials, manufacturing, formulations, analyses, and testing. The information provided in this chapter is fundamental to every chapter. Chapter 4, "Polyurethane Foams," is the most highlighted chapter because the polyurethane foam industry is the biggest segment of the polyisocyanate-based foam industry. This chapter and the following chapter include preparation, processing, and applications. Chapter 5 describes polyisocyanurate foams, which are growing rapidly in importance worldwide to meet stricter fire safety regulations. Urethane-modified foams are representative of the different polyisocyanurate foams. Other types of modified foams using higher temperature-resistant linkages than urethane linkage, such as imide and carbodiimide linkages, are also discussed.

Table 1.1 Classification of Isocyanate-Based Foams

Foam	Reaction	Foam Property
Polyurethane	Polyaddition	Flexible and rigid
Polyisocyanurate	Polycyclotrimerization	Rigid
Polyamide	Polycondensation	Flexible and rigid
Polyimide	Polycondensation	Semi-rigid and rigid
Polyurea	Polyaddition	Flexible and rigid
Polycarbodiimide	Polycondensation	Semi-rigid
Polyoxazolidone	Ring-opening polyaddition	Rigid and semi-rigid

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chapter two

Historical Developments of Polyurethane and Polyisocyanurate Foams

2.1 Introduction

The debut of Nylon 66, invented by W. Carothers of E.I. DuPont de Nemours & Co. in the mid-1930s, was a big stimulus to chemists for pioneering synthetic polymers. Since then, many exploratory studies in polymer synthesis have been carried out worldwide. For example, polyurethanes were first investigated by Otto Bayer and his collaborators at I.G. Farbenindustrie A.G. in Germany [1] and independently by T. Hoshino and Y. Iwakura of the Tokyo Institute of Technology in Japan [2], as well as a research group at E.I. DuPont de Nemours Co. in the United States [3].

Similarly, polyureas were synthesized by the reaction of diisocyanate with aliphatic diamines by the above-mentioned three research groups.

2.2 Isocyanate-Based Foams

The first invention of isocyanate-based polymeric foams was a polyamide foam, not a polyurethane foam. The polyamide foam was prepared by the two-step process in which the first step was preparation of carboxyl-terminated polyester-oligomer and the second step was a foaming reaction of the oligomer with a diisocyanate, for example, toluene diisocyanate (TDI). This method was invented by Hoechtlen and Dorste in 1941 [4]. Model reactions are shown in Equations 2.1 and 2.2.

Carboxyl-terminated polyester oligomer:

$$n\mathrm{HO{-}R{-}OH} + (n+1)\mathrm{HOOC{-}R'{-}COOH} \longrightarrow \mathrm{HOOC{-}(polyester\ oligomer)_n{-}COOH} \qquad (2.1)$$

Foaming Reaction:

$$\begin{gathered} n\mathrm{HOOC}-(\text{polyester oligomer})_n-\mathrm{COOH} + n\ \mathrm{OCN}-\mathrm{R''}-\mathrm{NCO} \longrightarrow \\ (-\text{polyester-oligomer}-\mathrm{CONH}-\mathrm{R''}-\mathrm{NHCO}-)_n + 2n\ \mathrm{CO_2} \end{gathered} \tag{2.2}$$

2.3 Polyurethane (PUR) Foams

The first patent of a flexible polyurethane foam preparation was given to Zaunbrecher and Barth in 1942 [5]. The one-step process is composed of simultaneous reactions of polyurethane formation and gas generation by admixing an organic TDI, a hydroxyl-terminated aliphatic polyester, and water in the presence of a catalyst. Polyurethane chains were formed by the reaction of isocyanate groups with hydroxyl groups. Carbon dioxide gas was formed by the reaction of diisocyanate groups with water. Model reactions of this process are shown in Equation 2.3.

One-Step Process:

$$\begin{gathered} n\mathrm{HO}-\mathrm{R}-\mathrm{OH} + n\mathrm{OCN}-\mathrm{R'}-\mathrm{NCO} \longrightarrow (-\text{polyurethane}-)_n \\ \mathrm{OCN}-\mathrm{R'}-\mathrm{NCO} + \mathrm{H_2O} \longrightarrow \mathrm{CO_2}\uparrow + (-\mathrm{R'}-\mathrm{NH}-\mathrm{CO}-\mathrm{NH}-)_n \end{gathered} \tag{2.3}$$

where R is polyester chain and R′ is isocyanate residue.

The one-step process was highly exothermic because of a primary OH-isocyanate reaction. Therefore, scorching or fire resulted in some cases, such as in foam block production. To avoid the exothermic reaction, the one-step process was switched to the two-step process as shown in Equations 2.4 and 2.5.

Two-Step Process, Step 1:

$$\begin{gathered} n\mathrm{HO}-\mathrm{R}-\mathrm{OH} + (n+1)\ \mathrm{OCN}-\mathrm{R'}-\mathrm{NCO} \longrightarrow \\ \mathrm{OCN}-[\text{polyurethane prepolymer}]_n-\mathrm{NCO} \end{gathered} \tag{2.4}$$

where R is polyester chain and R′ is isocyanate residue.

Two-Step Process, Step 2:

$$\begin{gathered} n\mathrm{H_2O} + n\mathrm{OCN}-[\text{polyurethane prepolymer}]\mathrm{n}-\mathrm{NCO} \longrightarrow \\ (-[\text{polyurethane prepolymer}]-\mathrm{NHCONH}-)_n + n\ \mathrm{CO_2}\uparrow \end{gathered} \tag{2.5}$$

An important development in polyols was the appearance of polyether polyols. Since then, polyether polyols have become major polyols in the polyurethane foam industry. In the early stage, polyether polyols were prepared by the single use of propylene oxide as monomer; accordingly, terminal groups were secondary OH groups. Therefore, the reactivity of polyether polyols was significantly slower than that of polyester polyol, and slower reactions lead to collapsed foams in one-step flexible foam preparation.

In the early years, polyether polyol-based flexible foams were prepared by the two-step process; the first step was the preparation of isocyanate-terminated urethane prepolymers, and the second step was the reaction of NCO-terminated prepolymers with water. The prepolymer process exhibited stable foam rise. Polyether-prepolymer-based foams were first proposed by Hill et al. of E.I. DuPont de Nemours in 1951 [3].

The prepolymer process was then replaced by the one-step process using 1,4-diazabicyclo [2,2,2] octane (or DABCO) [6] as a unique catalyst along with silicone surfactants. The debut of these raw materials led to considerable growth to the urethane foam industry.

DABCO accelerates the reaction of secondary OH groups with NCO groups. That is, it accelerates chain growth and carbon dioxide evolution in proper balance of the reactions. Therefore, the time-consuming preparation of prepolymers was eliminated. However, owing to the relatively high cost of DABCO, other catalyst combinations have been developed so that the combination catalyst consists of a tertiary amine and a tin catalyst.

Silicone surfactants composed of polysiloxane-polyoxyalkylene block copolymers have also been developed. These surfactants are effective in promoting foaming stability, and in the rigid foams the insulation property of resultant foams is increased.

In view of the foaming process developments, the process changes are as follows:

Polyester/polyurethane one step ⟶ Polyester/polyurethane two step
⟶ Polyether/polyurethane two step
⟶ Polyether/polyurethane one step

In addition to polypropylene ether polyols, advanced polyether polyols such as polymer polyols (or graft copolyols) and PHD polyols have been developed.

2.4 Physical Blowing Agents

The debut of the physical blowing agent CFC-11 (chlorofluorocarbon-11) opened a new era of urethane and related foams. This blowing agent invented by Frost of General Tire Corp. [7] would have been an ideal blowing agent if not for environmental problems such as ozone depletion potential (ODP). The CFC-based ODP theory was proposed by Molina and Rowland, (Nobel Prize winners in Chemistry in 1995) [8].

The advantages of CFC -11 as a physical blowing agent include noncombustibility, appropriate boiling point, good compatibility with urethane ingredients, and nontoxicity. However, owing to the ODP problem, the production and the use of CFCs were banned by the Montreal Protocol in 1987 [9]. Now, CFCs and hydrochlorofluorocarbons (HCFCs) have been completely phased out.

2.5 Third Generation Blowing Agents

The third generation, blowing agents are being investigated extensively. These blowing agents include C_5-hydrocarbons [10], halogen-free azeotropes [11, 12], liquid carbon dioxide, and water.

In addition, global warming potential (GWP) has become a serious problem. The problem initally discussed at the United Nations Framework Convention on Climate Change (UN/FCCC). The Conference of Parties, Third Section (COP 3) was held in Kyoto, Japan, in December 1997. The Kyoto Protocol will definitely regulate the use of blowing agents for foams in the near future.

Other environmental issues, for example, volatile organic compounds (VOCs) and acid rain may also result in regulation of the use of blowing agents.

Because of the significant changes in environmental regulations mentioned above, the isocyanate-based foam industry is facing a turning point. Many raw materials have to be modified to meet new blowing agent standards. Many revised formulation studies are being requested.

2.6 Fire Hazards

Urethane foams, both flexible and rigid, have been reported to create serious fire hazards in production and applications. Rigid urethane foams used as insulants for the iron frame of the 100-story John Hancock Building in Chicago were completely destroyed by fire due to a welding torch in 1967. Owing to this fire hazard, the U.S. government started a research group to provide data for fire protection.

Another example of a serious flexible urethane foam fire was a department store in Manchester, England, in the mid-1970s. The fire resulted in the loss of several lives. The International Isocyanate Institute and the governments of the United Kingdom, Germany, France, Italy, the United States, and Japan performed considerable work in the fire safety of urethane foams in the 1970s.

2.7 Polyisocyanurate (PIR) Foams

Polyisocyanurate foams of specific types are highly flame-retardant and heat-resistant [13] and can meet the increasing requirements of building codes. However, unmodified polyisocyanurate foams are extraordinary friable and therefore cannot be used for practical applications. Polyisocyanurate foams modified by urethane-linkages (trade name: Airlite Foam SNB) were commercialized in 1996 by Nisshinbo Inc. of Tokyo, Japan, using the Ashida patent [14]. The foam is remarkably flame-retardant and stable at high temperatures and is low in friability, so the foam has been used for highly flame retardant applications such as petrochemical plant insulation in Japan in 1996.

Independently, Haggis of I.C.I. in England also studied modified isocyanurate foams and developed a foam that was commercialized with the trade name Hexafoam in 1968 [15]. Similar foams were then commercialized in the United States by the Upjohn Co. in 1969 with the trade name Kode 25 and by Celotex Corp. with the trade name Thermax. Since then, urethane-modified isocyanurate foams have been employed worldwide in the building industry. In recent years, highly flame-retardant isocyanurate foams modified by thermally stable linkages such as amide, imide, and carbodiimide linkages have been reported [16–19]. These foams exhibit higher thermal stability and flame retardation than do urethane-modified polyisocyanurate foams.

2.8 Frothing Technology

The conventional foaming profile has a phase charge including the liquid state, creamy state, foaming bubbles, and jelled foam. However, frothing technology has no creamy state, its foaming profile is equal to shaving cream. This technology was developed by Knox of DuPont in 1961 [20] , and employed two blowing agents with two boiling points (b.p.): CFC-11 (b.p.: 23.8°C) and CFC-12 (b.p.: 29.8°C). Advantages of this technology include low foaming pressure, isotropic cell structure, and better density distribution in panel foams, and is suited for pour-in-place foaming for thin and large panels [21].

2.9 Phosgene-Free, Isocyanate Production Methods

Aromatic polyisocyanates, TDI and diphenylmethane diisocyanate (MDI), are key raw materials for urethane and related foams. Their production methods are phosgenation of aromatic amines. The methods remain unchanged from the early years of the polyurethane industry. Some phosgene-free methods have been developed, but commercialization was not attempted.

2.10 Recycling

Recycling of polyurethane foams has been a serious global problem. Overviews of chemical recycling of polyurethane and polyisocyanurate foams have been reported in many papers [22, 23]. However, economical problems in foam collection and recycling still have to be solved.

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chapter three

Fundamentals

3.1 Introduction

This chapter covers isocyanate chemistry, raw materials, foam preparation technologies, and calculations. These fundamental subjects are the foundation of the following chapters, that is, polyurethane foams (Chapter 4) and polyisocyanurate foams (Chapter 5).

3.2 Isocyanate Chemistry

Detailed reviews of isocyanate chemistry by Saunders and Slocombe [1], Arnold et al. [2], and Ozaki [3] have appeared in *Chemical Reviews*. In addition, Sayigh et al. [4] and Richter and Ulrich [5] described the isocyanate chemistry in detail. Saunders and Frisch described chemistry and technology in polyurethanes [6].

Isocyanate groups have six kinds of reactions: addition, (Equations 3.1 to 3.8), condensation (Equations 3.9 to 3.11), dimerization (Equation 3.12), cyclotrimerization, (Equation 3.13), radical polymerization (Equation 3.14), and thermal dissociation of addition compounds (Equations 3.15 and 3.16).

3.2.1 Addition Reaction

$$R-NCO + H-X \longrightarrow R-NH-CO-X \tag{3.1}$$

where $H-X$ is a reactive hydrogen-containing compound.

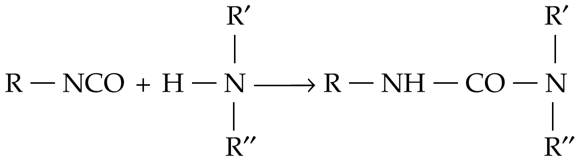
Any active hydrogen compound can react with isocyanate groups to produce addition compounds. These compounds include $N-H$ group-containing compounds, $O-H$ group-containing compounds, $S-H$-containing compounds, enolizable hydrogen-containing compounds, and so on. Polyurethanes can be prepared by the reactions of polyisocyanate having a functionality of at least two, and a polyol having a functionality of at least two. Typical active hydrogen compounds and their addition products are shown below:

Active Hydrogen Compound Addition Product

$$R-NCO + R'-OH \longrightarrow R-NH-CO-O-R' \text{ (Urethane)} \quad (3.2)$$

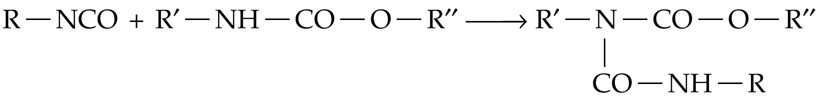
$$2R-NCO + H_2O \longrightarrow R-NH-CO-NH-R \text{ (Urea)} + CO_2\uparrow \quad (3.3)$$

$$R-NCO + R''-NH_2 \longrightarrow R-NH-CO-NH-R'' \text{ (Urea)} \quad (3.4)$$



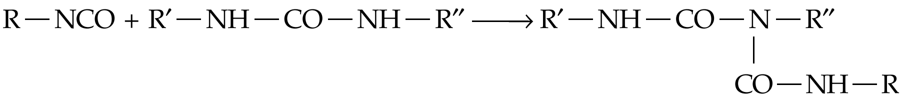
$$R-NCO + H-\overset{\displaystyle R'}{\underset{\displaystyle R''}{N}} \longrightarrow R-NH-CO-\overset{\displaystyle R'}{\underset{\displaystyle R''}{N}} \quad (3.5)$$

(Substituted Urea)



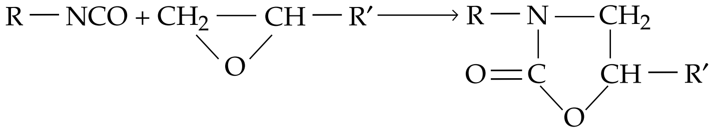
$$R-NCO + R'-NH-CO-O-R'' \longrightarrow R'-\underset{\displaystyle CO-NH-R}{N}-CO-O-R''$$

(Allophanate) (3.6)



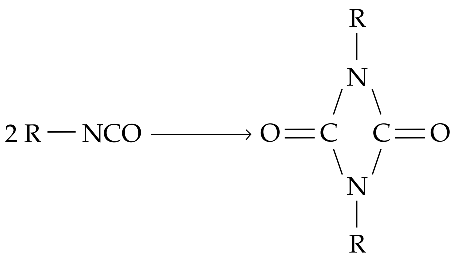
$$R-NCO + R'-NH-CO-NH-R'' \longrightarrow R'-NH-CO-\underset{\displaystyle CO-NH-R}{N}-R''$$

(Biuret) (3.7)



(2-Oxazolidone) (3.8)

3.2.2 Dimerization

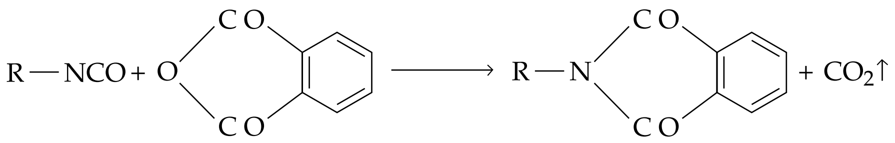


(3.9)

(Dimer)

3.2.3 Condensation Reaction

$$2\,R{-}NCO \longrightarrow R{-}N{=}C{=}N{-}R\ \text{(Carbodiimide)} + CO_2\uparrow \qquad (3.10)$$

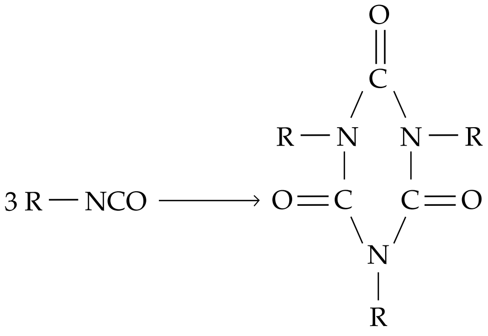


(Anhydride) (Imide)

(3.11)

$$R{-}NCO + R'''{-}COOH \longrightarrow \underset{\text{(Amide)}}{R{-}NH{-}CO{-}R'''} + CO_2\uparrow \qquad (3.12)$$

3.2.4 Cyclotrimerization Reaction

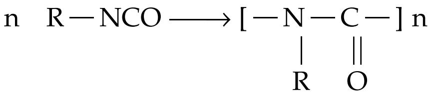


(Trimer)

(3.13)

3.2.5 Radical Polymerization

This reaction can occur only at low temperatures.



$$n\ \ R{-}NCO \longrightarrow [-\underset{\displaystyle R}{\underset{|}{N}}-\underset{\displaystyle O}{\underset{\|}{C}}-]\,n \qquad (3.14)$$

3.2.6 Thermal Dissociation of Addition Compounds

The urethane linkage thermally dissociates to produce the original compounds, that is, isocyanate and polyol. Likewise, the urea linkage dissociates to isocyanate and amine. Mukaiyama investigated this phenomenon in detail [7].

Model reactions are shown below:

$$\underset{\text{Urethane}}{R-NH-COO-R'} \longrightarrow R-NCO + R'-OH \tag{3.15}$$

$$\underset{\text{Urea}}{R-NH-CO-NH-R'} \longrightarrow R-NCO + R'-NH_2 \tag{3.16}$$

3.3 Raw Materials

The raw materials for making polyurethane and polyisocyanurate foams include polyisocyanates, polyols, blowing agents, catalysts, surfactants, and, optionally, flame retardants, antioxidants, fillers, colorants, and epoxides.

3.3.1 Polyisocyanates

Aliphatic isocyanates were first synthesized by Wurtz in 1849 [8]. Hoffmann [9] first prepared aromatic isocyanates by pyrolysis of symmetric diphenyloxamide in 1950. In 1884 Hentschel [10] reported the phosgenation method of amine and its salts. The method has become the predominant commercial method for the isocyanate production.

Model reactions are shown below:

$$R-NH_2 + COCl_2 \longrightarrow R-NH-CO-Cl + HCl \tag{3.17}$$

$$R-NH-CO-Cl \longrightarrow R-NCO + HCl \tag{3.18}$$

Aromatic polyisocyanates have been used for the preparation of isocyanate-based foams. Aliphatic isocyanates were not used because foaming reactions require high reactivity, and aliphatic polyisocyanates react slowly with OH groups. The major polyisocyanates employed are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) in oligomeric type. Their chemical structures are shown in Tables 3.1. and 3.2.

Table 3.1 Chemical Structure of TDI

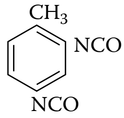
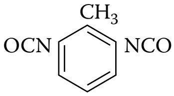
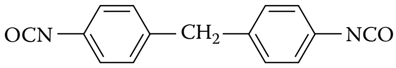
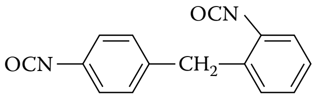
2,4-Isomer	
2,6-Isomer	

Table 3.2 Chemical Structures of MDI

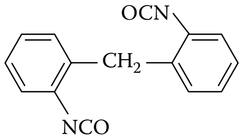


4,4-Isomer

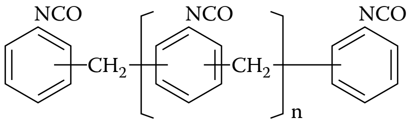
2,4-Isomer



2,2-Isomer



Polymeric MDI (oligomeric MDI), average functionality: 2,2–3,0



n : 0-3

TDI is manufactured by phosgenation of diaminotoluene, which is obtained by the reduction of nitrotoluene. Commercial products of TDI are mixtures of 2,4- and 2,6-isomers in the weight ratio of 80/20 or 65/35. TDI with a 80/20 isomer ratio is used mainly for flexible foams. Modified TDI and undistilled TDI are mostly used for rigid urethane foams and in part for semirigid foams. TDI is not suited for preparing polyisocyanurate foams.

MDI is obtained by the phosgenation of the condensation product of aniline with formaldehyde. Polymeric and oligiomeric MDI is in a liquid form. They are mainly 4,4′-isomer based and have small quantities of the 2,2′-isomer and up to 10% of the 2,4-isomer. Their average functionality is in a range of 2.3 to 3.0.

Pure MDI (or monomeric MDI) is obtained by the distillation of a crude reaction product and is used for elastomers and coatings. Polymeric MDI is used for rigid and semirigid urethane foams, as well as polyisocyanurate foams. Recently, polymeric MDI-based flexible foam technology has been developed. Tables 3.3. and 3.4 show the physical properties of TDI and MDI, respectively.

Table 3.3 Physical Properties of TDI

	Isomer Ratio (2.4 to 2.6)		
Item	**100**	**80:20**	**65:35**
Physical state at normal temperature	Liquid		
Color	Colorless to pale yellow		
Viscosity(mPas @ 25°C)	(3–6)	3–6	(3–6)
Purity	> 99.5%		
Specific gravity (g/ml)(@ 25°C)	1.21	1.21	1.21
Boiling point (°C)	251	251	251
Flash point (°C)	135	135	135
Fire point (°C)	142	142	142
Autoignition temp. (°C)	277	277	277
Freezing temp. (°C)	22	< 15	< 8
Vapor density (air = 1)	6.0	6.0	6.0
Vapor pressure (mbar @ 25°C)	0.03	0.03	0.03

Table 3.4 Physical Properties of MDI

Item	**MDI (monomeric)**	**MDI (polymeric)**
Physical state at normal temperature	Solid	Liquid
Viscosity (mPa at25°C)	—	100–800
Color	White to light yellow	Dark brown (opaque)
Specific gravity (@ 25°C)	1.22 (43°C)	1.23
Boiling point (°C)	171 (1.33 mbar) 200 (6.66.mbar) 230 decomposition	Polymerizes at ~260 with evolution of carbon dioxide
Flash point (°C)	199	Over 200
Fire point (°C)	232	Over 200
Freezing point (°C)	38	Below 10
Vapor density (air = 1)	8.5	8.5
Vapor pressure (mbar @ 25°C)	$< 10^{-5}$	$< 10^{-5}$

Phosgene-free methods of producing organic isocyanates have appeared in the literature. One method consists of reductive carbonylation of nitro compounds in the presence of a monoalcohol (monol) to produce a urethane compound, followed by the thermal decomposition of the resulting urethane compound, as shown below:

1. Reductive carbonylation

$$R-NO_2 \xrightarrow{3CO + R'-OH} \underset{\text{Urethane}}{R-NH-CO-O-R'} + 2\,CO_2 \tag{3.19}$$

2. Thermal decomposition

$$R-NH-CO-O-R' \longrightarrow R-NCO + R'-OH \tag{3.20}$$

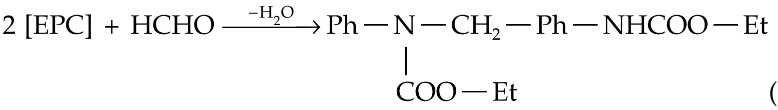
This method was developed for producing TDI by ARCO Chemical Corp. [11], Mitsubishi Chemical Corp. [12], Mitsui Toatsu Chemicals, Inc., [13] and Bayer AG [14].

Oxidative carbonylation was developed by Asahi Chemical Industry Co., Ltd. for producing MDI [15]. The process consists of three steps: (1) oxidative carbonylation, (2) condensation, and (3) thermal decomposition of the condensation product as shown below:

1. Oxidative carbonylation

$$\mathrm{Ph{-}NH_2 + CO + Et{-}OH + 1/2\,O_2 \longrightarrow \underset{[EPC]}{Ph{-}NHCOO{-}Et} + H_2O} \qquad (3.21)$$

2. Condensation
   Step 1: Condensation



$$\mathrm{2\,[EPC] + HCHO \xrightarrow{-H_2O} Ph{-}\underset{\displaystyle COO{-}Et}{\underset{|}{N}}{-}CH_2{-}Ph{-}NHCOO{-}Et} \qquad (3.22)$$

[N-benzyl Compound]

Step 2: Intermolecular Transfer Reaction

$$\mathrm{N\text{-}benzyl\ Compound + EPC \longrightarrow Et{-}OCONH{-}Ph{-}CH_2{-}Ph{-}NHCOO{-}Et + EPC} \qquad (3.23)$$

[4,4′- and 2,4- MDU]

3. Thermal decomposition

$$\mathrm{4,4'\text{-}\ and\ 2,4'\text{-}MDU \longrightarrow OCN{-}Ph{-}CH_2{-}Ph{-}NCO + 2\,Et{-}OH} \qquad (3.24)$$

[4,4′- and 2,4′- MDI]

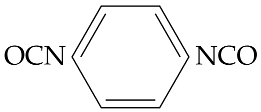
where Ph is phenyl or phenylene and Et is ethyl.

Another phosgen-free method was developed by Akzo Co. to produce p-phenylene diisocyanate [16]. Model reactions are shown below:

$$\mathrm{R{-}COOR \xrightarrow{NH_3} R{-}CO{-}NH_2 \xrightarrow{NaOCl} \underset{[I]}{R{-}CO{-}NH{-}Cl}} \qquad (3.25)$$

$$\mathrm{[I] \xrightarrow[-NaCl]{NaOH/HN(C_2H_5)_2} \underset{[II]}{R{-}NH{-}CO{-}N{-}(C_2H_5)_2}} \qquad (3.26)$$

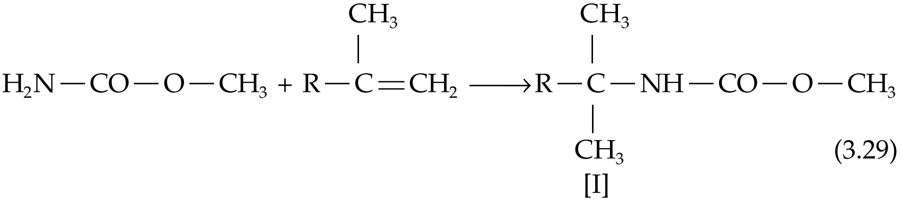
$$\mathrm{[II] \xrightarrow[-(C_2H_5)_2NH\,HCl]{HCl} \underset{[III]}{R{-}NCO}} \qquad (3.27)$$



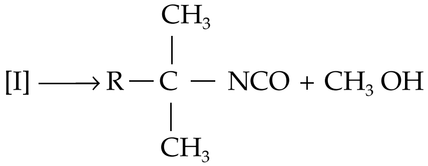
Akzo Corporation has developed a phosgen-free method of making benzene-1,4-diisocyanate (PPDI) [17], as shown below.

American Cyanamid Co. has commercialized tetramethyl xylene diisocyanate (TMXDI) in meta and para forms with a phosgen-free method [18]. The synthetic method is shown in Equations 3.28 to 3.30. The NCO groups are produced by the thermal decomposition of urethane groups. Recently, another similar method was disclosed by the same company [19]. The NCO groups are also produced by the thermal decomposition of urethane groups as shown below:

$$H_2NCONH_2 + CH_3\,OH \longrightarrow H_2NCOOCH_3 + NH_3 \qquad (3.28)$$



$$H_2N{-}CO{-}O{-}CH_3 + R{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 \longrightarrow \underset{\displaystyle [I]}{R{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}NH{-}CO{-}O{-}CH_3} \qquad (3.29)$$



$$[I] \longrightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - NCO + CH_3\,OH \qquad (3.30)$$

Modified polyisocyanates are prepared by incorporating at least one modifier linkage into monomeric polyisocyanates. Such linkages include urethane, carbodiimide, allophanate, biuret, amide, imide, isocyanurate, 2-Oxazolidone. These modifications give some advantages, for example, lower vapor pressure, increased viscosity for stabilized foaming, and controllable reactivity.

Some examples of modified polyisocyanates include isocyanate-terminated quasi-prepolymers (semi-prepolymers), urethane-modified MDI, carbodiimide-modified MDI, isocyanurate-modified TDI, and isocyanurate-modified isophorone diisocyanate.

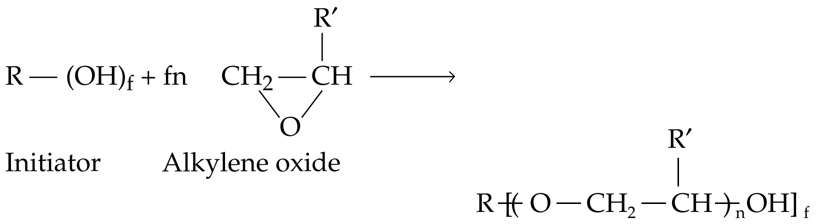
3.3.2 *Polyols*

The polyols for urethane foams are liquid oligomers or polymeric compounds with at least two hydroxyl groups. Such polyols include polyether polyols, polyester polyols, hydroxyl-terminated polyolefins, and hydroxyl-containing vegetable oils.

3.3.2.1 *Conventional Polyether Polyols*

Conventional polyether polyols are representative polyols for polyurethane foams. They are classified into four groups: polyoxyalkylene polyols, graft polyols, (polymer polyols), PHD polyols, and polytetramethylene ether glycol (PTMEG).

3.3.2.1.1 Polyoxyalkylene Polyols. Polyoxyalkylene polyols are prepared by the anionic polymerization of alkylene oxides, such as ethylene or propylene oxides as shown by Equations 3.21 to 3.23.



$$R-(OH)_f + fn\ \underset{O}{CH_2-\overset{R'}{CH}} \longrightarrow R\left[\left(O-CH_2-\overset{R'}{CH}\right)_n OH\right]_f \qquad (3.30)$$

where f is functionality of the initiator, R is the initiator, n is the number of moles of alkylene oxide molecules and R′ is H or CH_3.

3.3.2.1.1.1 Initiators for Polyether Polyols. The initiators are low molecular weight, active hydrogen compounds with 2 to 8 functionality as shown in Table 3.5.

The terminal groups of polyoxypropylene ether polyols mainly consist of secondary hydroxyl groups. The relative reactivity of primary vs. secondary hydroxyl groups with isocyanate groups is about 3:1 [20]. In order to

Table 3.5 Initiators for Polyether Polyols

Functionality 2	**Functionality 3**
Propylene glycol	Glycerol
Ethylene glycol	Trimethylolpropane
Water	1,2,6-Hexanediol
Methyldiethanolamine	Triethanolamine
	Phosphoric acid
Functionality 4	**Functionality 5**
Pentaerythritol	Diethylene triamine
Methyl glucoside	
Ethylenediamine	
Toluenediamine	
Functionality 6	**Functionality 8**
Sorbitol	Sucose

increase the reactivity of secondary hydroxyl groups with isocyanate groups, the polyoxypropylene ether polyol is capped with ethylene oxide.

The advantages of polyether polyols over polyester polyols are:

1. Various functionality polyols (2 to 8) are available.
2. Equivalent weight can be widely changed.
3. The viscosities are lower than those of polyesters.
4. Production costs are cheaper than those of aliphatic polyesters.
5. Resulting foams are hydrolysis resistant.
6. The functionality and equivalent weight of polyether polyols can be widely varied. This is a big advantage of polyether polyols over polyester polyols and therefore polyether polyols are extensively used for producing various polyurethanes such as flexible, semi-flexible, and rigid foams, elastomers, coatings, adhesives, sealants, and resins.

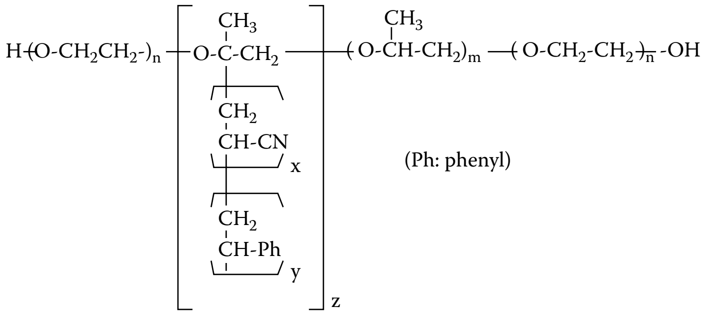
A disadvantage is lower oxidation resistance than that of polyester foams.

3.3.2.1.1.2 Catalysts for Polyether Polyols. The most widely used catalyst for polyoxyalkylation is potassium hydroxide (KOH). The KOH-catalyzed reaction is accompanied by side reactions; for example, the formation of allyl alcohol is caused by the isomerization of propylene oxide. The allyl alcohol yields vinyl-terminated polyether monols. The presence of monols results in many problems. Hence, the maximum molecular weight of conventional polyether polyols is limited to less than 5000.

Recently, a novel method to produce high-molecular-weight polyols with a trace amount of monols has been disclosed by ARCO Chemical Co. [20–22] and Asahi Glass Co. [23]. The specific catalyst employed for preparing low-monol and high-molecular polyether polyols are double metal cyanide complex catalysts [22] one example is zinc hexacyano cobaltate complex ($Zn_3[Co(CN)_6]_2 \times ZnCl_2$ y Glyme z H_2O). This catalyst was discovered in the 1960s by Herald and coworkers at the General Tire and Rubber Co. (now Gen Corp.) [24]. The catalyst can provide polyether polyols with low-monol and extra high OH-equivalent weights (i.e. 3000). The resulting polyols are used for HR foams [23], elastomers, sealants, films, and coatings.

Imidazole and alkyl imidazole have recently been found to be high-efficiency oxyalkylation catalysts [25]. An advantage of the catalyst is that it does not require any post-treatment after preparation. In contrast, the KOH catalyst needs a careful and critical neutralization process. The most promising application of this catalyst is considered to be the rigid polyol preparation, not the flexible polyol preparation.

3.3.2.1.2 Graft Polyols (Polymer Polyols). Graft polyether polyols (polymer polyols, copolymer polyols) appeared in the mid-1960s [27]. Graft polyols include acrylonitrile-grafted as well as acrylonitrile- and styrene-grafted



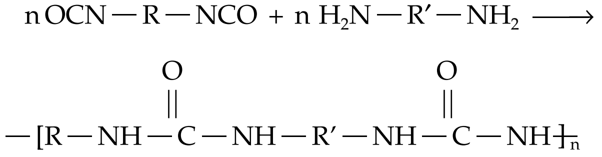
(Ph: phenyl)

Figure 3.1 Graft Polyols.

polyether polyols. The percent of grafting of the early polyether polyols was about 20 to 21%. However, polyether polyols with a higher percent of grafting, for example, about 30 to 50%, are available now as commercial products [27–32].

The chemical structure of acrylonitrile-styrene-grafted polyether polyol is shown in Figure 3.1.

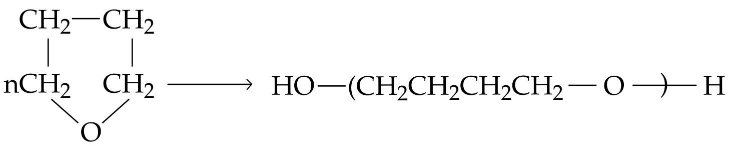
3.3.2.1.3 Polyurea dispersion Polyols. Polyurea dispersion (PUD) polyols (or polyharnstoff dispersion [PHD] polyols) were developed by Mobay Corp. [33]. PHD polyol is usually produced by reacting TDI with hydrazine-containing polyether polyols under vigorous stirring, and the products are dispersion of polyureas in polyether polyols.



$$n\,OCN-R-NCO + n\,H_2N-R'-NH_2 \longrightarrow -[R-NH-\overset{\overset{O}{\|}}{C}-NH-R'-NH-\overset{\overset{O}{\|}}{C}-NH]_n \qquad (3.31)$$

Advantages of the PHD polyol include high-load-bearing foam property. These polyols are preferably used for producing molded flexible foams, high-resilience foams with high-load-bearing properties, and cold-molded flexible foams.

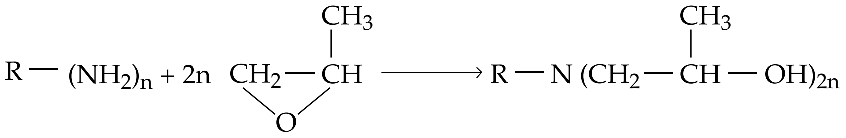
3.3.2.1.4 Polytetramethylene Ether Glycol (PTMEG). Another method of producing polyether polyols is the ring-opening polymerization of cyclic ethers such as tetrahydrofuran (THF) to produce PTMEGs or poly (oxytetramethylene) glycols, as shown below.



(3.31)

An anionic polymerization reaction is used for the polymerization of THF. PTMEG is used for producing thermoplastic polyurethanes (TPUs), elastomers, fibers, and films.

3.3.2.1.5 Amine-based Polyether Polyols. This type of polyol is prepared by the oxypropylation of amines such as ethylene diamine, aniline, and toluenediamine.



(3.32)

Amine polyols have t-amino groups, so they have better compatibility and catalytic activity to foam ingredients than neutral polyols do.

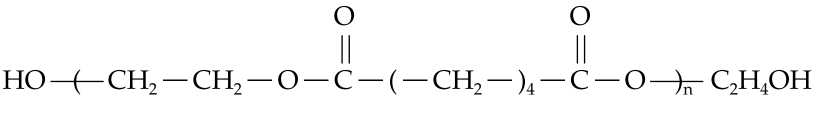
3.3.2.2 Polyester Polyols

The polyester polyols for urethane and related polymeric foams include aliphatic and aromatic polyesters.

3.3.2.2.1 Aliphatic Polyesters. Aliphatic polyesters are prepared by the polycondensation reaction of dibasic acids such as adipic acid, phthalic acid, and sebacic acid with glycols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, and 1,6-hexanediol. These polyesters have high viscosity and low functionality, for example, 2.0 to 2.1.

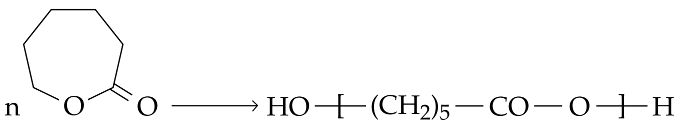
Polyethylene adipate is prepared by Equation 3.33.

$$(n+1)\ HO-C_2H_4-OH + n\ (CH_2)_4\ (COOH)_2 \longrightarrow$$



$$HO\!\left(-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(-CH_2-)_4-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)_n C_2H_4OH \qquad (3.33)$$

Aliphatic polyesters can also be prepared by the ring opening polymerization of lactones, for example, epsilon-caprolactone, as shown in Equation 3.34.



(3.34)

3.3.2.2.2 Aromatic Polyesters. Aromatic polyesters are prepared by the trans-esterification of recycled polyethylene terephthalate (PET), which includes medical films such as X-ray films and MRI films, and beverage bottles.

The reclaimed polyols are dark-colored liquids with a functionality of 2. This polyol can be used in part for rigid urethane foams and polyisocyanurate foams. Because of low compatibility of reclaimed polyester, blending it with aliphatic polyether polyols is recommended for PUR and PIR foams.

The general formula of the polyester is shown below:

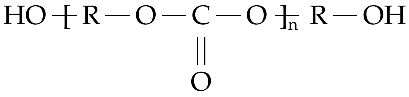
$$HOC_2H_4O \left[CO-C_6H_4-CO-O-C_2H_4-O \right]_n H$$

3.3.2.2.3 Caster Oil. Caster oil is a glycerole ester of ricinoleic acid, which contains secondary OH groups. Some attempts were made to prepare semirigid foams, but its commercialization was not reported.

3.3.2.3 Other Types of Polyols

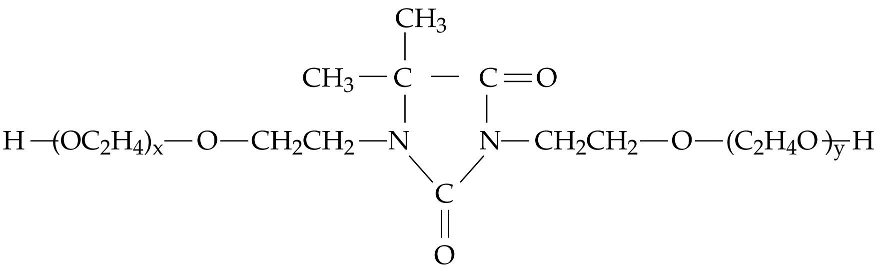
Other types of polyols include polycarbonate polyol (Duracarb, PPG Ind. Inc.), hydantoin-containing polyol (Dantocol DHE, Lonza Inc.), polyolefinic polyol (Poly bd, Atochem Co.), and its hydrogenated polyol, Polytail, (Mitsubishi Kasei Corp.). An application of polyolefinic polyols for foams has been reported [34]. The chemical structures of these polyols are shown below.

Polycarbonate polyols (Duracarb™)



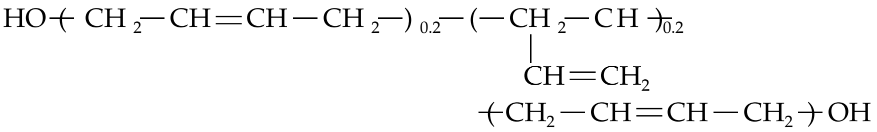
$$HO \left[R-O-\underset{\underset{O}{\|}}{C}-O \right]_n R-OH$$

Dimethylhydantoin polyols (Dantocol DHE™)



The hydantoin ring has an $-N-CO-N-CO-$ linkage that is similar to the urea linkage; and therefore the resulting foams are substantially flame-retardant. The obtained foam showed a high oxygen index, for example, 29 [35].

Polybutadiene polyols (Poly bd™)



$$HO\!-\!(CH_2\!-\!CH\!=\!CH\!-\!CH_2\!-)_{0.2}\!-\!(-CH_2\!-\!\underset{\substack{|\\ CH=CH_2}}{CH}\!-)_{0.2}\!-\!(CH_2\!-\!CH\!=\!CH\!-\!CH_2\!-)\!-\!OH$$

3.3.3 *Blowing Agents*

Gas generation is an essential part of plastic foam formation. In preparing polyurethane and polyisocyanurate foams, two kinds of gas generation methods are used: chemical gas generation and physical gas generation, as well as combinations thereof.

Chemical blowing agents are chemical compounds that react with isocyanate groups to generate carbon dioxide gas. A typical chemical blowing agent is water (Zaunbrecher's patent) [36]. Other chemical blowing agents include enolizable organic compounds and boric acid [37].

Physical blowing agents are liquids that have low boiling points and nonreactivity to isocyanate groups; they vaporize by the exotherm of foaming reaction. Physical blowing agents include various fluorine-containing compounds such as C5-hydrocarbons, azeotropes with or without halogen, and liquefied carbon dioxide.

3.3.3.1 *Chemical Blowing Agents*

The conventional gas generation reaction for flexible urethane foams is the water–isocyanate reaction [36] as shown by the following model reaction:

$$2\,R-NCO + H_2O \longrightarrow CO_2\uparrow + R-NH-CO-NH-R \quad (3.35)$$

The foaming reaction is composed of two simultaneous reactions: generation of carbon dioxide gas and formation of substituted ureas. This reaction is complicated. According to Naegeli and coworkers, the reaction mechanism consists of three routes as shown in Figure 3.2 [38]. Shkapenko and coworkers traced the mechanism in detail and confirmed that it was correct [39].

Water has been used as a chemical blowing agent since the beginning of the urethane foam industry for both flexible and rigid foams. In mid-1995, low-density urethane foams, both flexible and rigid, were blown by the co-use of water and a physical blowing agent, CFC-11. However, owing to the ban of use of CFC-11, the use of water alone as a blowing agent for foams is being developed.

The use of water alone has the following disadvantages: (a) Increased use of water results in higher reaction exotherm, which is the cause of scorching or fire. (b) System viscosity is high, so the flowability of foaming systems in the mold becomes worse. (c) In two component-rigid foam systems, mixing ratios become high, so mixing efficiency becomes worse.

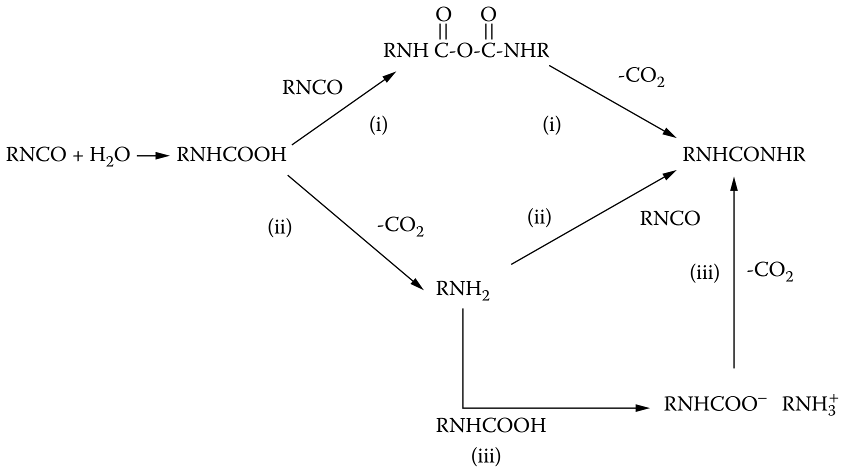


Figure 3.2 Mechanism of Isocyanate-Water Reaction, [3.99].

(d) System costs are high because using water consumes higher amounts of costly polyisocyanates, but system development efforts have overcome these disadvantages. Most flexible foams are now produced by using water as a sole blowing agent. For rigid-foam blowing agents, water-blown foams have been studied, and many papers were presented at the Polyurethane Technical/Marketing Conferences [39].

Other chemical blowing agents include enolizable organic compounds as shown in Table 3.6. The gas generation mechanism is composed of the following steps: addition of isocyanate to enol form hydroxyl groups, prototropy of hydrogen atoms, formation of phenyl carbamic acid, decomposition to aromatic amine, and formation of carbon dioxide and urea as shown in Figure 3.3 [37].

Table 3.6 Enolizable Compounds [37]

Type	Typical Compounds	Chemical Structure	Enol Form
$C=N-OH$	Nitroalkane	$R-CH_2-NO_2$	$R-CH=\overset{O}{\overset{\vert}{N}}-OH$
$C=N-OH$	Aldoxime	$R-CH_2-CH=N-OH$	$R-CH=CH-NH-OH$
$N=N-OH$	Nitrourea	$H_2N-CO-NH-NO_2$	$H_2N-CO-N=\overset{O}{\overset{\vert}{N}}-OH$
$N=C-OH$	Acid amide	$\overset{H}{\overset{\vert}{HN}}-\overset{R}{\overset{\vert}{C}}=O$	$HN=\overset{R}{\overset{\vert}{C}}-OH$
$C=C-OH$	Active methylene compounds	$R-CO-CH_2-CO-R'$	$R-CO-CH=\overset{R'}{\overset{\vert}{C}}-OH$

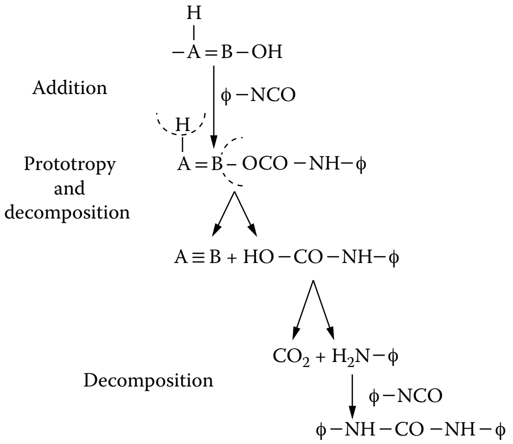


Figure 3.3 Mechanism of CO_2 Generation from Enolizable Compounds, [3.172].

Boric acid is another type of chemical blowing agent. Ashida et al. used boric acid as a blowing agent for flexible and rigid polyurethane foams [40]. A comparison study between water-blown rigid urethane foam and boric acid-blown rigid urethane foam showed the same physical properties at the same foam densities. The gas generation mechanism from boric acid is discussed in detail in Figure 3.4 [37]. A comparison between water-blown and boric acid-blown foams is shown in Figure 3.5 [37].

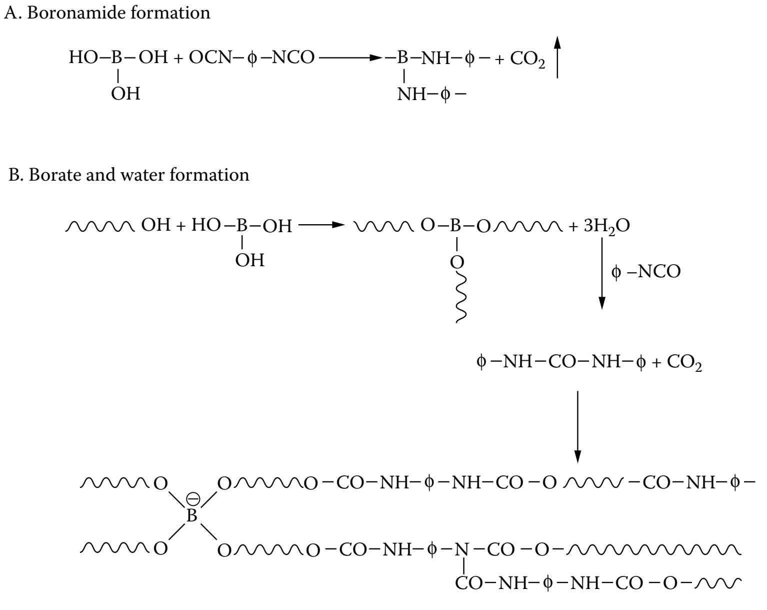


Figure 3.4 Mechanism of CO_2 Generation from Boric Acid [3.172].

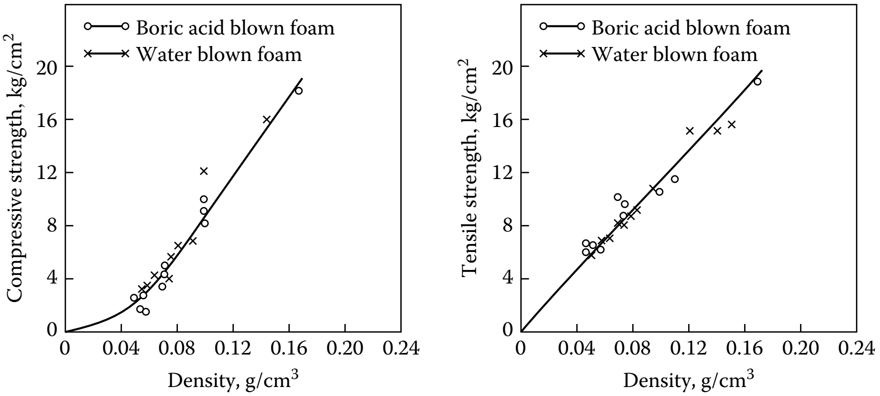


Figure 3.5 Comparison of Physical Properties Between Water Blown- and Boric Acid Blown-Foams [3.172].

3.3.3.2 Physical Blowing Agents

Physical blowing agents are inert liquids with low boiling points, and they evaporate by the exotherm of the foaming reaction. This chapter describes a variety of physical blowing agents, which include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorinated hydrocarbons (PFCs), hydrofluorocarbon ethers (HFEs), liquid carbon dioxide, C_5-hydrocarbons, halogen-containing azeotropes, halogen-free azeotropes, methylene chloride-hydrocarbon blends, and blends of zero ozone depletion potential (ODP) blowing agents.

3.3.3.2.1 Chlorofluorocarbons (CFCs). CFCs were representative physical blowing agents and were used for about 30 years in the foam industry [41]. Table 3.7 lists two kinds of CFCs in which trichloromonofluoromethane, CCl_3F (CFC-11), was the ideal physical blowing agent for both flexible and rigid foams.

The advantages included nonflammability, nontoxicity, good compatibility with foaming ingredients, low molecular weight, and moderate boiling point. It was used extensively for flexible and rigid foams including polyurethane and polyisocyanurate foams.

Table 3.7 Chlorofluorocarbons (CFCs)

Abbreviation	Composition	BoilingPoint(°C)	ODPHGWP*	GWP**
CFC-11 (R-11)	CCl_3F	23.8	1	4000
CFC-12 (R-12)	CCl_2F_2	–29.8	1	3800

* Halocarbon global warming potential (CFC–11 = 1.0)

** CO_2 = 1.0; 100-year time horizon

Table 3.8 Hydrochlorofluorocarbons (HCFCs)

Designation	Formula	Boiling point (°C)	ODP*	HGWP**	GWP***
HCFC-21	$CHCl_2F$	8.9	< 0.05	–	–
HCFC-22	$CHClOF_2$	–40.8	0.055	–	1500
HCFC-31	CH_2ClF	–9.1	0.05	–	–
HCFC-123	$CHCl_2CF_3$	27.9	0.02	0.02	–
HCFC-124	$CHClFCF_3$	–11.0	0.02	0.10	–
HCFC-132a	CH_2ClCF_3	6.1	< 0.05	–	–
HCFC-132b	$CH_2ClCClF_2$	46.8	< 0.05	–	–
HCFC-141b	CCl_2FCH_3	32.1	0.11	0.15	630
HCFC-142b	$CClF_2CH_3$	–9.8	0.06	0.36	–

* Ozone depletion potential (CFC-11 = 1.0)

** Halocarbon global warming potential (CFC-11 = 1.0)

*** Global warming potential (CO_2 = 1.0; 100-year time horizon)

In flexible foam production, CFC-11 reduced reaction exotherm and made it possible to produce large slabstocks in low densities. Furthermore, CFC-11-blown rigid foams had excellent thermal insulation properties. However, because of the ozone depletion potential of CFCs in the stratosphere, the Montreal Protocol was made in 1987 resulting in CFCs and HCFCs being phased out.

3.3.3.2.2 Hydrochlorofluorocarbons (HCFCs). An alternative blowing agent for CFCs is HCFCs, as shown in Table 3.8. These blowing agents still have ODP problems, and were phased out by 2003.

3.3.3.2.3 Hydrofluorocarbons (HFCs). HFCs are one of major candidates for the third generation of blowing agents. Table 3.9 shows representative HFC blowing agents such as HFC-245fa and HFC-365mfc. However, because of high global warming potential (GWP), the use of HFCs will be

Table 3.9 Hydrofluorocarbons (HFCs)

Abbreviation	Composition	Boiling Point (°C)	ODP*	HGWP**	GWP***
HFC-134a	CF_3CH_2F	–26.2	0	0.28	1300
HFC-152a	CHF_2CH_3	–24.7	0	0.03	—
HFC-245ca	$CHF_2CHF_2CH_2F$	25.4	0	0.12	490
HFC-245fa	$CF_3CH_2CHF_2$	15.3	0	0.24	990
HFC-245eb	CF_3CHFCH_2F	22.7	0	0.12	490
HFC-365mfc	$CF_3CH_2CF_2CH_3$	40.2	0	< 0.3	810
HFC-365mffm	$CF_3CH_2CH_2CF_3$	24.0	0	0.21	860
HFC-356	$CF_3CH_2CH_2CH_3$	24.6	0	0.03	—
HFC-227ea	CF_3CHFCF_3	30.0	0	—	—

* Ozone depletion potential (CFC-11 = 1.0)

** Halocarbon global warming potential (CFC-11 = 1.0)

*** Global warming potential, (CO_2 = 1.0; 100-year time horizon)

Tale 3.10 Perfluorocarbons (PFCs)

Designation	Formula	Molecular Weight	B.P (°C)	ODP
PF-5040	C_4F_{10}	238	–2	0
PF-5050	C_5H_{12}	288	30	0
PF-5060	C_6H_{14}	338	56	0
PF-5070	C_7H_{16}	388	80	0

restricted to some extent in the future. The high costs of HFCs also limit their applications. Many papers on HFC blowing agents have appeared in the SPI and API Polyurethane Conferences since 1994 [42].

3.3.3.2.4 Perfluorocarbons (PFCs). Some PFCs have been proposed as blowing agents [43]. However, the Environmental Protection Agency (EPA) pointed out that all PFCs have lifetimes in the stratosphere, up to 50,000 years [44]. Therefore, PFCs cannot be used as blowing agents. Table 3.10 lists PFCs.

3.3.3.2.5 Hydrofluorocarbon Ethers (HFCEs). Some HFCEs [45–47] are shown in Table 3.11. HFCEs have an advantage of better compatibility with polyols during the foaming press.

Table 3.11 Hydrofluorocarbon Ethers (HFCEs)

Designation	Formula	B.P (°C)	ODP	Reference
HFCE-245	$CF_3CH_2-O-CF_2H$	27	0	45
HFCE-356	$CF_3CHFCF_2-O-CH_3$	58	0	45
HFCE-347mcf	$CF_3CF_2CH_2-O-CF_2H$	46	0	46
HFCE-347pcf	$CF_2HCF_2-O-CH_2CF_3$	56	0	46
HFE-254pc**	$CHF_2CF_2-O-CH_3$	37	0	41
HFE-236pc**	$CHF_2CF_2-O-CHF_2$	28	0	41
HFE-347mcc**	$CF_3CF_2CF_2-O-CH_3$	34	0	41

3.3.3.2.6 Liquid CO_2. Liquefied CO_2 appeared as blowing agent in the European foam industry in the 1980s. This blowing agent has zero ODP, low GWP, and low cost. It is used in producing very low-density, flexible slabstock foams [48]. CO_2 is a gas at normal pressure and temperature, and therefore, when a CO_2-containing system is dispensed from a mixing head, the system immediately turns to froth, without the cream time. Special foaming machines and equipment have been developed (see Section 3.4.2.3.7).

3.3.3.2.7 C_5-Hydrocarbons. As an alternative blowing agent for CFC-11, cyclopentane has been used in Europe for appliance and building insulation since the early 1990s. Some papers were available from recent SPI conferences. For example, cyclopentane-blown foams [49–54] and n-pentane-blown foams [55,56] have been reported to be used for rigid urethane foam preparation.

Table 3.12 C_5-Hydrocarbons (C_5-HC_5)

Name	Structure	Boiling Point (°C)	ODP*	GWP**
Pentane	$CH_3(CH_2)_3CH_3$	35	0	11
Isopentane	$C_2H_5CH(CH_3)_2$	30	0	11
Cyclopentane	$(CH_2)_5$	50	0	11

* Ozone depletion potential

** Global warming potential (CO_2 = 1.0;100-year time horizon)

Cyclopentane-blown polyisocyanurate foams have cleared some building codes [57], and a blend of cyclopentane and butane has been proposed as a blowing agent [58]. In addition, a blend of iso- and n-pentane or iso-pentane-blown rigid urethane foams for appliances have been proposed [59]. Surfactants suited for hydrocarbon-blown foams have been evaluated [60]. Table 3.12 lists C_5-hydrocarbons.

3.3.3.2.8 Azeotropes.

3.3.3.2.8.1 Halogen-Containing Azeotropes. Dorge and others investigated halocarbon-based azeotrope blowing agents. Some examples are 2- methylbutane/1,1-dichloro-fluoromethane (HCFC-141b), [61] and CFC-11/methyl formate [62]. Barthelmy reported another type of halogen-based azeotropic mixture: HFC-365mfc/C_5 hydrocarbons (e.g., cyclopentane, isopentane) [63–65].

Advantages of azeotropic blowing agents include better compatibility with foaming ingredients and lower boiling points than those of comparable components. Table 3.13 shows halogen-containing azeotropes. These blowing agents have no ODP but have high GWP.

Table 3.13 Halogen-Containing Azeotropes

Azeotropic Mixture	Boiling Point (°C)	Flammable	ODP	Reference
HFC-365mfc/cyclopentane	32.0	Yes	0	63
HFC-365mfc/n-pentane	27.5	Yes	0	63
HFC-365mfc/iso-pentane	22.5	Yes	0	63
HCFC-14lb/iso-pentane	25.7	Yes	NA	61
CFC-11/methyl Formate	20.0	Yes	NA	62
Azeotropic fluoride ether composition		No	NA	66
CF_3CHF_2/Isobutane	—	Yes	0	67
HFC-225/chloroform	—	No	0	68
HFC-365mfc/HFC-245fa blend: 50/50	24	No	0	65
** HFC-365mfc/HFC-245fa Blend:95/5	37	No	0	65
** HFC-365mfc/HFC-134a Blend:93/7	20	No	0	65

** Zeotrope (non-azeotrope)

Table 3.14 Halogen-Free Azeotropes [70]

Azeotropic Mixture	Weight Ratio	Boiling Point (°C)
Pentane/methyl formate	47.2/52.8	21.7
Pentane/ethyl formate	70/30	32.5
Pentane/methyl acetate	78/22	34.1
Pentane/methyl ethyl ketone	32/68	33.4
Pentane/ascetone	79/21	31.9
Pentane/isoprene	26.5/72.5	33.6
Pentane/ethyl ether	32/68	33.4
Cyclopentane /methyl formate	34.0/66.0	26.0
Cyclohexane/ethyl formate	45/55	42.0
Cyclopentane/methyl acetate	62.1/37.9	43.2
Cyclopentane/acetone	64/36	41.0
Cyclohexane /2-butanone	60/40	71.8
Methyl formate/ethyl ether	56/44	28.2
Isoprene/methyl formate	50/50	22.5
Isoprene/acetone	20/80	30.5

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3.3.3.2.8.2 Halogen-Free Azeotropes. Ashida [69] has proposed halogen-free azeotropes. Examples of halogen-free azeotropes are shown in Table 3.14.

An example of a halogen-free, azeotropic blowing agents is a n-pentane/methyl formate (NPT/MFT) blend at a 47.2/52.8 weight ratio. Foams were prepared by using different molar ratios of the NPT/MFT blend, keeping the same molar amount (0.25 moles) of the blend to 100 parts by weight of the polyether polyol.

The effect of the blend ratio (NPT/MFT) on foam density is shown in Figure 3.6. Likewise, the effect of the blend ratio of cyclopentane (CPT)/MFT

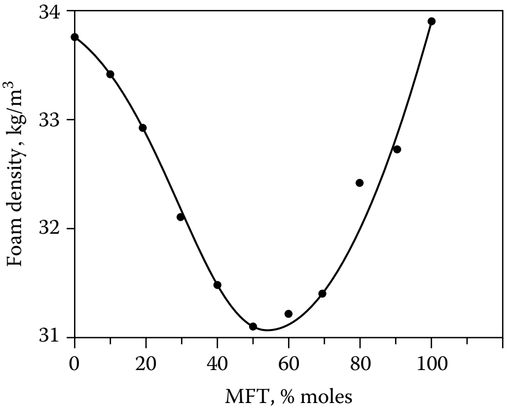


Figure 3.6 Effect of Blend Ratio (NPT/MFT) on Foam Density, [3.126].

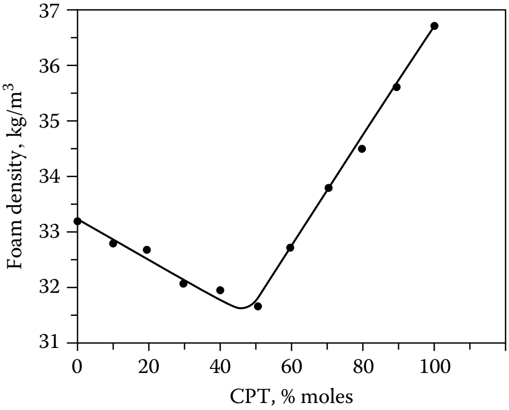


Figure 3.7 Effect of Blend Ratio (CPT/MFT) on Foam Density, [3.126].

on foam density is shown in Figure 3.7. The effect of the blend ratio of NPT/MFT on thermal conductivity is shown in Figure 3.8, and the effect of the blend ratio of CPT/MFT on thermal conductivity is shown in Figure 3.9. From these figures, it is interesting to note that azeotrope blowing agents gave the lowest foam density and the lowest thermal conductivity.

Figure 3.10 shows the relationship between the boiling point of physical blowing agents and the resulting foam densities, with 0.25 moles of blowing agent per 100 parts by weight of polyol. This study employed physical blowing agents with different boiling points. The figure shows a logarithmic straight line relationship which indicates that the lower the boiling point of blowing agent, the lower the resulting foam density. In other words, the same density foams can be obtained by using smaller amounts of azeotrope blowing agent.

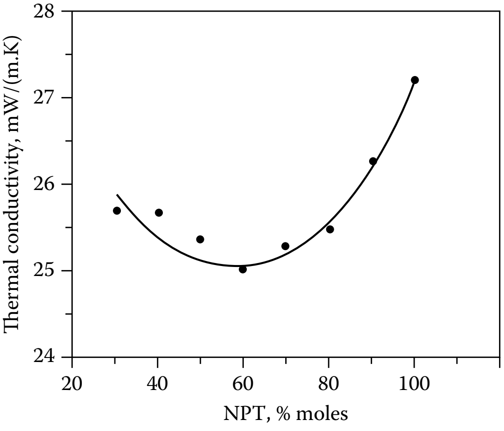


Figure 3.8 Effect of Blend Ratio (NPT/MFT) on Thermal Conductivity, [3.126].

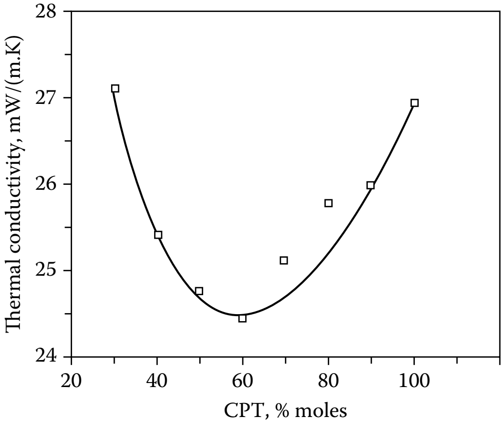


Figure 3.9 Effect of Blend Ratio (CPT/MFT) on Thermal Conductivity, [3.126].

Halogen-free azeotropes blowing agents have the following advantages over C_5-hydrocarbon blowing agents:

1. Halogen-free azeotropes give lower foam density with lower thermal conductivity than the same number of moles of comparable C_5-hydrocarbon component.
2. Halogen-free azeotropes have better compatibility with polyols than C_5-hydrocarbons and result in better foam cell structures.
3. Halogen-free azeotropes can be used in traditional CFC-11-based formulations without any formulation studies.
4. Integral skin urethane foams, microcellular urethane foams, polyisocyanurate foams, etc. are easily prepared by azeotrope blowing agents.

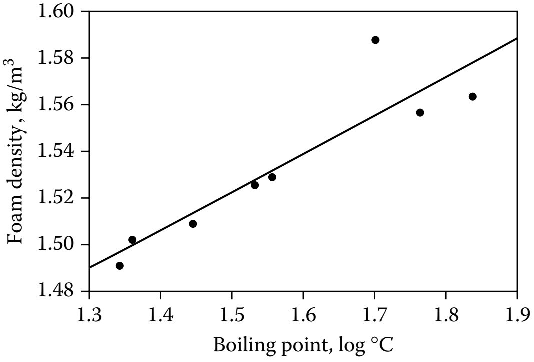


Figure 3.10 Boiling Point of Blowing Agent vs. Foam Density, [3.126].

Table 3.15 Blends of Zero-ODP Blowing Agents

Blend	Blend Ratio	Reference
HFC-365mfc/HFC-245fa	—	71
HFC-365mfc/HFC-227ea	93/7	72
	87/13	72
HFC-365-mfc/HFC-134a	93/7	73, 74
HFC-245fa/C_5—HCs	—	75, 76
HFC-245fa/water	—	77, 78
Cyclopentane/HFC-134a	—	79

Halogen free azeotrope blowing agents have the disadvantage of being flammable. However, flammable C_5-hydrocarbon blowing agents are widely used in Europe and the Far East. Consequently, one can substitute C_5-hydrocarbon blowing agents with halogen free blowing agents in these locations.

3.3.3.2.9 Blends of Zero ODP Blowing Agents. Because of the relatively high cost of HFCs, various blends of HFCs with less expensive blowing agents such as C_5 hydrocarbons and water have been reported. Examples of these blends are listed in Table 3.15.

3.3.3.2.10 Methylene Chloride–Hydrocarbon Blends. Methylene chloride was used in part as an alternative blowing agent for CFC-11 for producing slabstock flexible urethane foams, but regulation of the use of methylene chloride is under consideration in some countries because of its toxicity.

Recently, a method for solving these problems has been patented [80]. This method employs a blend of a liquid hydrocarbon and a halogenated hydrocarbon, such as, a blend of pentane and methylene chloride. This method is convenient for producing various rigid foams such as polyurethane foams, polyisocyanurate foams, and polyoxazolidone foams. Methylene chloride and pentane have nearly equal boiling points and act like a single solvent.

The use of 100% methylene chloride results in foam collapse because of its high solubility, but a blend of methylene cloride and pentane does not result in foam collapse. A blend of 80/20 and 90/10 wt.% of methylene chloride and pentane is substantially noncombustible and can be used as the blowing agent for polyisocyanurate-based foams. For rigid polyurethane foams, a blend of about 50/50 wt.% is suitable. These blends could solve the disadvantages of water-blown foams.

3.3.4 Catalysts

The catalysts for isocyanate-based polymeric foams include gelling catalysts, blowing catalysts, cyclotrimerization catalysts, oxazolidone catalysts, and carbodiimide catalysts.

For flexible urethane foam preparation, two kinds of reactions, an isocyanate– hydroxyl reaction and an isocyanate–water reaction, are employed, hence two types of catalyst are necessary.

Tin catalysts promote mainly isocyanate–hydroxyl reactions and they are considered "gelation catalysts." In contrast, tertiary amine catalysts accelerate mainly the water–isocyanate reaction, which generates CO_2. And they are considered "blowing catalysts."

Figure 3.11 [37] shows a concept of open cell formation in flexible foams. Only a good balance of gelation vs. blowing results in open-cell foams. A greater amount of blowing (or higher amine concentration) results in collapsed foams, and a greater amount of gelation (or a higher amount of tin catalyst) results in closed-cell foams, resulting in shrinkage.

Tertiary amine catalysts are listed in Tables 3.16 and 3.17. Delayed action catalysts are used to control reactivity profiles for molded foams of flexible

Table 3.16 Tertiary Amine Catalysts-A 叔胺催化剂-A

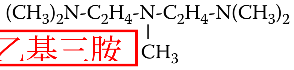
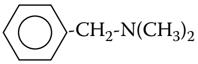
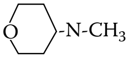
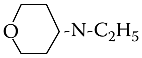
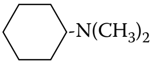
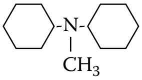
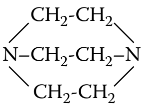
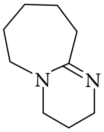
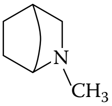
Aliphatic tertiary amines	
Bis-2-dimethylaminoethyl ether 双-2-二甲基氨基乙基醚	$(CH_3)_2N\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}N(CH_3)_2$
N,N,N′,N′-Tetramethylpropylene diamine N，N，N'，N'-四甲基丙二胺	$(CH_3)_2N\text{-}C_3H_6\text{-}N(CH_3)_2$
N,N,N′,N′-Tetramethylhexamethylene diamine N，N，N'，N'-四甲基六亚甲基二胺	$(CH_3)_2N\text{-}C_6H_{12}\text{-}N(CH_3)_2$
N,N,N′N′N″-Pentamethyldiethylene triamine N，N，N'N'N'' - 五甲基二亚乙基三胺	 $(CH_3)_2N\text{-}C_2H_4\text{-}\underset{CH_3}{\underset{\vert}{N}}\text{-}C_2H_4\text{-}N(CH_3)_2$
Aromatic and alicyclic tertiary amines	
N,N-Dimethylbenzylamine N，N-二甲基苄	
N-Methylmorpholine N-甲基吗啉	
N-Ethylmorpholine N-乙基吗啉	
N,N,-Dimethylcyclohexylamine N，N，- 二甲基环己胺	
N-Methyldicyclohexylamine N-二甲基二环己胺	

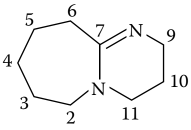
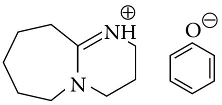
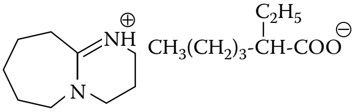
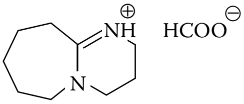
Table 3.17 Tertiary Amine Catalysts-B

Heterocyclic amines	
Triethylenediamine (1,4-diazabicyclo-2,2,2,octane), (DABCO$^{\text{TM}}$) **(82a)**	
1,8-Diazabicyclo,5,4,0,undecene-7, **(83)** 1,8-二氮杂二环，5,4,0，十一碳烯-7	
2-Methyl-2 azanorbornane, **(123a)** 2-甲基-2氮杂降冰片烷	

and rigid foams [81]. Delayed action catalysts are blocked amines, thermo-activated amines, and thermo-sensitive amines.

Blocked catalysts are various amines partially or totally neutralized with carboxylic acids. These acids can react with isocyanate groups, and the resulting primary amines react with isocyanate groups. Some of these catalysts are shown in Table 3.18.

Table 3.18 Delayed Action Catalysts

1,8-Diazabicyclo (5,4,0) undecene-7, DBU$^{\text{TM}}$ (82) 1,8-二氮杂双环（5,4,0）十一碳烯-7	
Polycat SA-1$^{\text{TM}}$ (82, 83)	
Polycat SAS-102$^{\text{TM}}$ (82, 83)	
Polycat SA-610/50$^{\text{TM}}$ (82, 83)	

Automotive interior foams include seat cushions, head restraints, sun visors, and headliners. Amine catalysts remaining in the foam structure evaporate and release an amine odor and deposit inside the windshield. This phenomenon is called fogging. (Silicone surfactants and antioxidants also cause fogging problems.) Volkswagen A.G. recently requested all foam makers not to use amine-emission catalysts [84]. The problem can be solved by using nonemission catalysts such as tertiary amines that have isocyanate reactive groups such as OH- or NH_2. The reaction products are chemically bonded in the foams and no amines emission occurs [82, 85]. Table 3.19 shows examples of reactive t-amines.

Table 3.19 Reactive Amine Catalysts 活性胺催化剂

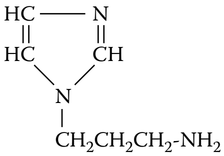
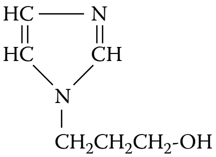
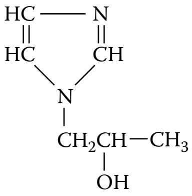
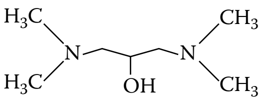
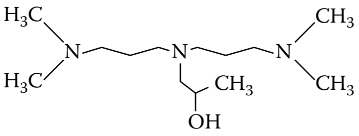
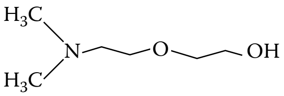
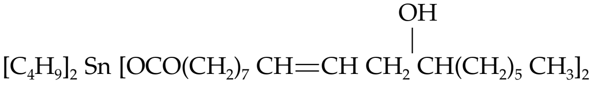
1-(3-Aminopropyl) imidazole **(84)** 1-（3-氨基丙基）咪唑	
1-(3-Hydroxypropyl) imidazole **(84)** 1-（3-羟基丙基）咪唑	
N-((2-Hydroxy)-propyl)-imidazole **(86)** N -（（2-羟基） - 丙基） - 咪唑	
Bis(dimethylamino)-2-hydroxypropanol **(86)** 双（二甲基氨基）-2-羟基丙醇	
Bis(dimethylaminopropyl)-amino-2-propanol **(86)** 双（二甲基氨基丙基） - 氨基-2-丙醇	
Dimethylaminoethyoxy-ethanol **(86)** 二甲基氨基乙氧基 - 乙醇	

Table 3.20 Tin Catalysts

Stannous 2-ethylhexanoate	$Sn\ [OCO\ CH(C_2H_5)\ (CH_2)_3CH_3]_2$
Stannous octoate	$Sn\ [OCOC_7H_{15}\ ]_2$
Dibutyltin dilaurate	$[C_4H_9]_2\ Sn\ [OCO(CH_2)_{10}CH_3]_2$
Dibutyltin 2-ethylhexanoate	$[C_4H_9]_2\ Sn\ [OCOCH(C_2H_5)(CH_2)_3]_2$
Dibutyltin diacetate	$(C_4H_9)_2Sn\ (OCOCH_3)_2$
Dioctyltin dimercaptide	$(C_8H_{17})_2\ Sn\ (SC_{12}H_{25})_2$
Dibutyltin diriicinolate [87]	 $[C_4H_9]_2\ Sn\ [OCO(CH_2)_7\ CH{=}CH\ CH_2\ \overset{OH}{\overset{\vert}{CH}}(CH_2)_5\ CH_3]_2$

Many tin catalysts appear in the literature. Some representative tin-catalysts are shown in Table 3.20. Tin-catalysts having hydroxyl groups, e.g., dibutyltin diricinolate, were disclosed by Ashida in 1962 [87]. The tin catalyst is prepared by the reaction of sodium ricinolate with dibutyltin dichloride. The OH group of the catalyst is reactive to isocyanate groups, thereby eliminating the odor and fogging problems. Ricinoleic acid employed for preparing dibutyltin diricinolate is available from castor oil.

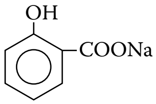
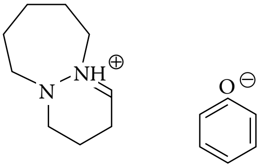
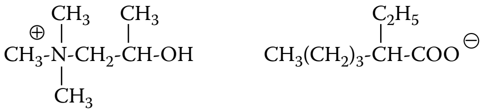
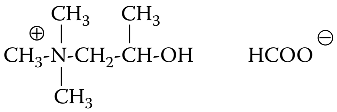
Polyisocyanurate foams are prepared by the trimerization reaction of monomeric polyisocyanates in the presence of modifiers such as polyols. Therefore, the preparation reaction consists of cyclotrimerization of polymeric isocyanates and polyurethane formation. Accordingly, co-catalyst systems consisting of a cyclotrimerization catalyst and a urethane catalyst are usually used. In some cases, use of a cyclotrimerization catalyst alone is possible.

Zhitinkina et al. [88] presented a comprehensive review of trimerization catalysts. Isocyanate cyclotrimerization catalysts are shown in Tables 3.21 to 3.25.

Table 3.21 Cyclotrimerization Catalysts-A

Potassium 2-ethylhexanoate [89]	$CH_3\ (CH_2)_3\ CH(C_2H_5)COOK$
Potassium acetate [90]	CH_3COOK
Alkali metal salt of aminocarboxylic acid [91]	$(CH_3)_2\ NCH_2COOK$
Metal alkoxide [90, 92, 93]	$NaOCH_3$, KOC_4H_9
Tertiary amines [94]	$N(C_2H_5)_3\ C_6H_5CH_2N(CH_3)_2$ $[(CH_3]_2NC_2H_4]_2\ O$
Alkali hydrosulfide [94]	$NaSH$
Alkali cyanide [95]	$NaCN$
Alkali polysulfide [96]	Na_2S_2
Titanium (IV) n-butoxide [97]	$Ti(O\ [CH_2]_3\ CH_3]_4$

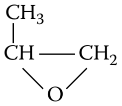
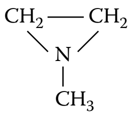
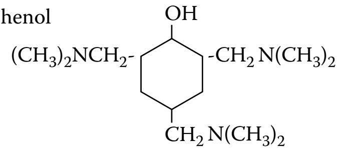
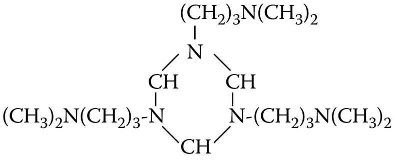
Table 3.22 Cyclotrimerization Catalysts-B

Sodium salicylate **(98)**	
Tri-n-butyl phosphine **(99)**	$(CH_3(CH_2)_3)_3P$
Group Va organometallics **(93, 99, 101)**	Bu_2SbO, $(iso\text{-}Bu)_3AsO$
Choline hydroxide **(102)**	$HOCH_2CH_2\overset{\oplus}{N}(CH_3)_3 \quad \overset{\ominus}{OH}$
Quaternary ammonium carboxylate 季铵羧酸盐	
(a) Polycat SA-1 **(83)**	
(b) Dabco TMR™ **(103, 104)**	 $\mathrm{CH_3\text{-}\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}\text{-}CH_2\text{-}\overset{CH_3}{C}H\text{-}OH} \qquad \mathrm{CH_3(CH_2)_3\text{-}\overset{C_2H_5}{C}H\text{-}COO^{\ominus}}$
(c) Dabco TMR-2™ **(103, 104)**	 $\mathrm{CH_3\text{-}\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}\text{-}CH_2\text{-}\overset{CH_3}{C}H\text{-}OH} \qquad \mathrm{HCOO^{\ominus}}$

Oxazolidone catalysts and carbodiimide catalysts are shown in Tables 3.26 and 3.27, respectively. These catalysts are used as modifiers for making thermally resistant polyisocyanurate foams [114].

Pankroatov et al. [121] reviewed the synthesis and properties of 2-oxazolidones and 2-oxazolidone-containing polymers. It is interesting to note that some isocyanate cyclotrimerization catalysts also act as catalysts for urethane, oxazolidone, and carbodiimide linkages.

Table 3.23 Cyclotrimerization Catalysts-C

Cocatalyst Combinations with Triethylene Diamine	
Butanedione **(105)**	$CH_3CO\text{-}COCH_3$
Alkylene oxide **(106)**	
N-substituted alkyleneimine **(106)**	
Aldehyde **(106)**	C_4H_9CHO
2,4,6-Tris(dimethylaminomethyl)phenol (DMP-30^{TM}) **(92)**	
N,N′,N″-Tris(dimethylaminopropyl) sym-hexahydrotriazine **(92)**	

3.3.5 *Surfactants*

Silicone surfactants appeared as commercial products in about 1958. The co-use of silicone surfactants and DABCO catalyst or a t-amine and a tin catalyst made possible one-shot production of polyether-based flexible foams. The general structure of silicone surfactants is shown in Table 3.28.

Structural parameters of silicone surfactants such as the ratios of ethyleneoxide (EO)/(EO + PO), and (EO + PO)/Si are major factors of silicone surfactants. Ashida [122] discussed some examples of the silicone surfactant structure for polyisocyanurate foams.

Burkhart, et al. [123] provides an overview of the structural parameters of silicone surfactants for different blowing agents, for example, cyclopentane, HCFC 141-b, and liquid CO_2.

Table 3.24 Cyclotrimerization Catalysts-D

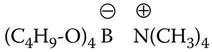
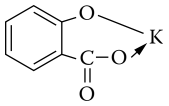
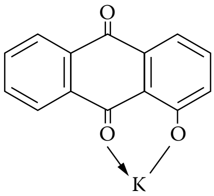
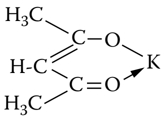
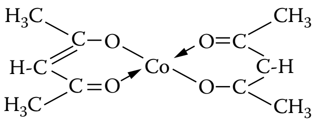
Titanates **(107)**	$Ti(OC_2H_4N(CH_3)_2)_4$
Silicates **(107)**	$Si(OC_2H_4N(CH_3)_2)_4$
Quaternary ammonium salt of tetrahedral boron-oxygen complex **(107)**	 $(C_4H_9\text{-}O)_4\overset{\ominus}{B}\ \overset{\oplus}{N}(CH_3)_4$
Salicylaldehyde sodium **(108)** 水杨醛钠	
Quinizarin potassium **(108)** 喹吖啶钾	
Potassium acetylacetonate **(108)** 乙酰丙酮钾	
Cobalt acetylacetonate **(108)** 乙酰丙酮钴	

Table 3.25 Cyclotrimerization Catalysts-E

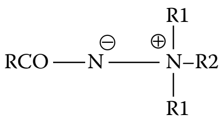
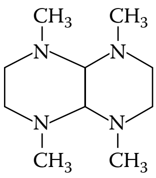
Combination Catalyst	
Tertiary amine/alkylene carbonate **(109)** 碳酸亚烷基酯	
Tertiary amine/alcohol **(110, 111)**	
Aminimides **(112)** 化酰亚胺	
Pyrazine compounds **(113)** 吡嗪化合物	

Table 3.26 Oxazolidone Catalysts

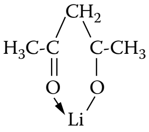
Tetraethylammonium bromide **(115)**	$\overset{\oplus}{(C_2H_5)_4N}\ \overset{\ominus}{Br}$
Alkoxides of II-a and III-a metals **(116)**	$Al(OC_2H_5)_3$
Complex of a magnesium halide and a phosphine oxide **(3.63)**	$MgCl_2\ [(C_6H_5\ P(O)]$
Alkali metal chelates **(117)**	
Lithium acetylacetonate	
Complexes of lewis acid and lewis base **(118)**	$AlCl_3 \cdot [(CH_3)_2N]_3\ P(O)$

Table 3.27 Carbodiimide Catalysts

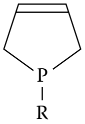
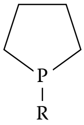
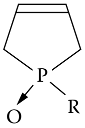
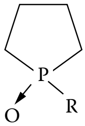
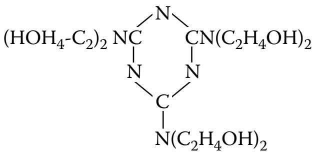
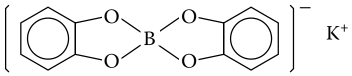
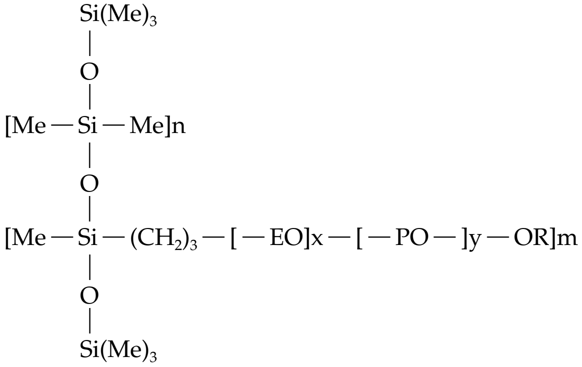
Phospholenes **(119)**	
Phospholanes **(119)**	
Phospholane oxides **(119)**	
Phospholene oxides **(119)**	
2,4,6-Tris(diethanolamino)-s-triazine **(120)**	
Potassium salt of catechol-boron complex **(107)**	

Table 3.28 Silicone Surfactants



$$\begin{array}{rcl} & \mathrm{Si(Me)_3} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{[Me-} & \mathrm{Si} & \mathrm{-Me]n} \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{[Me-} & \mathrm{Si} & \mathrm{-(CH_2)_3-[-EO]x-[-PO-]y-OR]m} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{Si(Me)_3} & \end{array}$$

Note:
Me: CH_3
EO: $-O-CH_2-CH_2-$
PO: $-O-CH_2-\underset{CH_3}{CH}-$

3.3.6 *Chain Extenders and Crosslinkers*

Low-molecular-weight diols such as ethylene glycol, diethylene glycol, and 1,3 -propylene glycol 1.4-butane diol are called chain extenders. Low-molecular-weight triols such as glycerol, trimethylol propane, tetrol (e.g., pentaerythritol), diamines (e.g., hexamethylene diamine), and aminoalcohol (e.g., diethanolamine) are called crosslinkers.

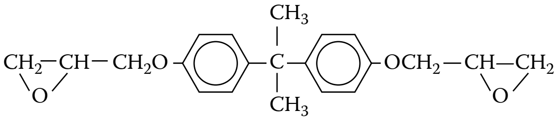
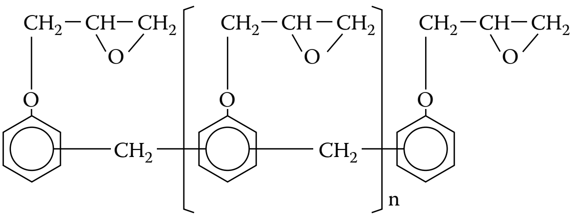
3.3.7 *Epoxides*

Epoxides are raw materials used to prepare poly-2-oxazolidone foams and oxazolidone-modified polyisocyanurate foams. In the foam preparation, fast reaction is essential, so only aromatic epoxides can be used. Aromatic polyepoxides include bisphenol A–based epoxides and novolac-based epoxides, as shown in Table 3.29.

3.3.8 *Flame Retardants*

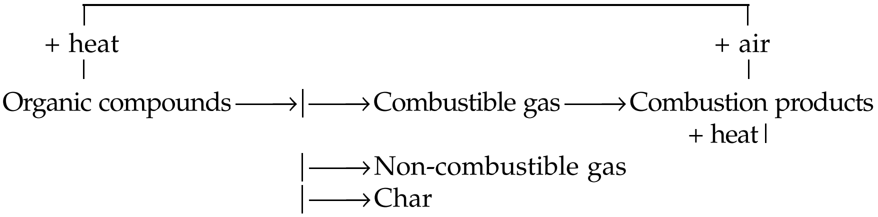
Because of serious fire hazards of flexible polyurethane foams, strict fire regulations have been enacted for the use of urethane foams in the areas of furniture, bedding, and public transportation. In addition, rigid urethane foams used as building insulants resulted in some serious fire hazards, and consequently building codes have become stricter.

Table 3.29 Aromatic Epoxy Resins

Bisphenol A–based epoxides	
Novolac-based epoxides	

Among the isocyanate-based foams, polyurethane foams, both flexible and rigid, are inherently flammable. Proper use of flame retardants can result to some extent in combustion-modified urethane foams.

The mechanism of combustion is schematically shown below:



The principle of flame retardation is to stop the combustion cycle as shown above. In view of the combustion mechanism, the principle of flame retardation can be drawn as follows:

1. By adding char-forming agents, that is, dehydration agents such as phosphates that can reduce generation of combustible gas
2. By adding radial scavengers, such as, Cl- or Br-compounds, because the combustion reaction is a radical reaction.
3. By adding fillers such as alumina trihydrate to reduce calorific value of combustion
4. By incorporating more thermally stable linkages such as isocyanurate linkages to reduce thermal decomposition (polyisocyanurate foams belong to this category)

Flame retardants are classified by different types, including, liquid, powder, reactive, nonreactive, radical scavenger, char-forming, noncalorific additives, and incorporation of more thermally stable linkages such as the isocyanurate linkage.

3.3.8.1 Example A: Liquid Flame Retardants

Halogen-containing organic phosphorus esters belong to this category. The phosphorus esters are classified into six types as shown below. Most commercial flame retardants are chlorinated phosphate esters. Excellent reviews of flame retardants are available [124,125].

1.	Phosphate:	$(RO)_3\ P(O)$
2.	Phosphonate:	$(RO)_2\ (R)\ P(O)$
3.	Phosphinate:	$(R_2)\ (OR)\ P(O)$
4.	Phosphite:	$(RO)_3\ P$
5.	Phosphine oxide:	$R_3\ P(O)$
6.	Phosphine:	$R_3\ P$

R group is a chlorine- or bromine-containing alkyl group.

Some examples of phosphates and phosphonates are tris(b-chloroprophyl) phosphate, tris(b-chloroethyl) phosphate, tris(b,b′-dichloroisopropyl) phosphate, and diethyl N,N-bis(2-hyroxyethyl) aminoethyl phosphonate.

3.3.8.2 Example B: Powder Flame Retardants

Powder flame retardants can be organic or inorganic compounds. Organic powder flame retardants include tetrabromobisphenol A bis(2-hyroxyethyl ether), melamine [129], guanidine [129] and pentabromodiphenyl oxide. Inorganic powder flame retardants include alumina trihydrate [16,126], ammonium polyphosphate [127], ammonium sulfate [128], boric acid [130], sodium borate, red phosphorus, magnesium hydroxide, calcium carbonate, and antimony oxide with PVC, clay, mica, etc.

3.8.8.3 Example C: Reactive Flame Retardants

Reactive flame retardants include halogen-containing alkylene oxide-based polyols. Examples include (a) thermolin RF-230TM (Olin Corp.) which is a reaction product of trichlorobutylene oxide and (b) phosphorous-based polyols, such as, phosphonate polyol. Hydroxyl-containing low-molecular-weight phosphates are also available in the market.

Another example is hydrophilic polyols which are used for making flexible polyurethane foams. The water kept in the foam retards heat for combustion and results in flame retarded foams [131].

3.8.8.4 Example D: Radical Scavenger Flame Retardants

This type of flame retardant is a halogen-containing liquid or solid compound described in the previous section.

3.8.8.5 Example E: Char-Forming Flame Retardants

The dehydration of various organic compounds results in much char formation and less generation of combustible gases. This type flame retardant includes various phosphorus esters, such as, phosphates and phosphonate as shown above. Sulfonates such as ammonium sulfonate also act as flame retardants of this type [128].

3.8.8.6 Example F: Noncalorific Additives

Alumina trihydrate (ATH) is a typical noncalorific additive [16, 126]. This is a compound with a high water content, and the latent heat of water retards the decomposition of organic compounds and results in reduced generation of combustible gases. Calcium carbonate, silica, and clay are also effective as flame retardant fillers.

3.8.8.7 Example G: Incorporation of Thermally Stable Linkages

Incorporation of thermally stable linkages, (e.g. polyisocyanurate linkages), into polymer structures retards generation of combustible gases and results in low combustible foams. It is important that the content of the linkage should be over a specific amount. The amount is affected by the NCO/OH equivalent ratio and the molecular weight of polyol [132]. A typical example is the incorporation of isocyanurate linkages [122]. Another example is the incorporation of thermally stable linkages such as amide, imide, and carbodiimide linkages [133].

3.3.9 Antioxidants

Decreasing foam density has long been a goal in the urethane foam industry. Increased use of water as a blowing agent has been a method to reach that goal. The use of increased water results in foam core scorching owing to high exotherm of the water–isocyanate reaction. Therefore, antioxidants are essential for producing such low density foam.

In addition, because of their ozone depleting potential, CFCs have been phased out as physical blowing agents. HCFC-141b, an alternative blowing agent, was also phased out by 2003 in the United States. As a result, a high level of water is necessary as a blowing agent in flexible urethane foam production. Increased exotherm owing to high levels of water results in scorching. In order to avoid scorching, the use of antioxidants is essential for flexible urethane foam production.

Antioxidants available for urethane foams are as follows:

1. Primary antioxidants:
    a. Hindered phenol
       BHT: (2,6-di-tert-butyl-p-cresol), 2,6-di-tert-butyl-4-butyl phenol
       2,5,7,8-tetramethyl-2(4,8,12-trimethyl tridecyl) chroman-6-ol
    b. Aromatic secondary amine
       Diphenylamine, 4,4′-di(a, a′- dimethylbenzyl) diphenylamine
2. Secondary antioxidants (hydrogen peroxide decomposer):
    a. Phosphite
    b. Thioether

BHT is a very effective antioxidant and has been widely used in the industry. However, because it is possibly a carcinogen, the industry has switched to other types of antioxidants [134]. Evaluation methods of novel antioxidants has appeared in the literature.

Reale et al. [135] reported on a microwave scorch test. Skorpenske et al. [136] evaluated antioxidants for flexible foam buns at a pilot plant. Statton [137] used the microwave scorch test to evaluate the use of hindered phenols as antioxidants. Barry et al. reported a synergy of antioxidants by a combined use of an amine and phenolic antioxidants [138]. Valentine et al. [139] discussed discoloration of foams by ultraviolet light. Perenice et al. reported another type of scorching test; that involved polyether polyols with various antioxidants that were analyzed by different scanning calorimeter (DSC) and titrated to determine the content of carbonyl and acid groups [140].

3.3.10 Colorants

Colored flexible urethane foams are required in some applications. Most colored foams are produced by adding pigment dispersions or spirit soluble dyes. These colorants are used for dispersion in polyols. Liquid polymeric colorants have also been reported [141, 142].

3.3.11 Mold Release Agents

Reaction injection molding (RIM) and reinforced RIM (RRIM) technology requires high productivity, therefore mold release agents are an important raw material to enhance productivity. Mold release agents are classified into two kinds: external mold release and internal mold release.

The compositions of external mold release agents are various blends of natural and synthetic waxes. Internal mold releases are long aliphatic carboxylates of calcium and magnesium. These release agents are used alone or in combination.

3.4 Foam Preparation Technologies

The preparation of isocyanate-based foams is a simultaneous occurrence of polymer formation and gas generation. Foams are prepared by mixing component A (isocyanate) and component B (a blend of polyol, catalyst, and surfactant) at room temperature. No heating is necessary. Examples of various isocyanate-based foam preparations will be explained in detail in the following chapters.

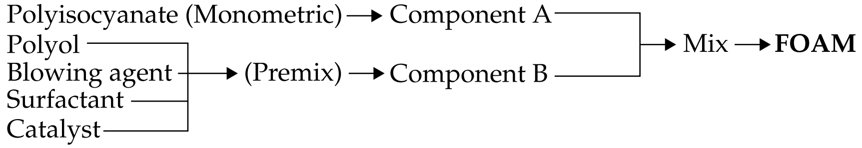
3.4.1 Foaming Systems

Foaming systems can be divided into three kinds of systems: the one-shot one-step system, the quasi-prepolymer system, and the full-prepolymer system.

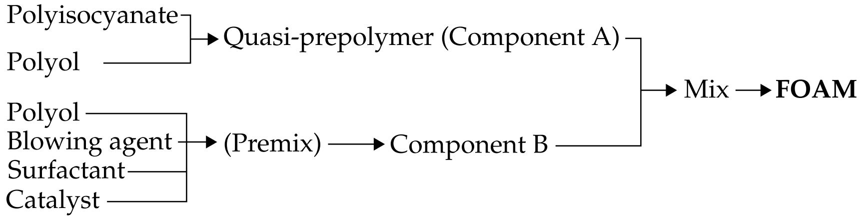
The one-step system and the quasi-prepolymer system are currently used in the urethane foam industry, in which the one-step process has become the major process for both flexible and rigid foams.

The full-prepolymer process was used only in the early years of the urethane foam industry and is now used only for preparing unconventional foam such as amide and imide foams [133]. Schematic diagrams of the systems are shown below:

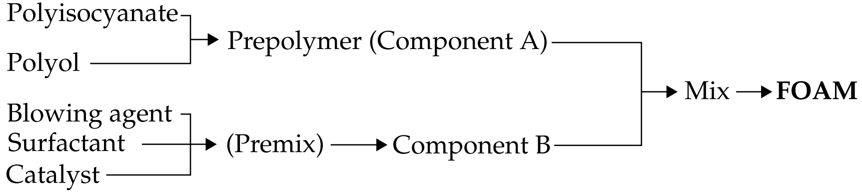
1. One-step system



2. Quasi-prepolymer system (semi-prepolymer system)



3. Full prepolymer system



These schematic diagrams show only the two-component systems. However, some modifications are possible. In slabstock flexible urethane foam production, three or four stream systems are employed for machine dispensing. For example, four-component systems consisting of polyol, a blend of blowing agent with polyol, a blend of surfactant with polyol, and a blend of catalyst with polyol are employed. These blends make accurate and easy metering and dispensing of components possible.

3.4.2 Foaming Processes

Formulation developments are usually established by the following three processing steps: cup foaming, box foaming, and machine foaming.

3.4.2.1 Cup Foaming

This foaming process is sometimes called hand mixing. It is used as a simple method of evaluating foaming systems for comparison of raw materials and resulting foam properties. Based on the optimum formulation obtained by cup foaming, scale-up foaming processes, that is, box foaming followed by machine foaming, are employed. The process requires the following:

1. Equipment and supplies:
   High speed electric mixer (one)
   Paper/plastic cups (about one liter capacity) (some)
   Top-loading balance (one)
   Micro syringes (0.1 g accuracy)
   Stopwatch
   Solvent for cleaning mixing blade (e.g., methylene chloride)
2. Safety: The fume hood should have an eye-level ventilation speed of at least 3 feet/second. Workers should be equipped with protective eyeglasses or goggles, lab coats, and latex gloves.
3. Foaming procedures: Good reproducibility of results is obtained by keeping foaming systems and the environment at a constant temperature.

An example of foaming procedures is as follows:

Step 1. Weigh 100g of a polyol or polyol blend into a 1-liter paper cup.

Step 2. Successively add surfactants, water, catalysts, and blowing agents into the polyol component with gentle stirring with a spatula. Tin catalyst, if used, is added as the last step of the addition to prevent hydrolysis of the catalyst.

Vaporization of the physical blowing agent must be avoided in the blending procedure. When the blowing agent is added and stirred, a portion of it evaporates, so its loss should be adjusted by adding more blowing agent. The addition and stirring are repeated at least three times to reach an exact amount. After the physical blowing agent is dissolved completely in the blend, the blowing agent does not evaporate within a short period of time.

Small amounts of additive such as catalysts and surfactants are conveniently added into the blend using microsyringes. When using microsyringes, the weights of the components are calculated by converting grams to milliliters. However, if an electronic top-loading balance with a 1000 to 2000g capacity and a readability of 0.01g is available, all weighing procedures can be done by using the balance without using syringes.

Step-3. Weigh the polyisocyanate component in a separate cup. The total amount is the theoretical amount plus the remaining amount in the cup after pouring. The remaining amount can be determined separately in advance.

Step-4. Thoroughly mix the polyol-containing blend for about 5 seconds. Then pour the polyisocyanate component into the polyol-containing blend and mix it for about 5 seconds.

Step-5. Allow the foaming mixture to expand in the same cup or pour it into a separate container. Measure cream, rise, and gel times.

Step-6. Clean the stirrer immediately after mixing by using methylene chloride or other solvents.

Step-7. Cure the foam block overnight at room temperature or by accelerated curing at 80 to 90°C for one hour. Cut samples for foam testing from the upper parts, not the lower parts, in the cup.

Figure 3.12 [37] shows foaming profiles. The definitions of terms used in the figure are explained below:

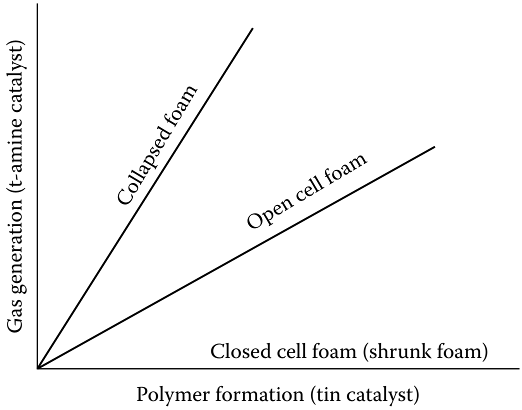


Figure 3.11 Concept of Open Cell Formation, [3.172].

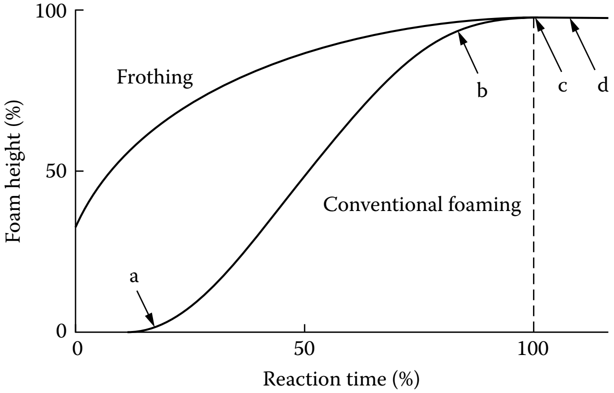


Figure 3.12. Comparison of Foam Rise Curves, [3.112].

Cream Time: (seconds) The bench type of mixing. The time interval between the final mixing of all the foam ingrediants and the time at which the clear mixture turns creamy and starts to expand (point a in Figure 3.12).

Gel Time: (seconds) The viscosity of the foaming liquid increases with reaction time due to the cross-linking reactions. To test for gel, touch the foam with a spatula and pull away; a thread will form between the spatula and the foam (point b in Figure 3.12).

Rise Time: (minutes to seconds) The time interval between the start of the final mixing and the time of complete expansion of the foaming mass. In machine mixing it is the time interval between pouring the foamable mass into the vessel and the time of complete of expansion of the foaming mass (point c in Figure 3.12).

Tack-free time: (minutes to seconds) The time interval between pouring the liquid mixture and the time when the surface of the foam does not show stickiness when touched with a spatula. This means that chemical reactions have been completed (point d in Figure 3.12). In some cases the tack-free time of rigid foams occurs before rise time.

3.4.2.2 Small-Box Foaming

Small-box foaming is better than cup foaming to obtain a sufficient amount of samples for evaluating foam properties before machine foaming. The sizes of the box range from 15 × 15 × 15 cm and 30 × 30 × 30 cm. Therefore, the necessary amount of raw materials is calculated depending upon the foam density expected. The inside of the box is lined with craft paper.

In the case of low-density foams, for example, 35 kg/m^3 density, 900 to 1000 g of foaming liquid is necessary to obtain about 30 × 30 × 30 cm^3 foams. Plastic containers of about 3 liters are used for weighing and mixing formations. The procedures are similar to those for cup foaming. Mixing is carried out with an electric drill equipped with a mixer. Immediately after mixing, the system is poured into the box and allowed to rise to obtain foams. Foam curing conditions are similar to cup foaming conditions.

3.4.2.3 Machine Foaming

A variety of machine foaming processes are available as shown below, and many machines and kinds of equipment can be chosen from the references [143,144].

3.4.2.3.1 Large-Box Foaming. This kind of foaming is a discontinuous process used to produce foam blocks in small-volume production. The sizes can be about 1 × 1 × 2 meters. The formulations obtained by small-box foaming can be used. However, because of the different exothermic conditions, formulations are slightly modified.

3.4.2.3.2 Slabstock Foaming. Slabstock foam is made by the continuous pouring of foamable liquids on a moving conveyer. A cut-off segment of the continuously produced foam loaf is called a block or bun [145].

In the case of polyether-based flexible urethane foam, a slabstock foam size can be about 1 meter high and 2 meters wide, with a foam density of 1.6 to 2.0 pound/ft^3

The cross section is rectangular with a crown-shaped top surface. The higher the crown, the less the yield of available foam. Two techniques can to used to reduce the crown. One method is to pull vertical sides of rising foam. Another technique is to compress the top of crown surface. Equipment for doing this is commercially available.

3.4.2.3.3 Pour-in-Place Foaming. This process involves pouring foaming ingredients into a closed void space to form an integral part of the foam and substrates. Commercial products that use this process include household refrigerators and deep freezers.

3.4.2.3.4 Sandwich Foaming. This process is used to produce sandwich panels with foam cores. Such panels can be produced continuously using a conveyer or discontinuously using jigs. Surfacing materials can be craft paper, aluminum sheet, copper sheet, etc.

3.4.2.3.5 Molding. This process is used for producing shaped foam products, such as seat cushions for automobiles and furniture. Foaming ingredients are poured into a mold cavity and cured in the mold. After curing, the molded foam is removed from the mold.

3.4.2.3.6 Spraying. This is a unique process used for urethane and isocyanurate foams. It creates seamless insulation layers not only on flat surfaces such as roofs, but also onto nonflat surfaces such as spherical tanks and pipes and building structures such as iron frames.

3.4.2.3.7 Frothing (Froth) Process.

3.4.2.3.7.1 Conventional Frothing Process. This process is a zero–cream time foaming process. The phenomenon is similar to that of shaving cream. This foaming process was developed by DuPont in 1960 [146]. When the foaming mixture is poured from a mixing head, the mixture immediately turns to cream and then to a solid foam through an exothermic reaction.

The most characteristic advantage of frothing over non-frothing is that it requires significantly low foaming pressure. Table 3.30 [35] and Figure 3.13 [147]

Table 3.30 Foaming Pressure of Panels [35]

Panel Thickness mm	Non-frothed Foam (MPa)	Frothed Foam(MPa)
50	0.0018	0.0048
75	0.017	0.0035
100	0.018	0.0022

Panel conditions: size: 50 × 50 × thickness (mm); temperature: 27°C; free rise foam density: 32kg/m^3

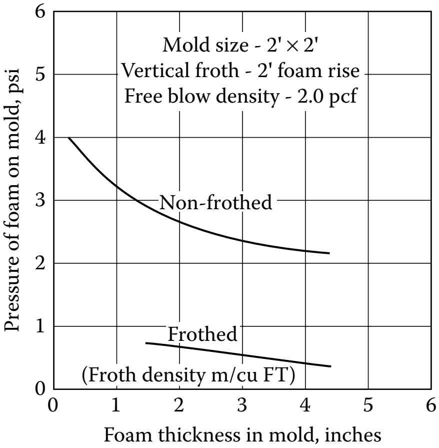


Figure 3.13 Effect of Void Thickness on Foaming Pressure, [3.112].

show this advantage of foaming pressure, which is about one-fourth to one-fifth of the foaming pressure of non-frothing processes. The cause of the low foaming pressure is lower ratios of foam expansion in the cavity than non-frothing processes. Figure 3.14 [37] shows the remarkable difference. Frothing has many other advantages including (a) better isotropicity, (b) lower skin foam density and therefore lower, overall foam density, and (c) possible thin and large cavity filling.

The isotropicity of foam properties is realized by the ratio of compressive strength parallel to foam rise to compressive strength perpendicular to foam rise. Conventional rigid foam cells are egg-shaped, so the compressive strength ratio is about 3.0/1.0. In contrast, the ratio of frothed foam is about 2.0/1.0. Figure 3.15 [147] shows these relationships. Figure 3.16 [37] shows a flow diagram of a frothing machine.

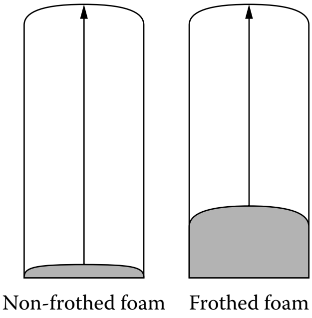


Figure 3.14 Expansion of Pour-in-Cavity Foam, [3.173].

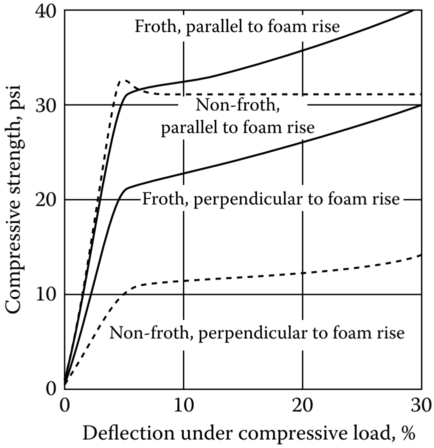


Figure 3.15 Comparison of Anisotropicity of Foams, [3.112].

Froth is formed by adding low-boiling-point liquids into a two-component urethane foam system. A turbulent flow mixer such as helix mixer is conveniently used as a mixing head. Figure 3.17 shows a schematic sketch of a helix mixer, and Figure 3.18 shows a prototype helix mixer [146]. The frothing agent developed by Du Pont was CFC-12, (CCI_2F_2) (boiling point [b.p.]:–30°C), and a mixing ratio of CFC–11/CC-22 = 3.0/1.0 was recommended [146]. However, because of the ban of the use of HFCs by the Montreal Protocol alternatives for CFC-12 include HFC-134a (b.p.: 26.2°C) and HFC-152a (b.p.: 24.7°C). Alternatives for CFC-11 include HFC-245fa (b.p.: 15.3°C) and HFC-365mfc (b.p.: 40.2°C).

The frothing process can be applied to on-site foaming (see Section 4.3.3). Figure 3.19 [148] shows an advantage of frothing-in-place; that is, horizontal foaming-in-place is possible. Therefore, the process can be applied to various

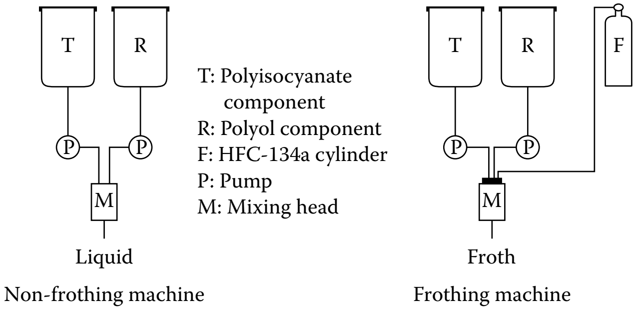


Figure 3.16 Flow Diagram of Dispensing Machine, [3.173].

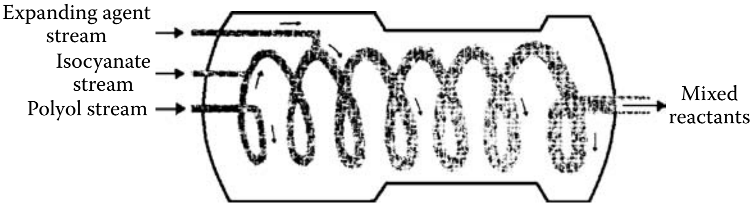
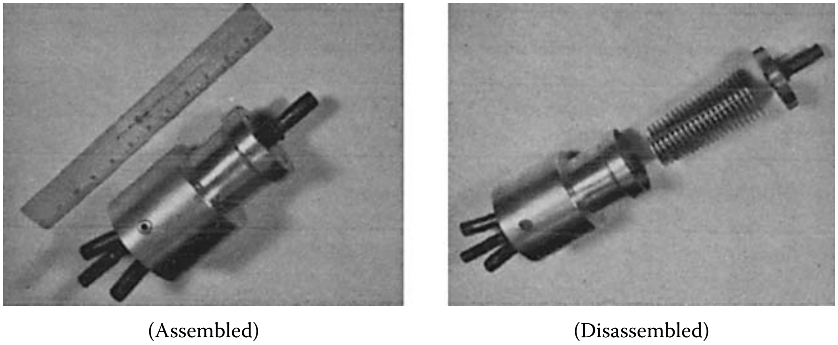


Figure 3.17 Skematic Sketch of Helix Mixer, [3.112].


(Assembled)

(Disassembled)

Figure 3.18 Prototype of Helix Mixer, [3.112].

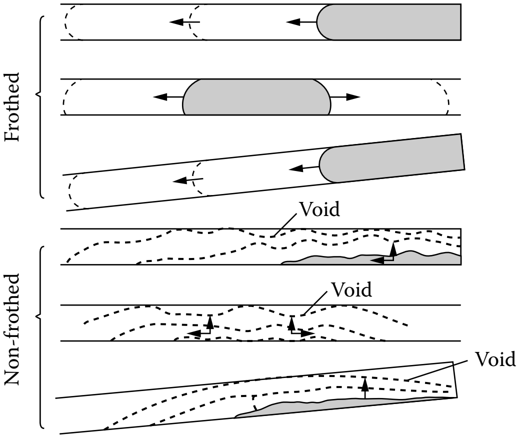


Figure 3.19 Horizontal Foaming-in-Place, [3.173].

kinds of on-site foaming, such as large tank top insulation, spherical tank insulation, refrigerated warehouse roof insulation, and etc.

3.4.2.3.7.2 Chemical Frothing Process. The addition of methyl alcohol to urethane foam systems enhances cream time and results in frothing foaming. However, the amount of added methyl alcohol should be accurate and limited because methyl alcohol is mono-functional and its molecular weight is small. A possible mechanism of the gas generation reaction seems to be dehydration of methyl alcohol by isocyanate groups, as shown below:

$$2\,CH_3OH + 2\,R{-}NCO \rightarrow R{-}NH{-}CONH{-}R + CO_2\uparrow + CH_3{-}O{-}CH_3$$

An advantage of this process is that frothing can be carried out at room temperatures and atmospheric pressure.

3.4.2.3.7.3 Thermal Frothing Process. Conventional two-component and nonfrothing systems can be used for the thermal frothing process. The systems have only liquid physical blowing agents dissolved in polyol components. When the polyol components are heated over the boiling point of the physical blowing agent, the systems can exhibit frothed foaming. The advantage of the thermal frothing process is that it can be made at atmospheric pressure and temperature.

3.4.2.3.7.4 Liquid Carbon Dioxide Process. A liquid CO_2 blowing agent has been developed in Europe to produce low-density flexible foams, (eg., 11 to 28 kg/m^3 density foams) [48]. When this foaming system is dispensed from the nozzle, the system immediately turns to froth, and no cream time is observed. One problem with this process is that it is difficult to obtain medium density foam. Furthermore, the prevention of large bubbles is difficult with this process.

Application of this process to rigid urethane foams is a future goal to be developed.

3.5 Chemical Calculations

The following equations are used for formulation studies:

$$\text{Amine Equivalent*} = \frac{(\text{Formula weight of NCO})(100)}{\%\,\text{NCO}} = \frac{(42.02)(100)}{\%\,\text{NCO}}$$

(*isocyanate equivalent, **isocyanate content, ***hydroxyl content, ****hydroxyl number)

$$\text{Isocyanate Index} = \frac{\text{Number of Amine Equivalent}}{\text{Number of OH Equivalent}} \times 100$$

$$\begin{array}{c}\text{\%NCO}\\ \text{(isocyanate content)}\end{array} = \frac{\text{(Formula weight of NCO)(100)}}{\text{Amine Equivalent}} = \frac{(42.02)(100)}{\text{Amine Equivalent}}$$

$$\begin{array}{c}\text{\%OH}\\ \text{(hydroxyl content)}\end{array} = \frac{\text{(Formula weight of OH)(100)}}{\text{OH Equivalent}} = \frac{(17.01)(100)}{\text{OH Equivalent}}$$

$$\text{OH Equivalent} = \frac{\text{(Formula weight of OH)(100)}}{\text{\% OH}} = \frac{(17.01)(100)}{\text{\%OH}}$$

$$\begin{array}{c}\text{OH Number}\\ \text{(hydroxyl number)}\end{array} = \frac{\text{(Molecular weight of KOH)(1000)}}{\text{OH Equivalent}} = \frac{(56.11)(100)}{\text{OH Equivalent}}$$

$$= \frac{\text{(\%OH)(Molecular weight of KOH)(1000)}}{\text{(Formula wt. of OH)(100)}} = \frac{\text{(\%OH)}(56.11)(1000)}{(17.01)(100)}$$

$$= (33.0)(\text{\%OH})$$

Table 3.31 American Society for Testing and Materials (ASTM) E-380-89a shows conversions from U.S. unit to SI units. SI units should be used as the primary units and U.S. units as the secondary units in official papers.

Table 3.31 Conversion Table (U.S. to SI)

	From	To	Multiply By
Density	pound/feet^3	Kilograms/meters^3	16.018
Pressure	pound/inches^2	MPa	0.006895
Drop impact	feet-pound	Joules	1.356
Notched Izod Impact	feet-pound/inches	Joules/meters	53.38
Tensile/impact	feet-pound/inches^2	Kilojoules/meters^2	2.103
Viscosity	Centipoise	MPa-s	1
Tear strength	pound/inches	KN/meters	0.175
Thermal conductivity,			
(Btu, international table)	feet/(h-feet^2 °F)	watts/(meters-K)	1.731
(Btu, thermochemical)	inches/(h-feet^2 °F)	watts/(meters-K)	1.730
(Btu, international table)	inches/(h-feet^2 °F)	watts/(meters-K)	0.1442
(Btu, thermochemical)	inches/(h-feet^2 °F)	watts/(meters-K)	0.1441

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chapter four

Polyurethane Foams

4.1 Introduction

Polyurethane foams are referred as urethane foams. The abbreviation PUR is commonly used for polyurethane. PUR foams can be classified into two categories: flexible foams and rigid foams. The PUR skeleton consists of polyol and polyisocyanate. Polyols can be considered the building blocks, and polyisocyanates can be considered the jointing agent. Therefore, polyurethane foam chemistry is considered a building block chemistry. All kinds of polyurethane foam are prepared by the proper choice of polyol and polyisocyanate in respect to chemical structure, equivalent weight, and functionality.

A classification of polyurethane foams is shown in Table 4.1 in terms of polyol components and elastic modulus [1].

In some cases semirigid foams and semiflexible foams are distinguished by the compression recovery phenomena. For example, semirigid foams, which have high stiffness, low resiliency, and complete recovery after deep compression, can be classified as flexible foams. In contrast, semirigid foams, which have incomplete recovery, are classified as rigid foams.

The essential raw materials for polyurethane foams are polyisocyanate, polyol, blowing agent, catalyst, and surfactant (see Section 3.3). In the early development, polyisocyanate-based polyurethane foams were polyester-based, but after the 1960s, polyether polyol-based foams became the most representative of both flexible and rigid foams.

An overview of the historical development of the flexible urethane foam industry is as follows:

Phase 1: A one-step process of reacting carboxyl-terminated polyester with TDI is described in a German patent [2]. The generation of the chemical blowing agent, CO_2 gas, is based on the reaction between isocyanate groups and carboxylic groups. A model reaction is shown below:

$$R-NCO + R'-COOH \longrightarrow R-NH-CO-R' + CO_2 \uparrow$$

The resultant polymer is polyamide, and not polyurethane. Also, low-boiling-point, and inert solvents were used as blowing agents

Table 4.1 Classification of Urethane Foams [1]

Polyol	Rigid Foam	Semirigid Foam	Flexible Foam
OH No.	350–560	100–200	5.6–70
OH Equivalent No.	160–100	560–280	10,000–800
Functionality	3.0–8.0	3.0–3.5	2.0–3.1
Elastic Modulus at 23°C			
MPa	> 700	700–70	< 70
lb/in^2	> 100,000	100,000–10,000	< 10,000

in the patent, which was the first patent in the isocyanate-based polymeric foams invented by I. G., Farbenindustrie GmbH. [2].

Phase 2: A two-step process consisting of (a) preparation of a toluene diisocyanate (TDI) polyester and (b) a prepolymer–water reaction [3]. The process reduces reaction speed and results in mild foaming.

Phase 3: A two-step process consisting of a polyether polyol–TDI prepolymer preparation and a prepolymer–water reaction [4].

The CO_2 gas generation is also based on the isocyanate–water reaction. The process increases the stability of the foam rise of polyether-based flexible foams.

Phase 4: A one-step foaming reaction of polyether polyol with TDI in the presence of water as a blowing agent [5]. The debut of the special catalyst (triethylene diamine or DABCO) and co-use with silicon surfactants made it possible to perform this one-step process. However, use of DABCO alone as a single catalyst was expensive. Therefore, DABCO was replaced in part by the the combined use of a tin catalyst and a tertiary amine catalyst, which resulted in cost savings. The one-step polyether process has significant advantages in both cost and processing, so it is being used extensively as the standard process for flexible and rigid foams [1, 6–10].

Phase 5: The co-use of a physical blowing agent, CFC-11 [6], and a chemical blowing agent, water. In 1963 the Frost patent [6] disclosed the use of trichloromonofluoromethane, CCl_3F, (boiling point [b.p.]: 23.8°C) as a physical blowing agent for both flexible and rigid foams. CCl_3F was considered to be the ideal blowing agent if ozone depression potential (ODP) was not considered.

Phase 6: The ban of CFCs. In 1987 the Montreal Protocol was issued and the production and use of CCl_3F were banned to eliminate the ODP, which is based on the chlorine-catalyzed theory presented by F. Shawood Rowland and Mario Molina (Nobel Prize winners in 1995). The ban had a serious impact on the urethane foam industry and resulted in the development of alternative blowing agents. The strong candidates for physical blowing agents include C_5-hydrocarbons (pentane, C_5H_{12}; b.p.: 35°C), isopentane (2-methylbutane, $C_2H_5CH(CH_3)_2$; b.p.: 30°C), cyclopentane (C_5H_{10}; b.p.: 50°C), and hydrofluorocarbons (HFCs), for example, HFC-245 fa (CF_3CH_2-CHF_2; b.p.: 15.3°C) and HFC-365mfc (CF_3CH_2-CF_2CH_3, b.p.: 40°C). Water, which is known as the oldest blowing agent [3], is now highlighted as a representative chemical blowing agent for both flexible and rigid urethane foams [1, 7–10]. Liquefied CO_2 and dry ice are also being developed as a physical blowing agents.

4.2 Flexible Polyurethane Foams

Flexible urethane foams are classified by polyol into polyether foams and polyester foams. They can also be classified based on process into slabstock foams and molded foams. They can be subclassified by means of physical properties or foaming processes as follows.

Slabstock foams include conventional polyether foam, high-resilience (HR) foam, viscoelastic foam, super-soft foam, energy-absorbing (EA) foam, semiflexible foam, and flexible polyester foam.

Molded foams are classified in two classes: hot molded foam and cold molded foam. Figure 4.1, [1] shows hysteresis curves of various flexible foams.

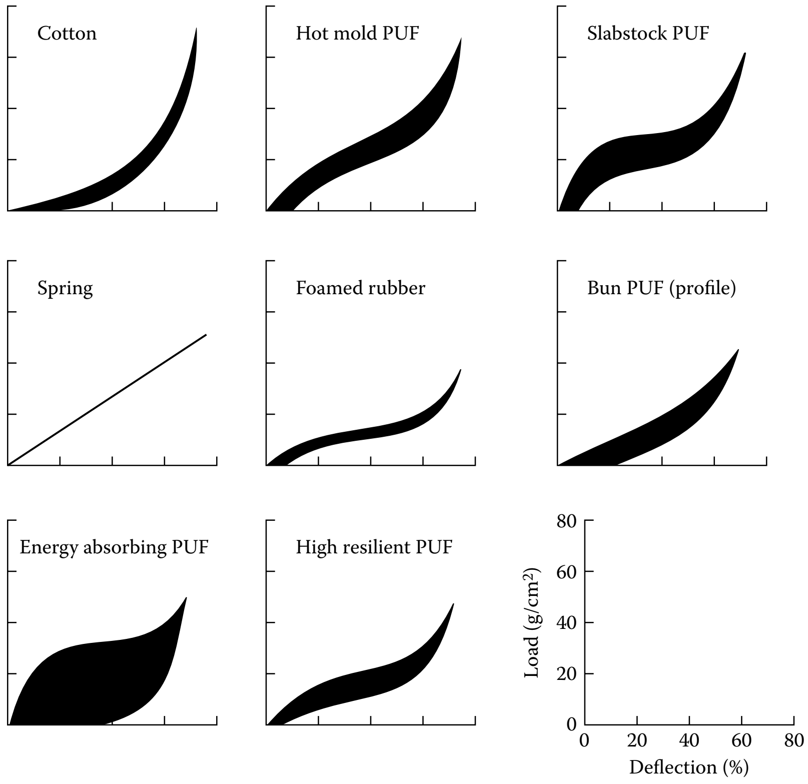


Figure 4.1 Hystersis Curves, [4.10].

Indentation load-deflection (ILD; ASTM D-3574), also called the comfort index, is the relationship of flexible foam and is expressed by the sag factor as follows:

$$\text{Sag Factor} = \frac{65\%\ \text{ILD}}{25\%\ \text{ILD}}$$

Flexible foams are also classified by sag factor as shown below.

Foam	Sag Factor
Flexible polyester foam	1.2–1.4
Flexible polyether foam	1.6–2.0
HR Foam	2.4–3.0

Figure 4.2 [1] shows the load-bearing properties expressed by compressive deformation curves of four kinds of foams: rubber foam (latex foam), slabstock urethane foam, profile-cut slabstock urethane foam, and hot-molded urethane foam. Every foam sample was 10 cm thick and their side surfaces were marked by parallel straight black lines at one inch intervals. The samples were loaded by metal disks of 1.0, 1.5, or 2.0 kg, and the load-bearing characteristics were compared by the deformation pattern of the lines.

The deformation characteristics corresponded to the hysteresis curves shown in the black-lined samples in Figure 4.2. Slabstock urethane foam showed small deformation at a 1.0-kg load, but significant deformation was seen at 2.0 kg, that is, a double weight load. The remarkable difference is illustrated in the deformation phenomenon related to the load-deflection curves in Figure 4.1. In contrast, molded foam deformation started at the center; that is, core foam and overall deformation curves were approximately proportional to the increased load. Foamed rubber and profile-cut slabstock flexible urethane foam exhibited nearly even deformation, that is, nearly linear S-shape curves in Figure 4.1.

Important cushioning properties of flexible urethane foam include compression-force deflection (CFD), indentation-force deflection (IFD), compression set, and humid aged compression set. These testing methods are described in ASTM: D 1564-86. CFD is the compression force of a foam sample when the entire sample is compressed by using a flat plate. In contrast, IFD is obtained by using an indentor.

4.2.1 Slabstock Foam

The continuous loaf of foam made by the continuous pouring of liquid foaming mixture on a moving conveyor is called slabstock foam, and a cutoff segment of the slabstock foam is called block foam or bun foam. The slabstock foam process is widely used in manufacturing of both polyether and polyester foams.

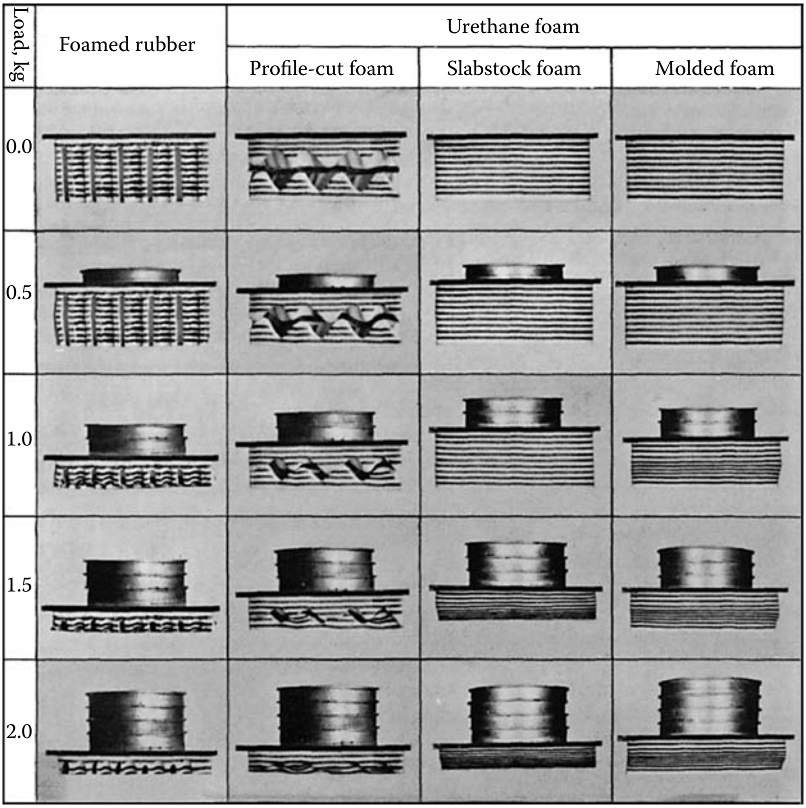


Figure 4.2 Compressive Deformation Characteristics, [4.10].

4.2.1.1 *Slabstock Foam Process*

The inclined conveyer process has been used since the beginning of the urethane foam industry. Figure 4.3 [1] shows a scheme of a continuous production line of slabstock foam.

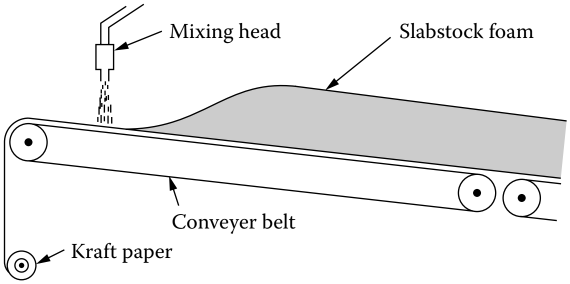


Figure 4.3 Slabstock Foam Production Line, [4.10].

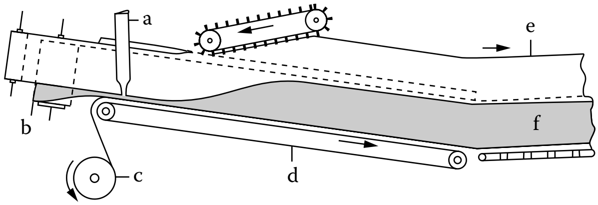


Figure 4.4 Draka-Petzetakis Process, [4.7].

The cross section of slabstock foams produced by the inclined conveyer process is not exactly rectangular and has crown shape. A crown-shaped cross section of foam bun results in a lower yield of fabricated foams. Accordingly, some improved processes to obtain rectangular cross sections have been proposed. Examples of these processes include the Draka-Petzetakis process shown in Figure 4.4 [11]. The Maxfoam process is shown in Figure 4.5 [11], and the Hennecke-Planiblock process is shown in Figure 4.6 [11]. A vertical continuous process, the Verifoam process, proposed by Hyman International Limited is shown in Figure 4.7 [12]. An advantage of the Varifoam process is that it reduces plant space by 15%.

Regarding the foaming systems for slabstock foam production, a one-step process (see Section 3.4.1) is widely used. All ingredients are pumped into the mixing head through several streams and are poured from the mixing head onto the moving conveyer. From the standpoint of viscosity and metering accuracy, some ingredients are preblended. These blends include a blend of water and amine catalyst, a blend of tin catalyst and polyol, and a blend of physical blowing agent and polyol.

The reaction temperatures in core foam usually reach about 160 to 170°C. The exothermic heat is mainly a function of the water–isocyanate reaction. The reaction temperatures are affected by the isocyanate index, water level, and catalyst concentration. When the core temperature reaches about

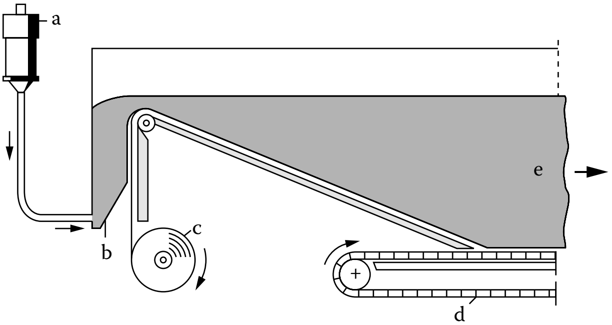


Figure 4.5 Maxifoam Process, [4.7].

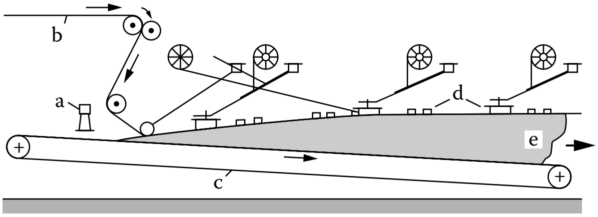


Figure 4.6 Henecke-Planibloc Process, [4.7].

190°C, discoloration or spontaneous fire may result. A stoichiometrically higher NCO/OH mixing ratio, such as unusually high isocyanate indices caused by pump-metering error, could result in spontaneous fire. Early in the flexible foam industry, some slabstock foam manufacturers experienced fires.

4.2.1.2 Polyether Slabstock Foam

From the beginning of the polyether foam industry, 3000 mol wt, tri-functional polyether polyols were used as a polyol component, and TDI (80/20 isomer ratio) was used as a polyisocyanate component. In 1980 the U.S. National Bureau of Standards (NBS) also selected a 3000 to 3500 mol wt, glycerine-based polyether polyol as the standard polyether polyol for round-robin tests [12]. Table 4.2 shows an example of conventional slabstock foam formulation and the physical properties of the resulting foam.

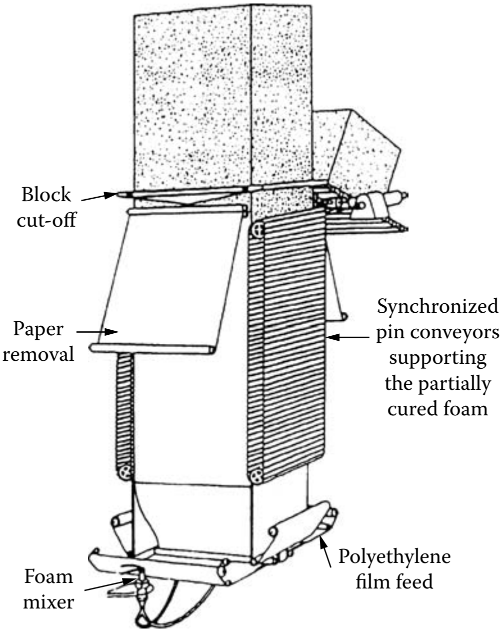


Figure 4.7 Verifoam Process, [4.103].

Table 4.2 Flexible Polyurethane Foam PRC-# GM-21 [12]

Formulation		**Weight Percent**
Polyol-Glycerine-based poly(oxypropylene polyoxyethylene) polyol, 3500 mol. wt.		68.1
Isocyanate-TDI-80/20		23.5
Blowing agent-CO_2 produced by isocyanate reaction with water		1.7
Auxiliary blowing agent fluorocarbon		5.5
Catalyst-organotin salt		0.2
Catalyst-tertiary amines		0.3
Surfactant-silicone copolymer		0.7
Physical Properties	**U.S. Unit**	**SI Unit**
Density, pounds/cubic feet (kg/m^3)	1.80	29.0
ILD		
25 % R, pounds/50 inches^2 (N/323 cm^2)	27.0	120.0
65 % R, pounds/50 inches^2 (n/323 cm^2)	53.0	236.0
Sag factor	1.96	1.96
Tensile strength, pounds/inches^2 (N/m)	12.0	83.0
Elongation, %	200.0	200.0
Tear strength, pounds/inches (N/m)	1.6	280.0
Compression set, %	7.5	7.5
Rebound, %	50.0	50.0

In the past decades, the chemical blowing agent employed was the co-use of water and CFC-11. Because of the ban of CFCs and HCFCs, alternative physical blowing agents have been developed, which include HFCs (HFC-245fa, HFC-365mfc, etc.) and blends thereof. However, owing to their high costs, flexible slabstock foams are currently blown with the water as the only blowing agent. The maximum amount of water to be used is about 4.6 to 4.8 parts per 100 parts of polyether polyol. Higher water levels than this may result in foam scorching or fire. Therefore, the lower limit of foam density for production is in the range of 21 to 22 kg/m^3. The co-use of physical blowing agents, for example, HFCs and methylene chloride, can result in foams with densities less than 20 kg/m^3. The densities of commercial slabstock foam can be varied in the range of 10 to 30 kg/m^3 (0.63 to 1.9 pcf). Liquid carbon dioxide-blown polyurethane foams are being developed.

Foam scorching is another problem of flexible urethane foam. The causes of scorching include high water level, high isocyanate index, low-acidity isocyanates, flame retardants, methylene chloride blowing agents, high humidity, low air flow cells, foam block size, and the ethylene oxide content of polyether polyol. Antioxidants, therefore, play an important role.

Antioxidants are classified into two groups: primary and secondary antioxidants, as shown in Table 4.3. [13]. A radical scavenger type of antioxidant,

Table 4.3 Examples of Antioxidants [17]

Primary Antioxidants
Hindered phenol
- 2,6 -Di-tert-butyl-4-methytphenol (BHT)
- 2, 6-Di-tert-butyl-4-sec-butylphenol, [Vanox^R PC]
- Aromatic sec-amine

Diphenylamine
- 4,4′-Di α, α–dimethylbenzyl-diphenylamine

Secondary Antioxidants
- Phosphine
- Thioether

BHT (2,6 Di-tert-butyl-4-methylphenol), is recognized to be an excellent antioxidant, but it is carcinogenic [14], hence noncarcinogenic antioxidants are being investigated [15–18]. Moy et al. [19] proposed a scorching reduction by means of bun cooling. Mechanisms of antioxidation are shown in Figure 4.8.

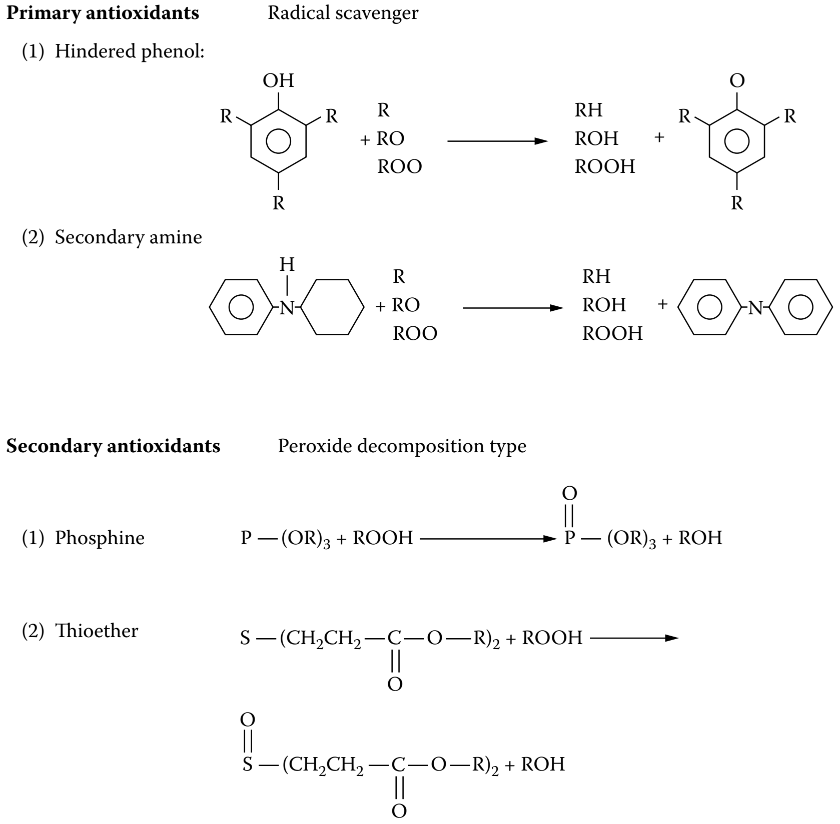


Figure 4.8 Mechanisms of Antioxidant, [4.70].

Antioxidant evaluation methods include carbonyl group titration [16], microwave oven scorch test [20], and antioxidant determination after the foam cure [15].

Hill [21] investigated fogging on the inside surface of the windshield (also mentioned in Section 3.3.4). C. Valetile et al. [22] investigated discoloration of foam caused by ultraviolet light.

4.2.2 Molded Flexible Foams

Molded flexible urethane foams have been used for producing intricately shaped products, such as automotive seats, child seats, head restraints, vibration damping for automobiles, arm rests, furniture cushions, and mattresses either by the hot molding process or by the cold molding process.

Hot-molded flexible foams are prepared based on polyether triols with secondary-OH terminal groups and 3000 to 3500 mol wt. Cold-molded foams are prepared based on polyether triols capped with primary-OH terminal groups.

The density distribution of molded foams is composed of high-density skin foam and low-density core foam. An example of density distribution of a 10-cm-thick hot-molded mattress foam is shown in Figure 4.9. Compression force deflection curves are relatively linear in comparison with slabstock foam as shown in Figure 4.1. In the molding process mixed foaming ingredients are poured through a mixing head into a preheated mold made of aluminum, steel, or epoxy resin. The mixed ingredients flow and expand in the mold, and then the molded foams are kept at the required curing temperature for a limited time, which is followed by demolding.

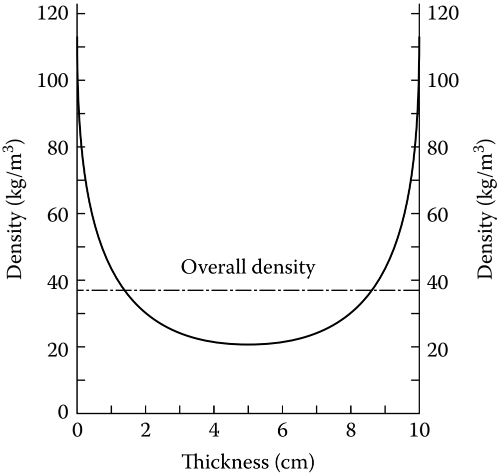


Figure 4.9 Density Profile of Molded Flexible Foam, [4.10].

4.2.2.1 Hot-Molded, Flexible Urethane Foam

Hot-molded foam is produced by using a formulation consisting of conventional polyether polyols (e.g., 3,000-mol wt, tri-functional oxypropylene triol) with TDI 80/20. Table 4.5 shows a formulation example of hot-molded flexible foam.

In 1961 Nisshinbo Industries Inc. in Japan commercialized hot-molded urethane foam mattresses that provided better sleeping comfort than slabstock foam mattresses and greater durability. J. Kohara of Chiba University, Japan, proved the advantages of the molded mattress by means of ergonomic studies [23]. Because of the relatively higher cost, however, the molded mattress was not competitive with slabstock foam mattresses, and production was discontinued.

4.2.2.2 Cold-Molded, Flexible Urethane Foam

Cold-molded, flexible urethane foam is prepared at low mold temperatures (e.g., 60 to 70°C) in 10 minutes of mold retention time, then post-cured in a separate oven or at room temperature.

Table 4.6 shows some formulation examples of all water-blown cold-molded foam [24–32]. Most of the polyisocyanate components employed are blends of TDI and polymeric diphenylmethane diisocyanate (MDI) as shown in the references listed in Table 4.6.

Almovist [28] reported an example of an all MDI-based formulation. Most of the polyols employed were polymer polyols (graft polyols). Hatano et al. [27, 30] reported the use of high molecular weight polyols, in the 8,000 to 10,000 mol wt range.

Dual-hardness automotive seats are prepared via the polymer polyol route [31, 32]. Making dual-hardness foams in a one-step process includes a two-mixing-head process, (2) a two-isocyanate index system, different foam densities, and different amounts of polymer polyol. Westfall [31] prepared dual-hardness foam seats by using one kind of polymer polyol with TDI 80/20 for firm foam and two types of polymer polyols with TDI 80/20 for soft foam. Kleiner used one three-stream dispensing machine, that two polyols streams and one polyisocyanate stream [32].

4.2.2.3 High Resilience (HR) Foams

Table 4.4. [12] shows a formulation and foam properties reported by the NBS. Table 4.5 [24] shows another formulation, employed by Campbell et al., in which molding conditions were an oven-cure temperature of 190°C and in-mold time of 40 minutes.

Hot-molded automotive seats have an advantage over cold-molded foam in humid and aged compression sets.

HR foams have higher resiliency than conventional flexible foams. For example, the sag factor of HR foams ranges from 2.4 to 3.0 and the percent ball rebound is about 70 %.

Table 4.4 High-Resilience Flexible Foam, PRC-GM #25 [12]

Formulation	Weight Percent	
Polyol: glycerine-based polyoxypropylene and ethylene glycol capped with primary hydroxyl groups, 6000 mol wt	62.4	
Isocyanate: Toluene diisocyanate modified	30.5	
Blowing agent: CO_2 produced by isocyanate reaction with water	1.5	
Catalyst: tertiary amines	4.4	
Processing aid: phosphate ester	1.2	
Physical Properties	**U.S. Customary**	**Si Unit**
Density, pounds/cubic feet (kg/m^3)	2.75	44
ILD, 25 % R, pounds/50 inches^2 (N/323cm^2)	26	116
65 % R, pounds/50 inches^2 (N/323cm^2)	75	334
Sag factor	2.88	2.88
Tensile strength, pounds/inches^2 (kPa)	10	69
Elongation, %	100	100
Tear strength, pounds/inches (N/m)	0.8	140
Compression set, %	3.5	3.5
Rebound, %	73	73

High resilience (HR) foams are prepared with the cold-molded foam process. The formulation principle is to reduce intermolecular interactions such as hydrogen bonding of urethane linkages, irregular structures of polymeric molecule, and so on. Examples of polyether polyol include high-molecular-weight polyether polyols (e.g., 4,000 to 10,000 mol wt [26, 29, 33–36]) and graft polyols (polymer polyols) [2, 25, 29].

Examples of polyisocyanates include blends of TDI-8020/polymeric MDI in a 80/20 weight ratio [25, 28, 30, 31] and the single use of polymeric MDI [28, 37]. The blowing agent is water alone [24–32, 37–39]. No use of physical blowing agents has been reported.

Table 4.5 Hot-Molded, High Resilience Foam (24)

Component	Hot Foam	High Resilience Foam
Polyol	3000 mol wt poloxypropylene glycol	6000 mol wt capped glycol
Isocyanate	80–20 TDI	80–20 TDI + polymeric isocyanate
Blowing agent	Water	Water
Catalyst	Amine + tin	Amine
Surfactant	Effective	Noneffective or insufficient
Inmold cure	40 min. at 187°C	10 min. at 60–69°C
Demolded post-cure	None	30 min. at 121°C

Table 4.6 All-Water-Blown, Cold-Molded HR foam

Polyisocyanate	Polyol (mol wt)	Mold Cure (°C/min.)	Post-cure (°C/min.)	Reference
TDI/pMDI*	Polymer polyol	60–69/10	121/130	24
TDI/pMDI*	Polymer polyol	100/10	None	25
TDI/pMDI*	Polymer polyol	63/6	121/4	27
TDI/pMDI*	8,000–10,000	80/7	NA	30
TDI/pMDI**	Polymer polyol	120/8	120/30	31
TDI/pMDI***	Polymer polyol	NA	NA	32
All pMDI	4,8000–6,000	45–50/4–5	NA	28
TDI-80-20	Polymer polyol	70/5	NA	29

* pMDI = polymeric MDI, weight ratio of TDI/MDI = 80/20;

** Weight ratio of TDI/MDI = 78/22;

*** Weight ratio of TDI/MDI = 70/30

All-water-blown, cold-molded HR foam has appeared in the literature. Examples are shown in Table 4.6.

Almoquist [3] reported preparative methods of HR foam for furniture and automotive applications. The method employs a cold molding process that uses raw materials consisting of high-molecular-weight polyether polyol (e.g., 4000 to 6000 capped with primary OH groups), a mixture of TDI/polymeric MDI or all polymeric MDI, and water as the blowing agent.

4.2.2.4 Viscoelastic Foam

Viscoelastic (VE) foams are characterized by slow recovery after compression. The foam is also called low-resiliency foam, slow-recovery foam, ergonomic foam, better-riding comfort foam, and temperature-sensitive foam. VE foams were used by NASA in the early 1960s [40], but they have been highlighted only in recent years [40–45].

The foam, used in carseats, deformed to a large extent by heavy parts of the body such as hips, but is deformed to a small extent by light body parts such as backs.

VE foam is prepared using a polyol blend of high- and low-molecular-weight polyols. The polyisocyanate can be TDI 80/20, TDI 63/36 [43], or polymeric MDI [46]. In general, a low isocyanate index formulation is utilized, (eg. less than 100) [42, 43], but indexes of 100 or higher have also been reported [42, 46]. Hager investigated the relationship between the chemical structure and physical properties of VE foam using a new polyether polyol at 100 index [42].

TDI-based VE foams are soft to the touch and have very low resilience and slow recovery. MDI-based foams are easier to process and can be produced in a wider range of isocyanate indexes. However, physical strengths of MDI-based foams are lower, resilience is higher, and compression set is better than TDI-based foams.

However, VE foam has an inherent disadvantage for automotive seat cushions: the temperature dependence of its cushioning property. VE foam becomes significantly harder below the glass transition (Tg) temperature (–20°C) and significantly softer above Tg temperature. Farkus et al. [46] attempted to solve the temperature dependence by adjusting the Tg of the foam. They used blends of polyether polyol with a terminal primary OH group (equivalent weight [EW]: 1600 to 2000) at 40 to 60 %, copolymer polyol (EW: 2800), 10 to 20 %, crosslinker at 25 to 40 %, and water at 1 to 3 %, and the isocyanate employed was modified MDI (EW: 147) at an isocyanate index of 70 to 100. The molding condition employed was 5 min. at 65°C, followed by curing without heating. The resulting foam properties were: density: 65 to 73 kg/m^3, ball rebound: 21%, and Tg: –43°C.

Saiki and his collaborators [47] prepared MDI-based VE foam using MDI prepolymers, polyether polyols, polymer polyols, crosslinker, water, amine catalyst, silicone surfactant, and an isocyanate index of 80 to 110.

Kintrup et al. [43] disclosed formulations of TDI-based foam. Hager et al. [42] reported that a key factor is the choice of polyol composition.

The VE foam market includes seat cushions for people who spend a long time sitting such as truck drivers, office workers, and airline pilots, as well as for NASA's space shuttle seats, wheelchair seats, and so on; sporting goods that require energy absorption such as gym mats, helmet linings, leg guards for ice hockey, ski boots, and ice skates [28, 38].

A currently growing market is foam mattresses based on the concept of ergonomics. VE foams are used for top layers of mattresses, usually with a density of 60 kg/m^3 and a thickness of 2 to 3 inches [28]. Farkas et al. [46] discussed in detail the technology for molded VE foam for automobiles. Examples of molded VE foam parts for automobiles are head restraints and driver's seats.

4.2.2.5 Soft/Super-Soft Slabstock Foam

Soft/super-soft slabstock foams can be produced by using high-molecular-weight polyether triols such as 6,000 to 12,000 mol wt polyether triols [33–36, 45]. A suitable polyisocyanate is TDI 80/20. Isocyanate indexes are in a range of 92 to 104 [45].

The blowing agent can be water alone or co-use of water and a physical blowing agent. Super-soft foam has low cross-link density and low foam density, for example, 20 to 30 kg/m^3. The 25 % ILD of the foam is in the range of 30 to 40 N.

Recently, d'Andrea [45] reported a method of super-soft foam preparation that uses polyether polyols with a hydroxyl number of 42.0 mg KOH/g, a blend of water and liquid CO_2 as the blowing agent, and TDI 80/20 as the polyisocyanate. Almovist [28] reported a preparative method of High Resilience (HR) foam using 4,000 to 6,000 mol wt polyol, a mixture of TDI and polymeric MDI, and water as the blowing agent.

One market for super-soft foam is back pillows for high-quality sofas.

4.2.2.6 Semiflexible Slabstock Foam

Semiflexible slabstock foam and molded foams have high open cells and high load-bearing and energy-absorbing properties. These foams are used for various automotive applications, such as bumper cores, interior knee bolsters, side impact-absorbing door panels, and headliners underneath the automotive roof. The foam is characterized by high energy absorption, so it can be called energy-absorbing (EA) foam. Figure 4.1 showed a hysteresis curve of EA foam. EA foam for bumper applications was discussed in detail by Kath et al. [44].

4.2.2.7 Reticulated Foam

Reticulated foam has 100 % open cell skeletons with no cell membranes. The cell membrane removal method for polyester foam is to dissolve membranes with an alkaline solution [48]. Other cell membrane removal methods include compressed air treatment and explosion of hydrogen gas [48]. The removal of polyether foam membrane can be done by oxidation such as with a potassium perchromate–sulfuric acid solution [49]. Applications for reticulated foam include various filters, mats, and pads.

4.2.2.8 Integral Skin, Flexible Foam

Integral skin foam is called also self-skin foam. The foam consists of high-density skin foam and low-density core foam, that is, a sandwich structure, as shown in Figure 4.10.

In the past the blowing agent for integral skin foam was CFC-11. At present, alternative blowing agents are non-CFC and non-HCFC physical blowing agents that include HFCs (Section 3.3.2.3) and azeotrope blowing

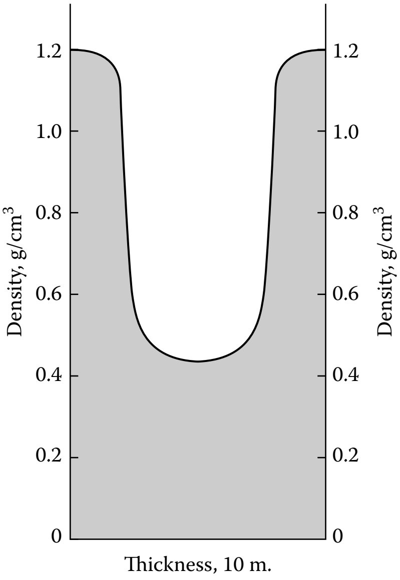


Figure 4.10 Density Profile of Integral Skin Flexible Foam, [4.10].

Table 4.7 Integral Skin Flexible Urethane Foam [51]

Formulation (pbw)	#1	#2	#3
Pluracol P-380*	160	160	160
1,4-Butanediol	20	20	20
Pluracol Pep 450*	20	20	20
Dabco 33LV**	2.4	2.4	2.4
CFC-11	30	0	0
n-Pentane	0	6.8	0
Methyl formate	0	6.4	0
Water	0	0	3.0
PAPI***, index	105	105	105
Mold temp. (°C)	32	32	32
Skin thickness (mm)	1.6	1.6	0.5

* BASF's trade name: Polyether polyol;
** Air Product's trade name: t-Amine catalyst;
*** Dow Chemical's trade name: Polymeric isocyanate

agents (Section 3.3.3.2.8) [32] because of easier processing and better efficiency of skin formation.

Table 4.7 [50] compares three kinds of blowing agents in the formation of foam skin in terms of skin thickness: CCl_3F, halogen-free azeotrope (methyl formate/pentane), and water. The mold temperature for integral skin foam preparation was carefully controlled at a range of 40 to 70°C.

C_5-hydrocarbons, however, are not recommended for integral skin foams because of poor compatibility with foaming systems. Water is not recommended either because it produces thin skins, although in some technical papers, water is used as a blowing agent.

Integral skin foams, both flexible and rigid, can be prepared either by the open mold process or by the reaction injection (RIM) process, described below.

4.2.2.8.1 Open Mold Process. A foaming system composed of two reactive components is mixed and poured into an open mold and the mold is immediately closed to allow foam expansion and curing. The foaming machine is a low pressure, high-shear type dispensing machine. This process is used for making automotive parts such as globe box lids, arm rests, head rests, and baby seats; motorbike seats; shoe soles; and mattresses.

4.2.2.8.2 Closed Mold Process (RIM Process). A foaming system composed of two reactive components is injected into a closed mold through a high-pressure impinging mixer. This process is suited to producing thin and large automotive parts such as bumper covers, air spoilers, deck lids, fenders, and steering wheel covers.

The RIM process has several modifications. Reinforced material, such as chopped glass fibers or mica, is added into foaming ingredients. The process is called reinforced RIM (RRIM), which is employed mainly for making rigid foam automotive panels.

Another reinforcement is fiber meshes. A sheet of fiber mesh is arranged in a closed mold, and a mixture of reactive components is injected into the mold. The process is called structural RIM (SRIM).

RRIM and SRIM processes are used to produce cellular and noncellular products, but mainly to manufacture automotive parts.

The RIM process can be applied not only to urethane systems, but also to various polymer systems, such as polyureas, polyisocyanurates, polyesters, polyepoxides, and nylon 6. In the case of polyurethane RIM foam, component A is polyisocyanate and component B is a blend of polyol, surfactant, catalyst, and blowing agent.

The physical structure of RIM foam consists of high-density skin and low-density core foam. An advantage of integral skin foam is that the structure gives more stiffness to molded foams. Another advantage of the RIM molding process is lower molding pressure than thermoplastic resins, for example, polypropylene and polystyrene. This advantage allows the use of a simple, light-weight mold and small-sized equipment, so investment costs are lower than for thermoplastic resins. Another advantage is that light-weight, large and thin molded products are obtained under relatively lower molding pressure than that of thermoplastic polymers.

4.2.2.9 Microcellular Elastomers

Microcellular urethane elastomers are also called foamed urethane elastomers. The density is in the range of about 320 to 960 kg/m^3 (20 to 60 pounds per cubic foot).

4.2.2.9.1 Preparation of Microcellular Foam. The major polyols employed include aliphatic polyester diols with a molecular weight of about 1000 to 3000 and the same molecular weight of poly-epsilon caprolactone and poly-(tetramethylene ether) glycols (PTMEG). The polyisocyanates employed include TDI-prepolymers and carbodiimide-modified MDI (liquid MDI) and urethane-modified MDI. Examples of chain extenders (functionality: 2) include ethylene glycol, 1,4-butane diol, MGCA, or MOCA (4,4′-methylene-bis-2-chloroaniline). Examples of cross-linkers (functionality: 3) are triethanolamine and trimethylolpropane.

The blowing agent for the foam is water. It is important to note that the amount of water is small but should be measured precisely. Its accuracy can be obtained by using a water-containing inert solvent such as liquid sodium sulfonate or vegetable oil, which contains a small amount of water. The use of water alone does not provide an accurate quantity.

Microcellular urethane elastomer is used for various shock-absorbing elements in vehicle suspensions, precision machines, shoe soles, sports shoes, etc.

4.2.2.10 Shoe Sole Foam

The advantages of polyurethane foam in shoe soles include high abrasion resistance, high flexibility, low density, high cushioning, and solvent resistance. In addition, the direct molding of the sole with the upper part of shoe makes it possible to increase production efficiency and lower production costs.

Casual shoes are produced using polyether-based foam systems. Some sports shoes such as tennis shoes are produced by polyester foam systems, because polyester-based foam has higher abrasion resistance, tensile strength, and elongation at break in comparison with polyether-based foams.

4.3 Rigid Polyurethane Foams

4.3.1 Introduction

Rigid polyurethane foams consist of a high percent of closed cells and have the following unique characteristics. (a) Foams are prepared at ambient temperatures without heating. (b) The foams adhere to many kinds of materials such as steel, wood, thermosetting resins and foams, and fibers. (c) The foam density can be varied in a wide range from 20 to 3000 kg/m^3. (d) They are resistant to petroleum, oils, and other nonpolar solvents. (e) Low-density foams have high thermal insulation properties. These characteristics are quite different from thermoplastic foams such as polystyrene and polyolefin foams as well as thermosetting foams such as phenolic foams. (f) They can be made with on-the-site foaming such as spray foaming, pour-in-place foaming, frothing-in-place, and one-component foaming by moisture in the air.

Rigid urethane foams are applied in many thermal insulation products such as refrigerators, freezers, refrigerated trucks, refrigerated containers, refrigerated warehouses, building and construction, chemical and petrochemical plants, water heaters, portable ice boxes, and thermos bottles. It should be noted that rigid urethane foam contributes considerably to energy savings on the earth.

The biggest technological event in the urethane foam industry in the past decade was the ban of the production and use of CFCs and HCFCs for preventing the ODP in the polar stratosphere. Accordingly, zero-ODP physical blowing agents, that is, the third generation blowing agents, are being developed. These blowing agents include HFCs, (e.g., HFC-245fa, HFC-365mfc, C_5-hydrocarbons), liquid carbon dioxide, and halogen-free azeotropes (see Section 3.3.3.2).

4.3.2 Production of Rigid Urethane Foam

4.3.2.1 Slabstock Rigid Foam

Slabstock foam is called bun foam or block foam. The essential raw materials for making rigid slabstock foam are polyisocyanate, polyol, catalyst, surfactant, and blowing agent as listed below (see also Section 3.3):

Polyisocyanate: Polymeric isocyanate or undistilled or crude TDI
Polyol: (a) Polyether polyol, OH-number in a range of about 350 to 500, (b) in part, aromatic amine-based polyether polyol, or (c) polyester polyol
Catalyst: Tertiary-amine catalyst; tin catalysts if necessary
Surfactant: silicone surfactant
Blowing agent: HFCs, C_5-hydrocarbons, liquid CO_2, azeotropic mixtures

An example of rigid slabstock formulations is shown in Table 4.8 [21].

Slabstock rigid foam is produced by a continuous process. Foam sizes are chosen based on applications. An example of foam sizes is 1.0 m wide × 0.5 m high × 4 m long. The slab foam is used by cutting for different applications such as core foam of sandwich panels and pipe covers.

As a nucleation agent, a small amount of water, for example, 0.5 parts per hundred (pphr), can be used with physical blowing agents. However, when water is used as a major or single blowing agent, the diffusion rate of

Table 4.8 Formulation of Rigid Urethane Foam (52)

	Parts by Weight	
Component A	I	II
Polyol: Voranol 360(#1)	100.0	100.0
Silicone surfactant L-5340 (#2)	1.5	1.5
Amine catalyst, Dabco 33LV (#3)	2.0	2.0
Metal catalyst, UL-6 (#4)	0.3	0.3
Fluorocarbon 11	28.4	47.0
Component B		
Polymeric MDI, index	105	105
#1: Dow Chemical's trademark		
#2: Union Carbide's trademark		
#3: Air Product's trademark		
#4: Witco's trademark		
Reactivity, Second		
Cream time	25	22
String time	36	45
Tack free time	45	59
Foam Properties		
Density lbs/ft^3 (core)	2.60	1.71
Compressive strength, psi		
Parallel	55.1	20.5
Perpendicular	17.7	8.2
K-factor, Btu/sq.ft.°F.hr/kn	0.135	0.109
Abrasion, weight loss %	1.4	2.2

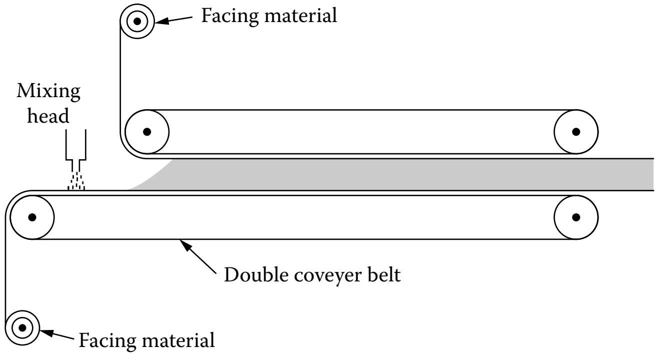


Figure 4.11 Continuous Production of Laminates, [4.10].

CO_2 gas generated from inside the foam cells outward is faster than the diffusion rate of air into foam cells. Therefore, the cell gas pressure becomes lower than the atmospheric pressure, which results in foam shrinkage. In order to prevent foam shrinkage, foam densities should be increased to resist to the atmospheric pressure; the necessary density is at least 3.0 pcf (48 k/m^3).

4.3.2.2 Laminates

Rigid foam laminates consist of rigid or flexible facings and a rigid core foam. A continuous production line of laminates is composed of a horizontal conveyer, facing feeder, foaming system dispenser, and laminate cutter as shown in Figure 4.11. Flexible facings include craft paper, aluminum foil, polyethylene-coated paper, and asphalt-coated paper. Rigid facings include steel sheet, aluminum sheet, and gypsum board.

In the case of small production, however, discontinuous processes are preferably employed; facings are adhered on both sides of the foam core board by a manual process.

Rigid urethane foam laminate is used for various applications, such as insulants for building walls, roofs, and refrigerated warehouses.

4.3.2.3 Sandwich Panels

Rigid urethane foam sandwich panels have a hexahedral structure composed of two sheets of large facing and four frames. The foaming mixture is poured into the closed cavity to allow for expansion. Both froth and non-froth processes can be applied. The panel position for pour-in-place foaming can be held in either vertical or inclined positions.

Panel production in small amounts is made by batch processes. In contrast, continuous processes have higher productivity, but the initial investment cost is higher. In addition, the change of process conditions is less flexible than with the batch process.

Recently, a low-vacuum-assisted foam injection process for producing sandwich panels in a discontinuous process was developed with the cooperation of Canon and three other companies [53, 54]. The vacuum-assisted system results in less foaming pressure; +0.2 bar, compared with around 0.45 bar in normal systems. Foam density has a better consistency of around 40 kg/m^3, and production cycle time is 5 to 10 min. per panel, depending on sandwich panel thickness. The sandwich panel thickness can be in the range of 5 to 13 cm.

Stengard studied the relationship between foaming pressure and foam thickness at different foam thicknesses using a mold size of 4 feet × 4 feet. His results are shown in Figure 3.15 in Chapter 3 [54]. For example a panel size of 2 feet × 2 feet × 4 inches gave a foaming pressure of 0.4 psi, compared to 2.2 psi with a non-frothing process. In contrast, a frothing process gives lower foaming pressure, which is about one-fifth of a nonfrothing process (Section 3.4.2.3.7).

Sandwich panels are widely used for refrigerated warehouses and transportation vehicles that carry refrigerated food. These vehicles include refrigerated trucks and refrigerated railroad freight cars.

4.3.2.4 Appliances

The appliance industry is a major user of rigid urethane foams, which includes household refrigerators, household freezers, and residential water heaters. As described previously, the development of physical blowing agents revolutionized the rigid urethane foam industry. At this time, the most viable physical blowing agents are HFCs including HFC-245fa, HFC-365mfc, HFC-134a, and HFC-227ea.

Because of the energy conservation regulations in the United States, C_5-hydrocarbons cannot be used as blowing agents in the U.S. appliance industry. However, European and Asian countries employ C_5-hydrocarbons such as cyclopentane as blowing agents because C_5-hydrocarbons are economical, have zero ODP and nearly zero global warming potential (GWP), and allow for thicker insulation wall thickness. C_5-hydrocarbons have some disadvantages such as higher K-factor, flammability, and high investment costs.

In principle, the required physical properties of appliance foam include low foam density, high dimensional stability, low K-factor, good adhesion to plastic door liners, zero ODP, and low GWP.

Another important application area of appliances is residential deep freezers. The wall thickness of the deep freezer is about 2 inches for a 4-cubic-foot-capacity freezer. In comparison, household refrigerators have wall thicknesses of about one inch.

In the past, residential water heaters were insulated with glass fibers, but they now are insulated with rigid urethane or urethane-modified isocyanurate foam. The insulation foam requires higher heat stability than conventional rigid foam. Ingold et al. [55] examined three leading blowing agent candidates (HFC-245fa, cyclopentane, and HFC-134a) to replace HCFC-141b.

4.3.2.5 Refrigerated Trucks

Refrigerated trucks are required to keep an inside temperature of −30°C. Therefore, wall thickness is about 10 cm (4 inches). Foaming-in-place is applied into separated cavities of preassembled refrigerated truck bodies. Another process is to assemble foam-filled sandwich panels.

4.3.2.6 Refrigerated Showcases

Refrigerated showcases are display cabinets of frozen or chilled food that are used in grocery stores. The required physical properties are the same as those of household refrigerators.

4.3.2.7 Vacuum Insulation Panels

It has been recognized that the overall thermal conductivity of rigid urethane foams consists of the factors shown below:

$$\lambda t = \lambda g + \lambda s + \lambda c + \lambda r$$

where λt is total thermal conductivity, λg is the conductivity of a cell gas, λs is the conductivity of a solid, λc is the conductivity of convection, and λr is the conductivity of radiation.

It is well known that a vacuum bottle (or thermos) has superior thermal insulation, but its disadvantages are weight and brittleness. The ideal vacuum panel theoretically has the following thermal conductivity:

$$\lambda t = \lambda s + \lambda r$$

Accordingly, vacuum insulation panels are considered to be the next generation of thermal insulation panels.

A method of making vacuum insulation panels was first proposed in Royalle's patent [56], which described the use of a plastic honeycomb as the core material and metal-plated plastic sheets as the facing material. The plastic honeycomb resists the atmospheric pressure when the panel is evacuated. Some studies have been conducted to make core materials by using open-cell urethane foams.

By Nakamura's method [57], rigid urethane foam board was treated under vacuum (e.g., 0.01 to 0.001 mm Hg at 100°C and 100% RH) to produce open cells.

Uekado and Okada [58] proposed an adiabatic box consisting of a vacuum panel and a rigid urethane foam core.

Kodama et al. [59] used calcium stearate as a cell opening additive to CFC–11 or HCFC-141b-blown urethane foam systems.

Open-cell, urethane-modified isocyanurate foam was prepared using methylene chloride and n-pentane blends as blowing agents and by controlling the foaming reaction with a choice of catalysts and without cell opener [60]. According to the paper, the following relationship can provide open cell foams:

$$(Tr - Tt)/(Tt - Tc) > 1.2$$

where Tr is rise time, Tt is tack free time, and Tc is cream time.

Bayer AG and Telwest Recycling GmbH [50] have developed a vacuum panel technology using recycled rigid foam fluff from old refrigerators for new refrigerators. Finely ground open-celled fluff is molded into sheet forms, with polymeric MDI as a binder using heat and pressure. These sheet forms are sealed within a gas-impermeable plastic film to produce 25-mm-thick vacuum insulation panels.

Tabor prepared microcellular polyurea xerogels from PAPI 27™ (a polymeric MDI) and applied them as a core material for vacuum panels [61, 62]. Burkhart discussed the mechanism of open-cell rigid foam by means of an additive approach [13]. Glicksman [63] chose glass as the rigid supporting structure for vacuum panels.

4.3.2.8 Molded, High-Density, Rigid Foams

Molded, high-density, rigid urethane foams are prepared either by the open-mold process or by the closed-mold process. The closed-mold process is RIM. Molded foams have integral skin structures consisting of high-density skin foam and low-density core foam. This integral skin structure significantly enhances the mechanical strength of the product.

4.3.2.8.1 Open-Mold Process. The open-mold process is a casting process consisting of turbulent mixing of two reactive components, pouring the mixed components into an open mold, and closing the mold cover for foaming and curing. Overall foam densities can vary from about 300 kg/m^3 to over 800 kg/m^3 depending upon the structure and thickness. Application examples of the open mold foam process include furniture, decorative doors, and picture frames.

4.3.2.8.2 Closed-Mold Process (RIM Process). The RIM process consists of mixing two reactive components and injecting the mixture into a closed mold through a high-pressure impinging mixer. This process can produce thin and large products. Examples of rigid foam RIM products include chair shells, office machines, computer housings, and automotive parts such as air spoilers and fenders.

RRIM is produced by adding reinforcements such as 1/16th-inch-long glass fibers. RRIM panels were used for automotive door panels Fiero automobile (General Motors). SRIM is produced by the injection of a mixed system into a closed mold in which a fiber mesh has been set. SRIM technology is used to make bumper cores for automobiles

4.3.3 On-Site Foaming

4.3.3.1 Spraying

The spraying process provides seamless insulation layers on flat or waved roofing or tank surfaces. This process, however, has disadvantages of loss of urethane due to the wind, environmental issues, and the effects of atmospheric and object temperatures. At below 15°C, foaming efficiency becomes low and adhesive strength becomes poor.

Spray systems consist of two components, and the mixing ratio is about 1.0/1.0. The spraying machine is a high-pressure impinging type. Current blowing agents include HFCs and their blends, for example, HFC-365mfc with HFC-245fa, HFC-365mfc with HFC-234a, and HFC-365mfc with HFC-134a (see Section 3.3.3.2). Spraying by froth systems is also available [54]. Recently, CO_2-blown spraying was announced [64].

C_5-hydrocarbons cannot be used because of flammability. An all-water blowing agent is not practical because isocyanate–polyol mixing ratios are far from the required 1.0/1.0 ratio, and its viscosity is high.

4.3.3.2 Frothing-in-Place

The frothing process is very well suited for filling a large cavity such as large tanks by means of frothing-in-place, not by spraying. Advantages of this process are as follows.

1. Large-area cavity filling at one injection is possible (e.g., cavity filling of 10 cm thick, 100 cm wide and 200 cm high), allowing for low foaming pressure.
2. Effect of ambient temperature on foaming is low, so adhesion and other physical strengths of the foam are good. Accordingly, frothing-in-place in winter is possible, even if ambient temperatures are lower than 15°C. (In contrast, spray foaming requires ambient temperatures of higher than 15°C.)
3. Spray foaming has significant loss of foaming material due to wind, but frothing-in-place has no wind effect.
4. The helix mix-head is compact and portable and as easy to use as on-the-site-foaming.

Further advantages are described in Section 3.4.2.3.7 in Chapter 3.

Application examples of an LPG spherical tank insulation by frothing-in-place are described below.

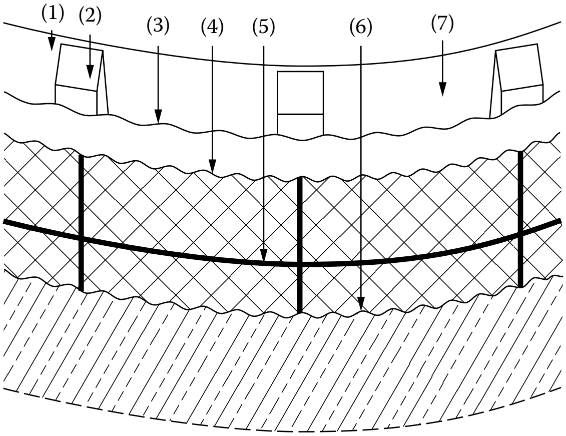
Sanshin Seinetsu Co. Ltd. of Japan developed an insulation process that involved frothing and applied it to a spherical LPG tank. Figure 4.12 shows the insulated spherical tank. Figure 4.13a shows a cross section of the cavity on the tank surface, and Figure 4.13b shows the operation onto the tank surface cavity. Huge LPG tank surfaces of an LPG cargo ship were frothed in place at Mitsubishi Heavy Industries Co. Ltd. in Japan in 1963 (Figure 4.14). A liquefied natural gas (LNG) transportation pipe (Figure 4.15) was also frothed in place at the Chiba-Petrochemical Complex in Japan [65].

4.3.3.3 Storage-Stable, Two-Component, One-Package Systems

Storage-stable, two-component, one-package, systems are possible by means of thixotropic systems [66–69]. Polyisocyanate gels can be obtained by dissolving dibenzal sorbitol into polyisocyanates such as TDI, polymeric isocyanate, and their prepolymers. The chemical structure of dibenzal sorbitol is shown in

Figure 4.12 Spherical LPG Tank Insulated by Frothing-in-Place [4.54].

Figure 4.16 [66]. The storage-stable, one-package, two-component system is prepared by mixing the polyisocyanate and dibenzol sorbitol at elevated temperature. In one example 100 g of polymeric isocyanate and 2.0 g of dibenzal sorbitol in the presence of catalyst (sulfuric acid) were stirred at 80°C for 30 min.



(1) Tank wall
(2) Foam spacer
(3) Polyethylene film
(4) Wire mesh
(5) Steel belt
(6) Mortar, water proofed
(7) Cavity for frothing-in-place

Figure 4.13(a) Frothing-in-Place into Cavity of Tank Surface [4.54].

Figure 4.13(b) Frothing-in-Place Operation onto Tank Surface [4.54].

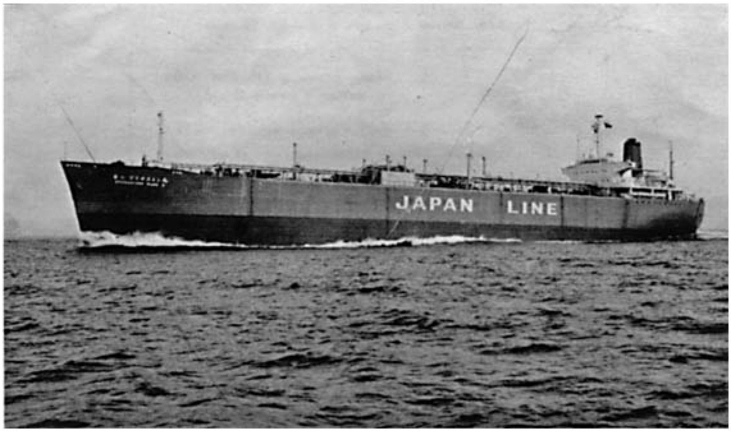


Figure 4.14. LPG Cargo Ship Insulated by Frothing-in-Place [4.54].

Figure 4.15 LNG Pipe Lines Insulated by Frothing-in-Place [4.54].

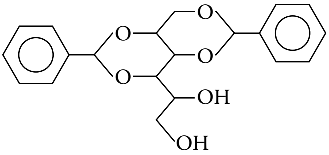


Figure 4.16 Dibenzol Sorbitol, [4.99].

Another method of making a polyisocyanate gel is the use of polycarbonate using similar conditions as just described [69]. By adding 1.07 wt of polycarbonate in pellet or powder form to the polyisocyanate without catalyst and heating it at 150°C for 3 hours, gelled polymeric isocyanate is obtained. Polyisocyanate gels are used as nonsagging, moisture-cured sealing foams and are storage-stable, one package, two-component systems. Polyol thixotropic components can be made by dissolving dibenzol sorbitol into a polyol component [68]

The two-components of the storage-stable, one-package urethane foam system can be stored in a single rigid container, with both components separated using a polyethylene bag. When the bag is broken, and the two components are mixed, the urethane foam formation occurs.

4.3.3.4 One-Component, Moisture-Cure Systems

This kind of system is used for foam sealants based on frothing. It is composed of a mixture of MDI-prepolymer, surfactant, and a low-boiling-point physical blowing agent such as HFC-134a with no catalyst. The system is kept in a pressurized container. Frothed foam systems can be injected in small cavities. The injected foam reacts with moisture in air and solidifies gradually. The one-component system is used in the construction industry to fill narrow cavities with rigid foam.

4.3.3.5 Foam Composites

Foam composites have two major applications: wood substitutes and cryogenic insulants, which are described in part in the previous section. Figure 4.19 shows the Young's modulus of various materials, one can see that foam composites show high ratios of modulus per density [71].

Foam composites, in general, consist of a rigid foam matrix and reinforcing glass fiber. Matrix foam can be either urethane or modified isocyanurate foam, and foam density can vary from low density to high density, depending upon the application [71, 72].

The type of reinforcing fiber can be selected from the group consisting of continuous roving, continuous strand mat, and chopped glass fiber [73, 74].

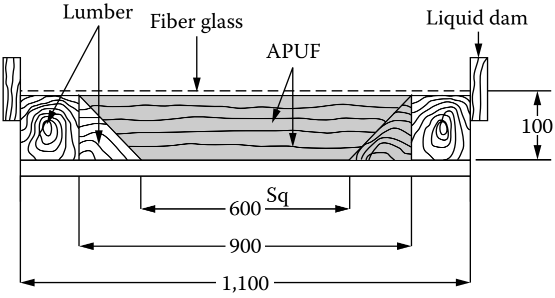


Figure 4.17 Conch-Methane-Service Test Box, [4.57].

4.3.3.5.1 Structures of Foam Composite. Figure 4.21 shows a schematic diagram of five kinds of foam composites. The orientations of reinforcing fibers are classified into five categories: (1) mono-axial, (2 and 3) two-dimensional, (5) three-dimensional, [75] and (4) combinations thereof [72, 74].

Figure 4.20 shows the excellent water resistivity of foam composite, which is the main reason it is used as a wood substitute.

Foam composites can be produced by closed mold processes. Spray processes and continuous processes have also been proposed. Figure 4.18 shows a process in foam composite production in which glass wool was used as the reinforcement [76]. The process is a continuous production process.

Figure 4.22 shows a combination structure of foam composite that was produced by a continuous process at NPC Corp. Its registered trade name is Synwood.

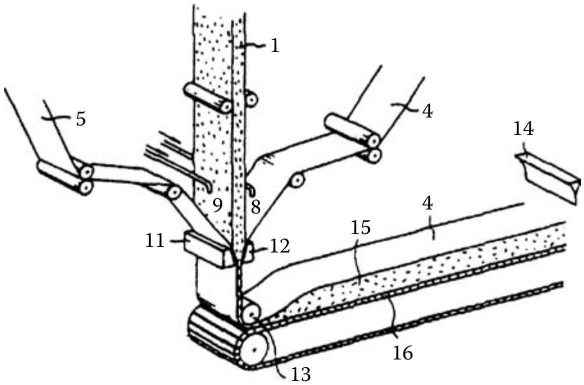


Figure 4.18 Continuous Foam Composite Production Process, [4.89].

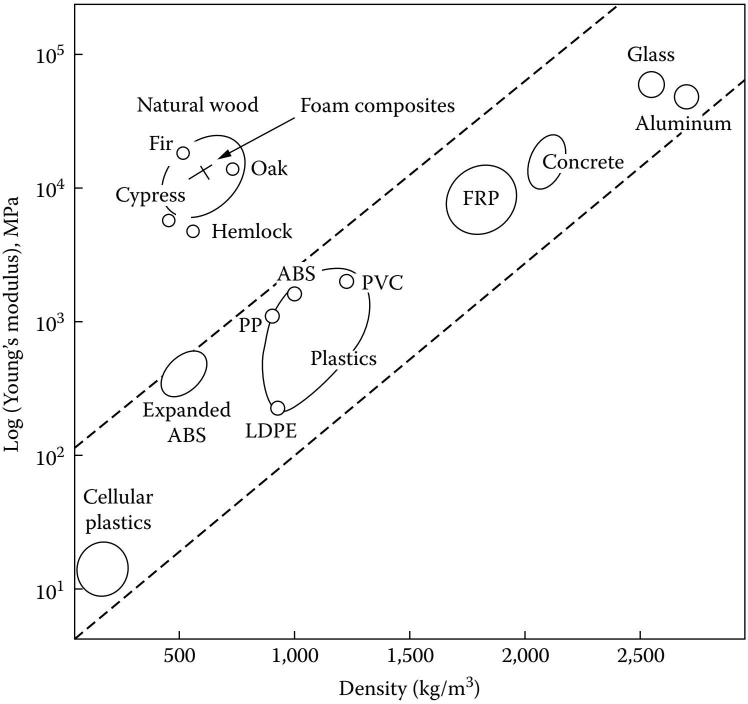


Figure 4.19 Comparison in Strengh of Various Materials, [4.90].

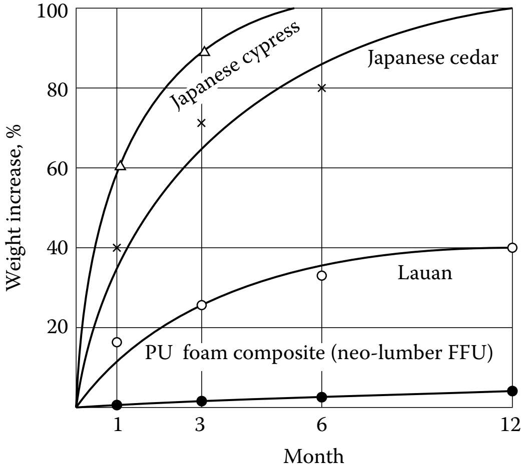


Figure 4.20 Water Absorption of Foam Composite and Wood, [4.90].

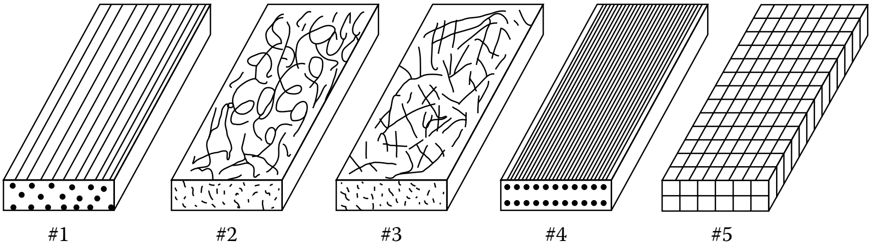


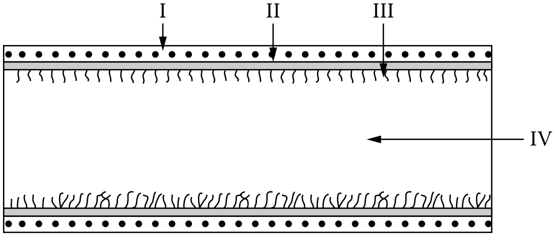
Figure 4.21 Schematic Diagram of Foam Composites [4.91].

4.3.3.6 *Cryogenic Insulation*

Natural gas is recognized to be a clean energy source. It is delivered through the pipelines on land, but when transported to a distant place by boat, it must be stored and carried as liquid at –162°C. Toyo Rubber & Tire Company's method for insulating LNG tanks [77] is called the mesh-lining (ML) system. The insulation layers are composed of multiple layers of sprayed rigid foam, and the top layer surface is lined with glass fiber mesh. Figure 4.23 shows the insulation structure. The ML system is very effective for crack prevention.

Toyo Rubber and Tire Co. emphasized the three important requirements to prevent crack formation: the safety coefficient of polyurethane foam, spray foaming technology, and mesh lining. The safety coefficient is defined by the following equation.

$$\text{Safety coefficient} = \frac{\text{Tensile strength at cryogenic temperature}}{\begin{array}{c}\text{Thermal stress at cooling from ambient}\\ \text{to cryogenic temperature}\end{array}}$$



I: Continuous roving
II: Continuous strand mat
III: Chopped glass fiber
IV: Foam core

Figure 4.22 Synwood™ Foam Composite, [4.94].

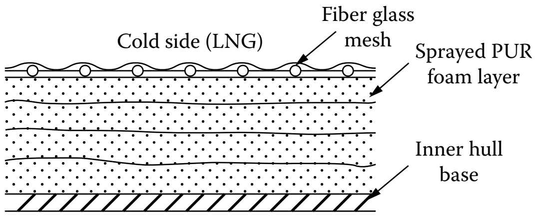


Figure 4.23 Cryogenic insulation Structure by Toyo Rubber Co., [4.101].

Spray foam has the remarkable advantage of higher strength in the parallel direction and higher elongation in the perpendicular direction to foam rise. The mesh lining on the cryogenic side was proven to be most effective for crack prevention.

Mitsubishi Heavy Industries Co. Ltd.'s insulation method for cryogenic storage [78, 79] is simultaneous spraying of rigid urethane foam and chopped glass fiber onto the inner surface of the LNG storage tank.

Cryogenic insulation requires absolutely no foam crack formation. An authorized evaluation method for cryogenic insulation is the Conch-Methane Service Ltd.'s test method. Figure 4.17 shows the test apparatus that is used to examine possible crack formation caused by liquid nitrogen at 196°C. Figure 4.24 shows the cryogenic insulation structure developed by the joint work of Mitsubishi Heavy Industries Co. Ltd. and Mitsubishi Chemical Ind. Co. Ltd.

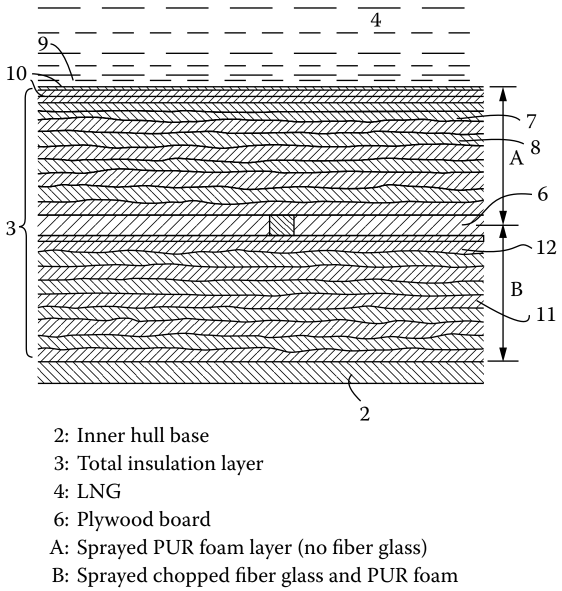


Figure 4.24 Cryogenic Insulation Structure by Mitsubishi Heavy Ind. Corp. [4.101].

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chapter five

Polyisocyanurate Foams

5.1 Introduction

The isocyanurate linkage is obtained by the cyclotrimerization of isocyanate groups as shown in Figure 5.1 [1]. The linkage was first reported by Hoffman in 1885 [2]. Zhitinkina et al. published a review article in 1985 [3].

The chemical structure of the urethane linkage has a labile hydrogen atom and it dissociates at relatively low temperatures as shown in Figure 5.2 [4].

In contrast, the isocyanurate linkage has no labile hydrogen. This is the reason for its high temperature stability. Figure 5.3 [5] compares thermal stability in terms of activation energy. In the figure thermal stability is in the following increasing order:

Urethane linkage < 2-Oxazolidone linkage < Isocyanurate linkage

The first patent literature regarding isocyanurate linkage–containing urethane foams was presented by Windemuth of Bayer A. G. [6]. Its objective was to increase crosslink density by incorporating 3-functional linkages into urethane foams using low-viscosity polyesters. In other words, incorporation of isocyanurate linkages with the co-use of low viscosity and low functionality polyester polyols resulted in rigid urethane foams. The patent, however, did not show how to obtain substantially flame- and heat-resistant rigid foams by means of polycyclotrimerization.

Nicholas and Gmitter [7] reported that polyisocyanurate-containing foams were prepared by the cyclotrimerization of NCO-terminated toluene diisocyanate (TDI) prepolymers. The thermo gravimetric analysis (TGA) data of these foams, however, showed that there is no visible increase in thermal stability owing to the low trimer content. In other words, the resulting foams did not show heat- and flame-resistance in terms of TGA.

Polymeric foams prepared by the polycyclotrimerization of aromatic polyisocyanates without the use of modifiers have highly crosslinked structures. Therefore, the resulting foams are extremely brittle and friable

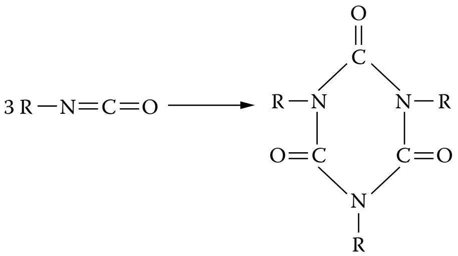


Figure 5.1 Cyclotrimerization of monoisocyanate.

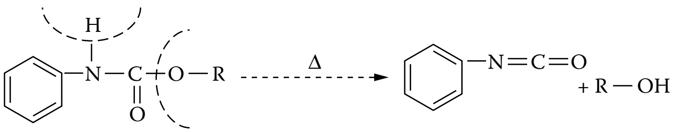


Figure 5.2 Labile Hydrogen Atom of Urethane Linkage.

and not resistant to handling and transportation stresses. In addition, when exposed to flame, the foam burst into fragments like popcorn. These disadvantages have made it impossible to use the foam for practical applications.

A dramatic breakthrough technology in the production of heat- and flame-resistant rigid foams with low friability was invented first by K. Ashida at Nisshin Boseki Co. Ltd. (Nisshinbo Industries Inc.) in Japan in 1966 [1]. The principle of the Ashida patent is the reduction of crosslink density by modifiers. The modifiers employed include polyether polyols

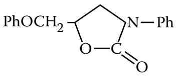
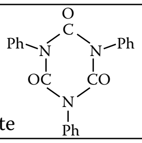
Model compound	Chemical formula	MP °C	T °C	$10^3 \times k$ min^{-1}	Correlation coefficient r	Activation energy kJ (kcal)	Frequency factor A min^{-1}	T_D (°C) at k = 0.005
I		135	330	1.629	0.980			
			350	5.649	0.996	201.1(48.1)	4.306×10^{14}	348
oxazolidone			370	19.2	0.996	r = 0.999		
II		282	400	1.683	0.989			
			420	5.638	0.998	252.2(60.3)	6.15×10^{16}	417
isocyanurate			440	20.906	0.997	r = 0.999		
III	$PhNHCOO-Bu$	62	280	6.447	0.995			
			300	19.816	0.995	161.8(38.7)	1.230×10^{13}	277
urethane			320	69.567	0.989	r = 0.999		

Figure 5.3 Kinetics of the Thermal Degradation of Model Compounds, [5.37].

with 300 or greater molecular weight with a functionality of at least three. The commercialization of the patent was launched in 1966 for the insulation of petrochemical plants in Chiba Prefecture, Japan. The foam's trade name was Airlite Foam SNB (super-non-burning). The foam was recognized as the first polyisocyanurate foam with high heat and flame resistance and low friability [8].

In addition, substantially nonflammable foam compositions with high heat and flame resistance and low friability were prepared by incorporating inorganic fillers into the system of Airlite Foam SNB. Examples of the inorganic fillers include graphite, talc, and inorganic fibers. The trade name of the foam was Airlite Foam USNB(ultra-super-nonburning). The foam exhibited outstandingly high flame and heat resistivity [9].

Two months after the priority claim date of the Ashida patent [1], Haggis of I.C.I. Ltd. independently registered a Belgian patent in which the modifiers employed were less than 300-molecular-weight polyether polyols [10]. One year after the priority claim date of the Ashida patent, Haggis registered another Belgian patent in which the employed modifiers were more than 300-molecular-weight polyether polyols [11]. Commercialization of the I.C.I. technology was reported by Ball et al. in 1968 [12]. The registered trade name of the foam was Hexafoam. Since then, extensive process developments were conducted by Upjohn Co. (trade name: Kode 25, 1969) [13], Jim Walter Corp. and its subsidiary Celotex Corp. (trade name: Thermax) [14], as well as other companies.

The modification methodology of polyisocyanurate foams includes a choice of modifiers, NCO/OH equivalent ratio, and blowing agent. Figure 5.4 shows a general formula for modified polyisocyanurate [15].

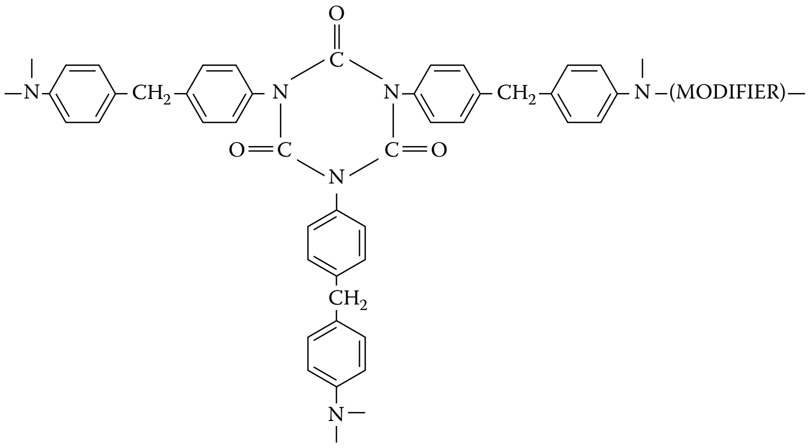
The manufacturing processes for modified polyisocyanurate foams are the same as those for polyurethane foams, an include slabstock processes, laminate processes, spraying processes, frothing-in-place processes, and molding processes.

Applications of modified polyisocyanurate foams include insulants for buildings, foam core laminates for wall panels, roof insulation panels, insulants for liquefied petroleum gas (LPG) cargo ship tanks, and on-ground liquefied natural gas (LNG) storage tank insulants [16].

5.2 Methods of Preparing Modified Polyisocyanurate Foams

As described above, the main objective of modification of polyisocyanurate foams is to reduce their friability by lowering crosslink density. The methods of modification include modifiers, blowing agents, and NCO/OH equivalent ratio (or isocyanate index).

The modifiers employed include (a) urethane linkages by adding aliphatic polyols [1, 17] or aromatic polyester polyols [18–20, 22], (b) amide linkages by adding dicarboxylic acids [23], (c) 2-oxazolidone linkages by



Modifiers:

Urethane linkage
Amide linkage
Oxazolidone linkage
Carbodiimide linkage
Imide linkage
Substituted urea linkage
Resole linkage

Figure 5.4 Modified Polyisocyanurates.

adding polyepoxides [23], (d) imide linkages by adding aromatic dianhydride, [24], (e) carbodiimide linkages by adding catalysts [24, 25], (f) acyl ureas by adding aromatic secondary diamines [26], and (g) phenolics by adding resole resins [27]. These modification methods will be described in detail in the following sections.

The blowing agents to be employed include hydroflurocarbons (HFCs), hydrocarbons (HCs), water, mixtures thereof, and nonhalogen azeotropes. The NCO/OH equivalent ratio usually varies from 2.8 to 5.0.

5.2.1 Urethane-Modified Polyisocyanurate Foams

5.2.1.1 Polyether-Polyol Modified Polyisocyanurate Foams

5.2.1.1.1 Modified Polyisocyanurate Foam Structure and Fire Endurance of Foams. An outstanding feature of polyisocyanurate foams is their fire endurance. These foams have superior flame and heat resistance compared to urethane foams [4].

The evaluation method employed for fire endurance was the Bureau of Mines Flame Penetration Test [28]. Anderson and Downing pointed out that the

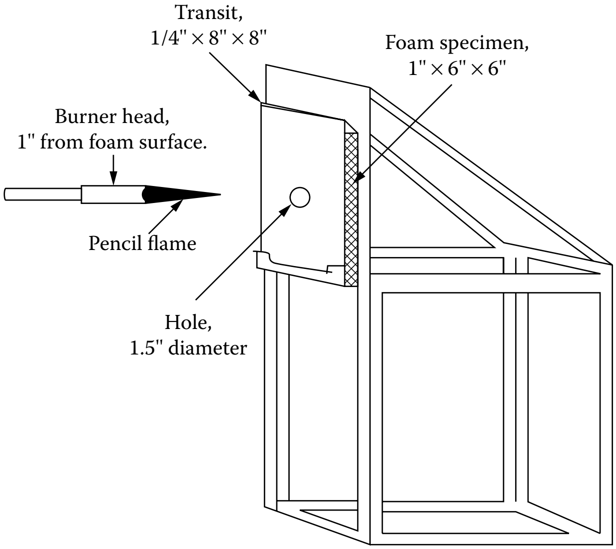


Figure 5.5 Bureau of Mines Flame Penetration Test Apparatus, [5.8, 5.84].

flame penetration test had poor reproducibility [29]. Ashida established an improved test method [4]. An example of the reproducible test results are below:

Number of samples: 10
Mean of burn through time: 28.3 minutes
Standard deviation: 1.9 minutes
Coefficient of variation: 6.7 %

Because of the better reproducibility, the method was employed throughout the study for the evaluation of the fire endurance of foams. Figure 5.5 [13, 30] shows the apparatus employed for the flame penetration test.

The formulations for isocyanate comparison in fire endurance are shown in Table 5.1, and the results are shown in Figure 5.6 [4]. This figure clearly shows the difference between the fire endurance of TDI and diphenylmethane diisocyanate (MDI) in terms of burn-through time. MDI-based foams show that at higher equivalent ratios, flame penetration times reached about 2000 seconds (about 33 minutes). In contrast, burn-through times of TDI-prepolymer-based foams were about 20 seconds at all ranges of the NCO/OH equivalent ratio. The reasons for the poor fire endurance are (a) that cyclotrimerization is retarded by the steric hindrance of the ortho methyl group of TDI and (b) thermally dissociated TDI monomer ignites immediately after dissociation in the presence of air, because the dissociation temperature of the TDI-based urethane linkage begins at about 150°C, which is higher than the inherent flash temperature of TDI (i.e., 132°C). Therefore, only polymeric MDI can be used for polyisocyanurate foams.

Table 5.1 Formulations for Isocyanate Comparison in Fire Endurance [4]

Polyether polyol:	Sucrose-based, OH No. 560.
Organic isocyanates	(a) Polymeric (MDI) isocyanate, 30.5% NCO or (b) TDI-prepolymer; 30% NCO
Equivalent ratio, NCO/OH	1.0, 2.0, 3.0, 4.0, & 5.0
Blowing agent:	CFC-11
Catalyst:	50% 2-ethylhexanoic potassium in polyether polyol
Silicone surfactant	L-544 (U.C.C.)
Foam density (kg/m^3)	46–48

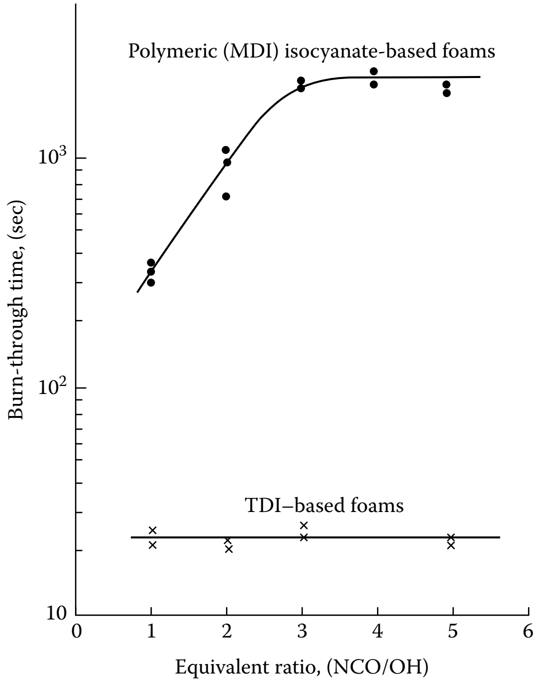


Figure 5.6 Comparison of Polyisocyanurates in Burn-Through Time, [5.11].

5.2.1.1.2 Effect of the Weight Ratio of Polyisocyanate/Polyether Triol on Fire Endurance. The fire endurance of foam is related to the content of the isocyanurate linkage (% trimer). The percent of trimer in foam is calculated by the following equation:

$$\%\,\text{Trimer} = 42 \times \frac{\text{E1} - \text{E2}}{\text{W1} + \text{W2}} \times 100$$

where E1 is the isocyanate equivalent and E2 is the hydroxyl equivalent. W1 is the weight of the isocyanate and W2 is the weight of the polyol. The number 42 is the formula weight of NCO. At a higher trimer content, the combustibility of foam significantly decreases, but friability increases to an unacceptable level of more than 30% weight loss, which is defined by the ASTM tumbling friability test [30]. However, lower-trimer-content foams increase combustibility but decrease the percent weight loss of the tumbling friability test.

The aliphaticity index defined by the following equation was used throughout the formulation study [4].

$$\text{Aliphaticity Index} = \frac{\text{Weight of Polyether Polyol}}{\text{Weight of Polymeric Isocyanate}}$$

The aliphaticity index is a ratio of the combustible components in the foam. Polyether polyol is regarded as a combustible component, and polymeric isocyanate is regarded as a noncombustible, char-forming component.

A systematic study of the fire endurance of foams was undertaken that examined the molecular weight of the modifier (polyether triol), the aliphaticity index, and the equivalent ratio of NCO/OH. The formulations employed for the comparison of polyether triols in the fire endurance are listed in Table 5.2. The optimum formulation that gives a flame penetration

Table 5.2 Polyether Triol Comparison in Fire Endurance [4]

Polymeric isocyanat, g.	652–405	Varied[a]
Polyether triol, g.	98–345	Varied
TG-300 (OH No: 517)		
TG-400 (OH No: 437)		
TG-500 (OH No: 325)		
TG-700 (OH No: 224)		
TG-1000 (OH No: 166)		
TG-1500 (OH No: 124)		
TG-2000 (OH No: 78.5)		
TG-3500 (OH No: 48.3)		
Catalyst, NKA, g.	12–18	Varied[b]
TCEP, g.	115[c]	
CFC-11, g.	110	
Surfactant L-544, g.	10[d]	
NCO/OH	1.0–14.0	Varied
Aliphaticity index	0.1–0.6	Varied

[a] Polymeric MDI, %NCO: 30.5

[b] Cyclotrimerization catalyst, 50% 2-ethylhexanoic potassium in polyether polyol

[c] Tris(chloroethyl) phosphate

[d] Silicone surfactant

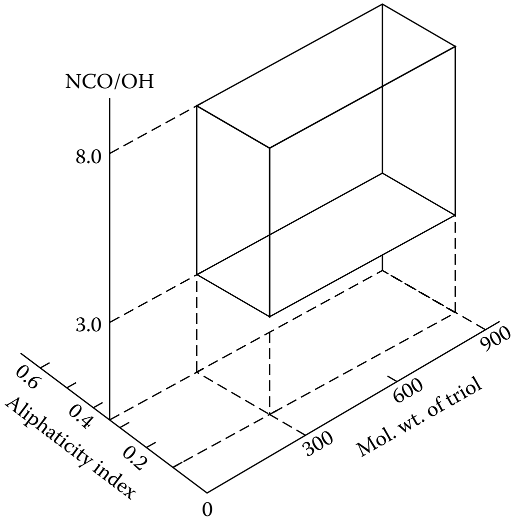


Figure 5.7 Optimum Range of Polyether Triol, [5.11].

time of at least 30 minutes is shown in Figure 5.7. Furthermore, the optimum formulas of a polyether triol-modified polyisocyanurate foam is listed below:

NCO/OH equivalent ratio: 3.0 to 8.0
Molecular weight of polyether triol: 300 to 900
Aliphaticity index: 0.1 to 0.3

5.2.1.1.3 Effect of the Functionality of the Polyether Polyol on Fire Endurance. The effect of the functionality of polyether polyols on burn-through time was investigated at different NCO/OH equivalent ratios. The formulations employed are shown in Table 5.3 [4], and the results are shown in Figure 5.8 [4]. Among the polyether triols employed, TG-260 (OH equivalent weight: 86.7) and glycerol (OH equivalent weight: 30.7) gave relatively poorer fire endurance higher functionality polyols such as OC-460, HS-700, and TG-400 with equivalent weights in a range of 115 to 130. In view

Table 5.3 Comparison of Functionality of Polyether Polyol in Fire Endurance [4]

Polyol	Functionality	Base	OH Equivalent
OS-460	8	Sucrose	130
HS-700	6	Sorbitol	126
TG-400	3	Glycerol	115
TG-260	3	Glycerol	86.7
Glycerol	3	Glycerol	30.7

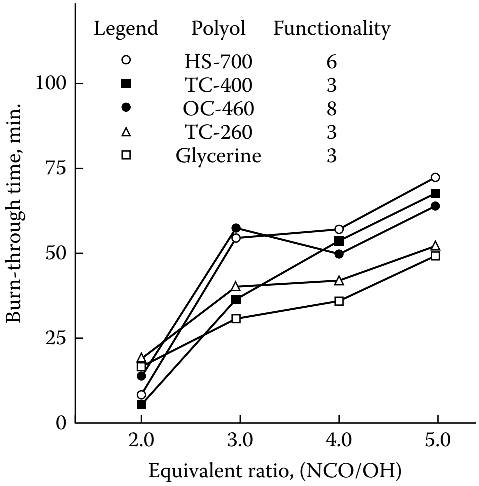


Figure 5.8 Effect of Functionality on Burn-Through Time at Different NCO/OH Ratios, [5.11].

of the accuracy of the burn-through time, no significant difference of functionality in fire endurance was observed among these polyols.

5.2.1.2 Glycol-Modified Polyisocyanurate Foams

Moss and Skinner investigated different modified polyisocyanate foams [31–35]. They conducted detailed studies on alkylene diols as modifiers. The foams were developed for producing laminates. The formulation employed is shown in Table 5.4 [35]. The formulation employed for continuous lamination was an ethyl glycol modifier as shown in Table 5.5 [35]. Moss and Skinner chose an optimum trimer level of 18 to 22% of trimer content [35].

Table 5.4 Glycol-Modified Foams for Laminates [35]

Formulation	No. 1	No. 2
Ethylene glycol	21	0
Propylene glycol	0	24
Mondur MR[a]	280	276
CFC-11	35–40	35–40
DC-193[b]	3–6	3–6
Aziridine/DMP-30[c]	3–5	3–5
Trimer, % Calculated	20	20

[a] Polymeric isocyanate (Mobay Chemical);

[b] Silicone surfactant (Dow Corning);

[c] 24, 6-tris(dimethylaminomethyl) phenol

Table 5.5 Laminate Foam Properties [35]

Subject	Properties
Trimer content	20 %
E-84 tunnel test:flame spread	25–26
:smoke development	< 100
Thermal conductivity (Btu-in/Hr.Ft^{2}F°	0.14
Dimensional stability (1″ × 5″ × 5″ sample at 70 °C, 95% RH, 28 days	2.0–2.5 % linear growth
Conventional and flame-retarded urethane foams	5–15% liner growth

5.2.1.3 *Aromatic Polyol-Modified Polyisocyanurate Foams*

Aromatic polyols include reclaimed PET (polyethylene terephthalate) and Mannich polyols. Advantages of aromatic polyols as modifiers are high char formation and less smoke generation from foams. Disadvantages include low polyol functionality (e.g., 2.0) and high viscosity. Low functionality of aromatic polyols results in low dimensional-stability foams, and the high-viscosity of aromatic polyols result in problems in handling and processing foam systems. System development studies, therefore, are being conducted at various companies [18–20, 22]. All water-blown polyisocyanurate foams that use aromatic polyester polyols have been reported [18, 20, 36].

5.2.1.4 *Resole Resin-Modified Polyisocyanurate Foams*

Resole resin have phenolic OH group and a methylol OH group, and these groups react with isocyanate to form a urethane linkage. Hodogaya Chemical has commercialized a series of systems named Danfunen NFPI for the production of metal-faced wall panels [27]. Table 5.6 shows some

Table 5.6 Resole-Modified Polyisocyanurate Panel Foam [27]

Weight ratio of components: A/B = 100/200 where A: resole-component B: MDI component
Foam properties
  Foam density (core): 28 kg/m^3
  Compressive strength (10%): 1.7 kg/m^3
  Thermal conductivity: 0.00330 W/m.Kg/100cm^2
  Water absorption: 0.9g/100cm^2
  Dimensional stability
    –20°C, dry, 48 hr.: –0.1% vol.
    90°C, dry, 48 hr.: –0.8%vol.
    70°C, 95% RH, 48 hr.: + 0.5 % vol
Foam flammability
  Oxygen index: 26
  ASTM E-84, flame spread: 20–22
    Smoke: 150–200
Adhesive strength to galvanized steel (tensile strength, cured at 2 min 60°C) 1.6 Kgf/cm^2

of the characteristics of foam systems and foam properties according to a Hodogaya Chemical technical bulletin. Figure 5.39 shows the wall panels.

5.2.1.5 Furan Resin-Modified Polyisocyanurate Foams

A furan resin was prepared by the reaction of furfuryl alcohol with formaldehyde. The resin contained 20 to 40% bis-(2, 5-hydroxymethyl) furan monomer, 2 to 3% furfuryl alcohol, and 1% water. Ashida and Jiang used the furan resin as a modifier for polyisocyanurate foam preparation. The resulting foams had excellent char-forming characteristics, for example, 98% weight retained by the Butler Chimney test. The modified isocyanurate foams also had high flexural and compressive strength [37].

5.2.1.6 Isocyanurate-Modified Urethane Foams

An isocyanurate linkage was used as a smoldering and ignition suppressant for TDI-based flexible foams. The addition of the linkage in small amounts (e.g., 115% isocyanate index) lowers the melting temperature of foams and results in melting out from fire zone. There are no char-forming effects [38].

5.2.2 Blowing Agents for Polyisocyanurate (PIR) Foams

This section is a review from the standpoint of blowing agents for PIR foam.

5.2.2.1 All-Water-Blown Polyisocyanurate Foams

Water blowing agents have the following advantages and disadvantages:

Advantages:
  1. No ozone depleting potential (ODP)
  2. Marginal global warming potential (GWP)
  3. Lower costs than HFCs (if the consumption of polyisocyanate is not considered)

Disadvantages
  1. Higher mixing ratio of components A/B than physical blowing agents
  2. Higher viscosity of system component B than physical blowing agents, resulting in flowability problems for systems
  3. Lower dimensional stability in low-foam-density foams in less than 3.0 pcf.
  4. Poor initial adhesion to steel, aluminum, or paper
  5. Poor storage stability of polyester polyol-based systems
  6. High friability of foam owing to reduced trimer content because of urea linkage
  7. High flammability owing to low trimer content

The problems of high friability and high flammability can be solved by the sole use of physical blowing agents, especially azeotrope blowing agents because of better compatibility [39].

Extensive studies on water-blown polyisocyanurate foams have been reported in several papers [18, 20, 25, 26, 36].

According to Skowronski et al. [36], the blowing agents evaluated included HCFC 22, n-pentane, water, a blend of water and HFCs, and water and CO_2 gas. This paper pointed out that the cause of poor dimensional stability of all-water-blown polyisocyanurate foams is due to the faster diffusion of CO_2 gas cells from foam cells and slow diffusion of air into foam cells. Therefore, good dimensional stability can be reached when utilizing higher densities of not lower than 2.7 pcf (43.2 kg/m^3). The use of HFCs, for example, HFC-245fa and HFC-365mfc, as co-blowing agents, gives better physical properties.

An example of production conditions of all-water-blown lamination foam is as follows:

Conveyer temperature: 122°F (50°C)
Isocyanate index: 240 to 260
Foam density: 2.82 pcf (45.1 kg/m^3)

All-water-blown polyisocyanurate foams were also studied by Moriya et al. [20] and Naruse et al. [19]. Moriya et al. selected an aromatic polyol, a catalyst, and a surfactant that improved the nonflammability characteristics of all-water-blown foams. Furthermore, this foam met the Japanese Industrial standard (JIS) A-1321 Grade 2 incombustibility standard [18]. However, the storage stability of all-water-blown foam systems was not satisfactory. Naruse et al. conducted studies to improve the storage stability of a polyol premix of all-water-blown polyisocyanurate foam systems [20].

5.2.2.2 C_5-Hydrocarbon (HCs)-Blown Polyisocyanurate Foams

Polyisocyanurate foams are widely used as the core material in metal-faced sandwich panels for building applications. The required foam properties, therefore, include low friability, good adhesion, good insulation, and low flammability. Current papers [22, 40, 41] discuss HC-blown polyisocyanurate foams.

Skowronski and Pignagnoli [40] reported that some HC blown systems meet the following standards: UL 723/ASTM E-84 Class 1, the German DIN 4102 B2, and the EN 13823 European standard. Singh et al. investigated the aging properties of pentane-blown polyisocyanurate panel boards [41]. Feske et al. [22] studied pentane-blown polyisocyanurate foams for roofing at low isocyanate indexes of 250 and 275. The results were unsatisfactory due to low isocyanate index.

5.2.2.3 HFC-Blown Polyisocyanurate Foams

Many papers on HFC blowing agents (i.e., HFC-245fa and HFC-365mfc) have appeared in the literature [38, 42–56] (see also Chapter 3). These blowing agents

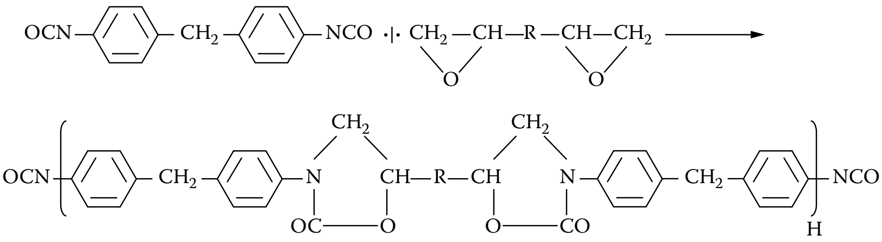


Figure 5.9 NCO-Terminated Poly-2-Oxazolidone Prepolymer [5.20].

are excellent not only for rigid urethane foams but also for polyisocyanurate foams. However, because of unusually high costs, their use is limited in the U.S. refrigerator and construction industries. Accordingly, developmental studies for polyisocyanurate foams are not being attempted.

5.2.2.4 Blends of Third Generation Blowing Agent-Blown Polyisocyanurate Foams

The main objective of blending is cost reduction. Another objective is to enhance the flowability of system injection into void spaces by means of the frothing action of small amounts of water in the system. The disadvantage of water addition is that it increases the component ratio A/B and decreases the storage stability of foaming systems.

5.2.2.5 Halogen-Free, Zero-ODP Azeotrope-Blown Polyisocyanurate Foams

A detailed description of halogen-free, zero-ODP azeotrope is available in Chapter 3. An application example is given in the *Journal of Cellular Plastics* [61]. The data shows good compatibility with foam formulations and efficient foaming properties.

5.2.2.6 Blend of C_5-hydrocarbon HC- and Methylene Chloride-Blown Polyisocyanurate Foams

Blends of HC and haloalkane have been found to be effective blowing agents for polyisocyanurate foams [55]. An example of the blend ratio is 20% by weight of pentane and 80% by weight of methylene chloride.

5.2.3 Polyisocyanurate Foams Modified by non-Urethane Linkages

5.2.3.1 2-Oxazolidone-Modified Polyisocyanurate Foams

Modified polyisocyanurate foams are substantially flame retardant without the addition of extra flame retardant materials. However, urethane-modified polyisocyanurate foams have relatively minor flame-retardant properties because the urethane modifier is a relatively low flame retardant. Therefore, the use of high-flame-retardant linkages as modifiers can improve the flame-retardant properties of urethane modified polyisocyanurate foams.

The 2-oxazolidone linkage is a temperature-resistant linkage in terms of activation energy, as shown previously in Figure 5.3 [5]. The figure clearly indicates that the order of thermal stability increases in the following order: urethane linkage, 2-oxazolidone linkage, isocyanurate linkage.

The 2-oxazolidone linkage is regarded as a cyclic urethane linkage, with no labile hydrogen. In contrast, the urethane linkage has a labile hydrogen and dissociates at elevated temperatures as shown previously in Figure 5.2. This difference is the reason for the temperature stability of the 2-oxazolidone linkage.

Pankratov et al. prepared an excellent review regarding 2-oxazolidones. [62]. Ashida and Frisch reported a method of producing oxazolidone-modified polyisocyanurate foams with higher properties in thermal stability, flame resistance, and low smoke generation. The method consists of a two-step process. In the first step NCO-terminated prepolymer is prepared and in the second step, the prepolymer is trimerized.

The optimum equivalent ratio of Epoxy/NCO is in the range of 0.05 to 1.5 as shown in Figure 5.10, when Epon 828TM (bisphenol A-epichlorohydrin) and polymeric isocyanate are used; DMP 30 (2,4,6-tris [dimethylaminomethyl] phenol) and CFC-11 were used as major raw materials. Figure 5.11 shows the effect of the epoxy/NCO equivalent ratio vs. burn-through time. Figure 5.12 shows the effect of the epoxy/NCO equivalent ratio vs. the percent weight loss of tumbling friability.

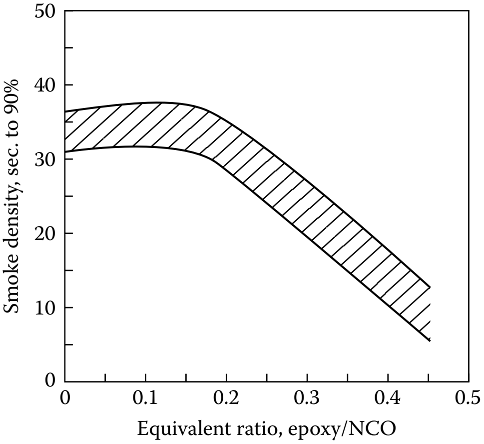


Figure 5.10 Effect of Epoxy/NCO Equivalent Ratio on Smoke Density, [5.11].

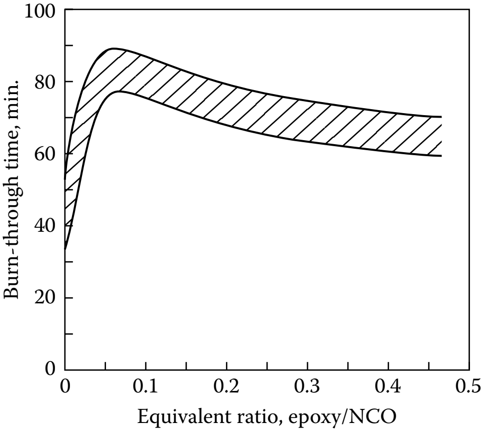


Figure 5.11 Effect of Epoxy/NCO Equivalent Ratio on Burn-Through Time, [5.11].

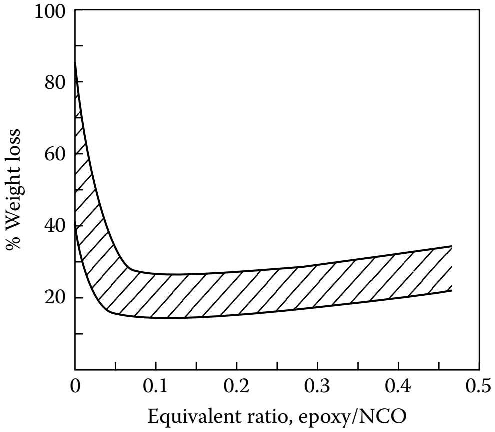


Figure 5.12 Effect of Epoxy/NCO Equivalent Ratio on Tumbling Friability, [5.11].

5.2.3.1.1 2-Oxazolidone Catalysts. Ashida has developed various oxazolidone catalysts. For example, Lewis acids (e.g., $FeCl_3$, $AlCl_3$, $ZnCl_2$) were found to be effective 2-oxazolidone catalysts that exist in polymeric isocyanates as impurities. It is interesting that pure MDI did not contain the Lewis acid as an impurity, so it did not produce 2-oxazolidones [63].

The second group of 2-oxazolidone catalysts includes metal alcoholates such as aluminum (Al) isopropoxide, calcium (Ca) ethoxide, and magnesium (Mg) ethoxide [63, 64]. Very effective catalysts discovered by Ashida are complexes consisting of Lewis acid and Lewis base [65, 66] such as $AlCl_3$-tetrahydrofuran, $AlCl_3$-N-methyl pyrrolidone, $AlCl_3$-hexamethyl phosphoric triamide, and $AlCl_3$-tris (2-ethylhexyl) phosphorine oxide, as shown in Table 5.7. Other types of 2-oxazolidone catalysts are also discussed in Chapter 3.

Table 5.7 Complexes Consisting of Lewis Acid and Lewis Base [65, 66]

Catalyst Type	Catalyst Amount (m.mole)	Yield (%)	Melting Point (°C)
$AlCl_3$ tetrahydrofuran	5.0	79.6	143
$AlBr_3$ tetrahydrofuran	5.0	79.2	143
AlI_3 tetrahydrofuran	5.0	68.8	143
$ZnCl_2$ tetrahydrofuran	5.0	19.0	143
$FeCl_3$ tetrahydrofuran	10.0	23.4	143
$AlCl_3$ dibutyl ether	5.0	77.3	145
$AlCl_3$ triethylamine	5.0	5.09	139
$AlCl_3$ n-metyl pyrrolidone	5.0	85.5	143
$AlCl_3$ hexamethyl phosphtic triamide	5.0	63.9	144
$AlCl_3$ tris(2-ethylhexyl) phosphine oxide	5.0	90.7	143

Test Condition: Phenyl isocyanate: 0.10 mole; phenyl glycidyl ether: 0.10 mole; benzene: 50 ml; heating: refluxing benzene for 7 hours

5.2.3.2 *Amide-Modified Polyisocyanurate Foams*

It has been recognized that the higher the thermal stability of polymers, the less generation of flammable gases from the polymers and, therefore, the less smoke that results. Hence using a more thermally stable linkage as modifier results in foams with low smoke density. The thermal stability of the amide linkage is higher than that of the urethane linkage and, therefore, the amide linkage is a suitable modifier. Figure 5.13 shows model structures of amide-modified polyisocyanurate foams [23]. This paper concluded the advantages as follows.

1. Higher weight retention percent in the Butler Chimney test
2. Higher thermal stability in terms of TGA profile
3. Smaller percent of tumbling weight loss
4. Finer cell size and higher closed-cell content
5. Better dimensional stability
6. Smaller aging of K-factor

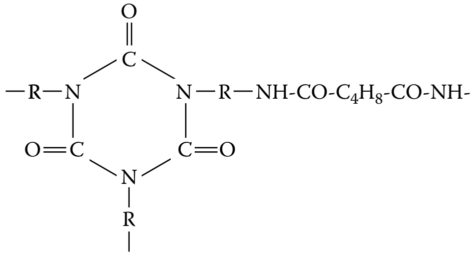


Figure 5.13 Amide-Modified PIR foam, [5.23].

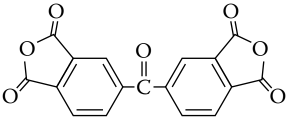


Figure 5.14 3,3′,4,4′, - Benzophenonetetracarboxylic Dianhydride (BTDA), [5.21].

5.2.3.3 Imide-Modified Polyisocyanurate Foams

Kashiwame and Ashida [67] studied the temperature stability of polyimide foams in terms of TGA. According to this paper, a 90% decomposition was found to occur at about 550°C [68].

Imide-modified polyisocyanurate foams were prepared by the one-step reaction of polymeric MDI with BTDA (benzophenone 3,3′,4.4′-tetracarboxylic dianhydride) at 120°C with no solvent. Figure 5.14 shows the chemical structure of BTDA, and Figure 5.15 shows a model reaction of imide-linkage formation using phthalic anhydride and phenyl isocyanate.

In addition to cyclotrimerization catalysts, an imide-forming catalyst, Kacac (potassium acetylacetonate in diethylene glycol), was used. Neither solvents nor physical blowing agents were used, since imide linkage formation generates CO_2 gas.

TGA profiles and smoke densities of imide-modified polyisocyanurate foams at different equivalent ratios were determined. The test results exhibited excellent properties. Figure 5.16 shows smoke density, and Figure 5.17 shows the TGA profile of imide-modified polyisocyanurate foams at different equivalent ratios.

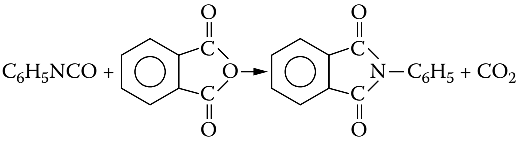


Figure 5.15 Model Reaction of Imide Linkage Formation [5.21]

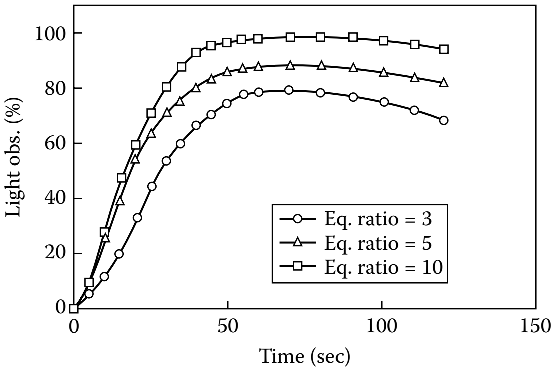


Figure 5.16 Smoke Densities of Imide-Modified PIR Foams, [5.21].

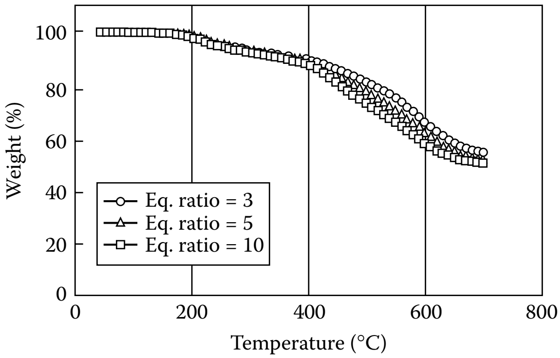


Figure 5.17 TGA Profiles of Imide-Modified PIR Foams, [5.22].

5.2.3.4 *Carbodiimide-Modified Polyisocyanurate Foams*

The carbodiimide linkage is obtained by the condensation reaction of isocyanate groups in the presence of a catalyst, such as 1-phenyl-3-methyl-2-phospholene-1-oxide (PMPO). This reaction is shown below:

$$2\ \mathrm{R{-}N{=}C{=}O} \longrightarrow \mathrm{R{-}N{=}C{=}N{-}R} + \mathrm{CO_2}$$

Foams were prepared by the one-step process at room temperature with no blowing agents [24]. Figure 5.18 compares the thermal stability of various foams by TGA profiles. Figure 5.19 shows various properties of carbodiimide- modified

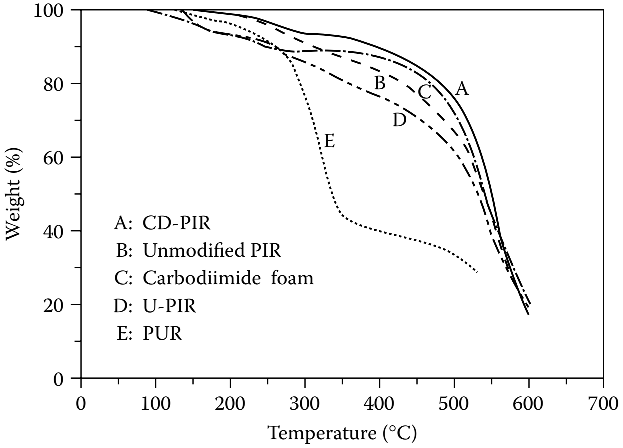


Figure 5.18 TGA Profiles of Various Modified PIR Foams, [5.22, 5.95].

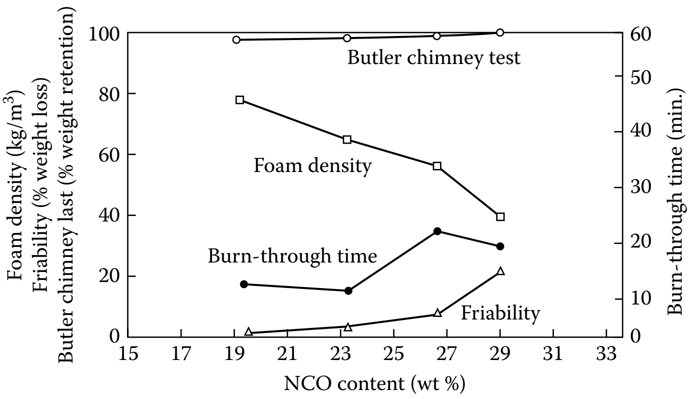


Figure 5.19 Relationship between NCO-content vs. Foam Properties of Carbodiimide-Modified PIR Foams, [5.22, 5.95].

polyisocyanurate foam. It is interesting of note that 99.1% of the weight was retained in the Butler Chimney test. Furthermore, the carbodiimide modified PIR foam exhibited a long burn-through time. These figures represent essentiall nonburning. In addition, carbodiimide modified PIR foams have remarkably low tumbling friability (e.g., 5 to 10%).

Another example of a modified polyisocyanurate foam is carbodiimide-blown polyisocyanurate foams (not water blown). These foams were used for metal-faced panel production [25]. Foams blown with water do not adhere well to facing metals. However, foams blown with carbodiimide exhibited improved strength of adhesion to steel facings.

5.2.3.5 Secondary Aromatic Diamine-Modified Polyisocyanurate Foams

Aromatic secondary diamine available in the U.S. market has the chemical structure shown in Figure 5.20. Its trade name is Unilink 4200 (UOP Inc., USA) [26].

Unilink 4200 produces N-substituted urea-modified polyisocyanurate foams by the reaction of the secondary amino group with the isocyanate group. A model reaction is shown in Figure 5.21.

The resulting foams have low tumbling friability (e.g., 9.0%), high Butler Chimney weight retention (e.g., 97.5%), and a high oxygen index (e.g., 26.5).

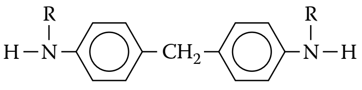
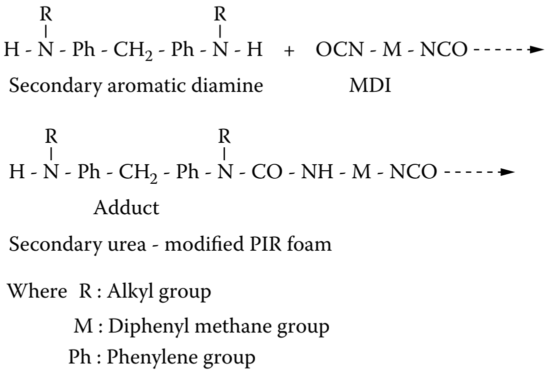


Figure 5.20 Unilink 4200™, [5.25].



$$H-\overset{R}{\overset{|}{N}}-Ph-CH_2-Ph-\overset{R}{\overset{|}{N}}-H \quad + \quad OCN-M-NCO \dashrightarrow$$

$$H-\overset{R}{\overset{|}{N}}-Ph-CH_2-Ph-\overset{R}{\overset{|}{N}}-CO-NH-M-NCO \dashrightarrow$$

Figure 5.21 The Use of Secondary Aromatic Diamine as Modifier for PIR Foam, [5.25].

5.3 Chemistry of Cyclotrimerization

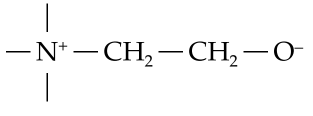
5.3.1 Kinetics and Mechanism of Cyclotrimerization

The mechanism of catalytic cyclotrimerization was reviewed comprehensively by Zhitinkina et al. [3].

Kogon [69] proposed a cyclotrimerization mechanism by tertiary amines as follows: Phenyl isocyanate was reacted with ethyl alcohol in the presence of a catalyst at room temperature, and the resulting product was ethyl carbonate. When the same two compounds were reacted at 120°C without a catalyst, the resulting products were a, b-diphenyl alliphanate and a trace of phenyl isocyanate dimer.

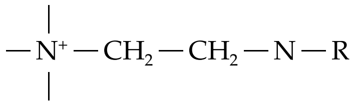
When N-methylmorphorine was added to the reaction system as a catalyst at 125°C, the reaction was altered and the product was triphenyl isocyanurate (isocyanate trimer) in excellent yield. Kogon's mechanism was supported by Taub et al. [70] based on their experimental data.

Jones et al. [71] investigated the co-catalyst mechanism of olefin oxides such as ethylene oxide, propylene oxide, styrene oxide, and epichlorohydrin with a trace amount of tertiary amines. They postulated that amine and olefin oxide produce zwitterions,



$$-\overset{|}{\underset{|}{N^+}}-CH_2-CH_2-O^-$$

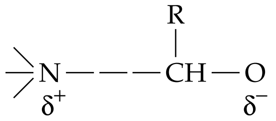
which are the active catalyst species for the trimerization of isocyanates. By analogy, the active catalyst species for the amine–imine combination should have the following structure [72]:



$$-\overset{|}{\underset{|}{N^+}}-CH_2-CH_2-N-R$$

where R is H, alkyl, P=O, or ureide groups.

The active species formed with aldehydes would presumably be:



Tsuzuki et al. [73] proposed that when propiolactone reacts with isocyanates in the presence of an amine catalyst, the following betaine analog is formed:

$$\overset{+}{R_3N}-CH_2-CH_2-CO-\overset{-}{O}$$

Sayigh [13] proposed different mechanisms of cyclotrimerization based on specific catalysts as shown in Figure 5.22. A kinetic study of cyclotrimerization catalyzed by cyclic sulfonium zwitterions was conducted by Kresta et al. [74], who varied the concentration of the catalyst as shown in Figures 5.23 and 5.24.

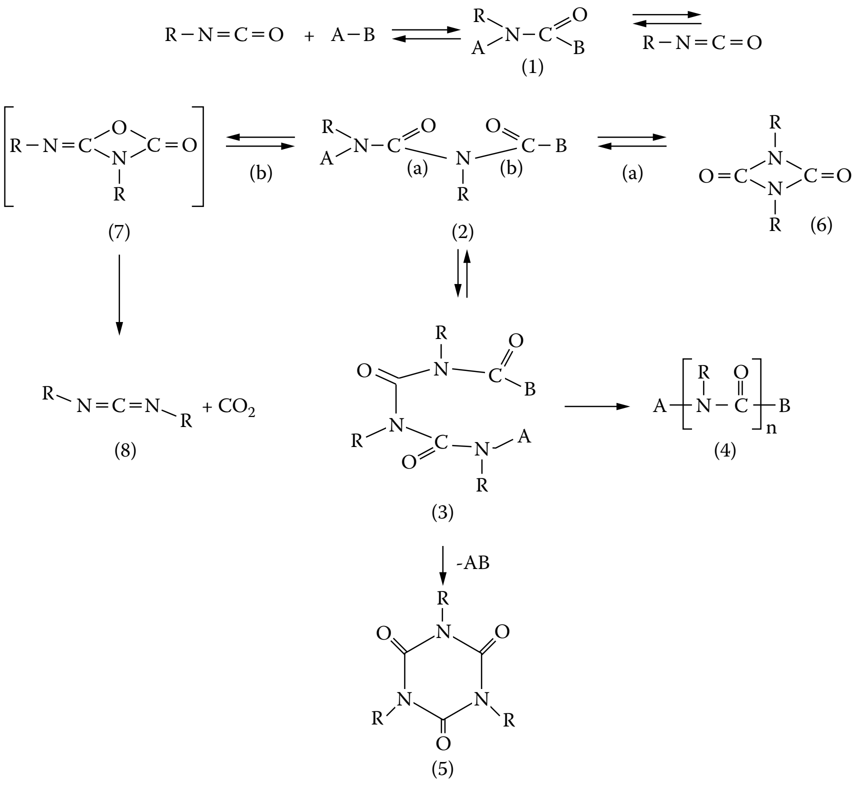


Figure 5.22a General Mechanism of Isocyanurate Formation, [5.8].

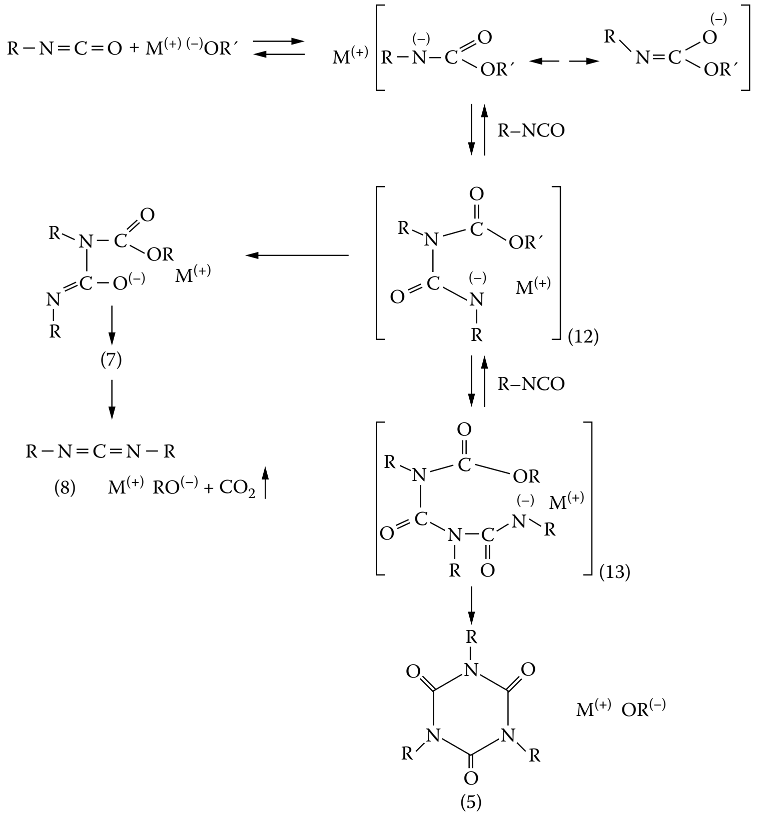


Figure 5.22b Base-Catalyzed Cyclotrimerization, [5.8].

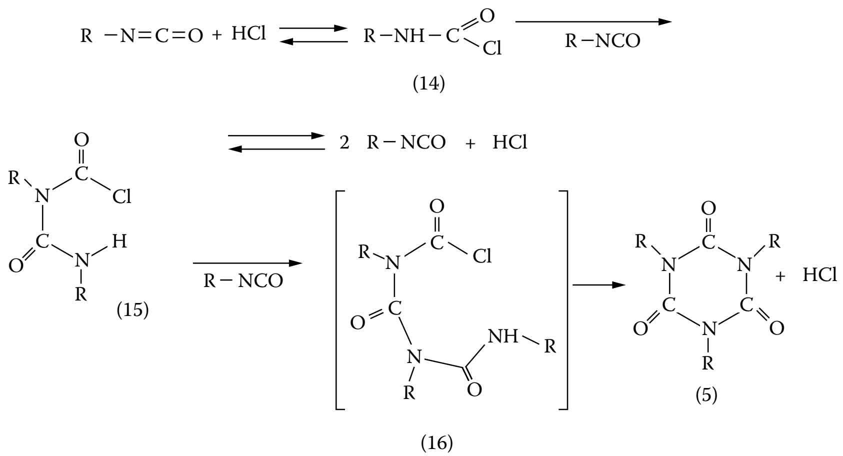


Figure 5.22c Acid-Catalyzed Cyclotrimerization, [5.8].

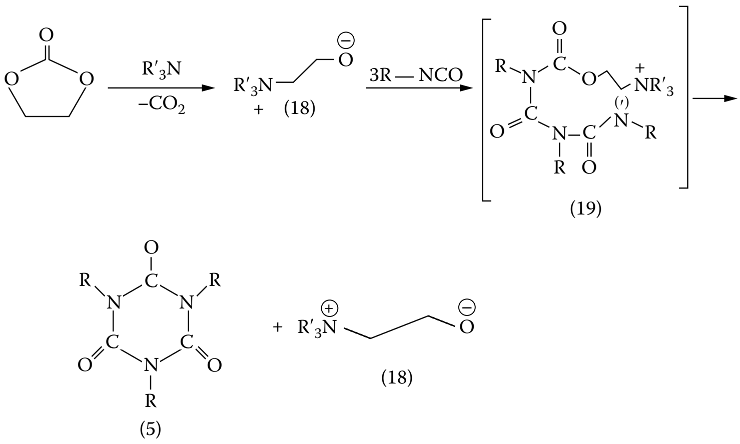


Figure 5.22d Amine-Alkylene Catalysis, [5.8].

Sehovic et al. [75] carried out a kinetic study on the cyclotrimerization of butyl and cyclophenyl isocyanates using quaternary ammonium salt of 2-ethylhexanoic acid. They found that the kinetics of the cyclotrimerization of butyl isocyanate using the 2-ethylhexanoic salt of trimethylaminopropanol-2 was first order with respect to the isocyanate and first order with respect to the catalyst. However, when salicylaldehyde-potassium was employed as catalyst, the cyclotrimerization of butyl isocyanate followed second-order kinetics with respect to the isocyanate and first-order with respect to the catalyst.

Kresta et al. [74] reported a kinetic study of the cyclotrimerization of isocyanates catalyzed by cyclic sulfonium zwitterions. The catalyst employed was 2-methyl-4-(1-thiolanylium) phenolate dihydrate. They concluded that the reaction followed second-order. Figure 5.23 and Figure 5.24 show their results.

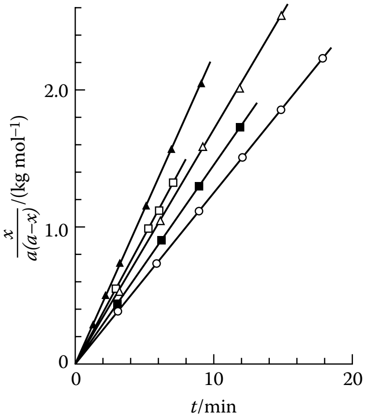


Figure 5.23 The Integral Foam of the Second Order-Time Plot for the Cyclotrimerization of Phenyl Isocyanate, [5.73].

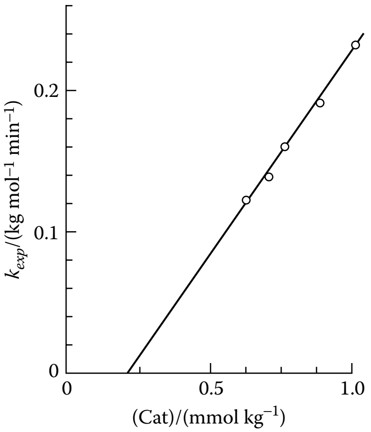


Figure 5.24 Relationship Between n K_{exp}. and Concentrtation of Catalyst, [5.73].

5.3.2 Relative Catalytic Activity Studies in Nonsolvent Systems

Cyclotrimerization catalysts are listed in Figures 5.26 and 5.27. Many kinetic studies by many investigators are available, but all of them were conducted in solvent systems. It should be noted that kinetic studies are significantly influenced by the solvent. An interesting investigation of the effects of solvents on the rate of trimerization of phenyl isocyanate is reported by Nicholas and Gmitter [7], Table 5.8 shows the data.

Ashida [37, 76] reported kinetic studies without solvents using gel time determination. Nonsolvent studies would simulate foaming systems. The experimental apparatus employed is shown in Figure 5.25, and the cyclotrimerization catalysts employed are shown in Figures 5.26 and Figure 5.27.

Some of the relationships between the catalyst concentration, C, and the gel time, *t*, at different temperatures are shown in Figure 5.28, and the same relationship at 120°C is shown in Figure 5.29. Since variables in both axes are expressed in logarithmic scales, the lines are expressed by the following equations.

$$\log t = \log a - b \log C$$

Table 5.8 Effect of Solvents on the Rate of Cyclotrimerization of Phenyl lsocyanate [7]

Solvent	Dielectric Constant at 20°C	Relative Reactivity
Benzene	2.28	1.47
Chlorobenzene	5.67	2.4
Acetonitrile	37.5	8.4
Dimethyl sulfoxide	45.0	12.3

11.9 g (0.1 M) of phenyl isoctanate; 13.1 g of solvent as above 0.1% of N, N′, N″, tris(dimethylaminopropyl) symhexahydrotriazine

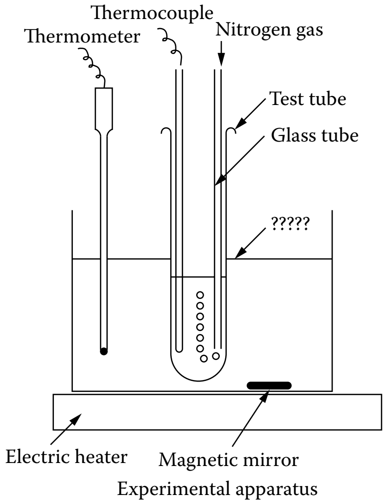


Figure 5.25 Gel Time Determination Apparatus, [5.72].

or

$$t = aC^{-b}$$

where t is the gel time in seconds, "C" is the catalyst concentration as a percent of weight, and a and b are constants.

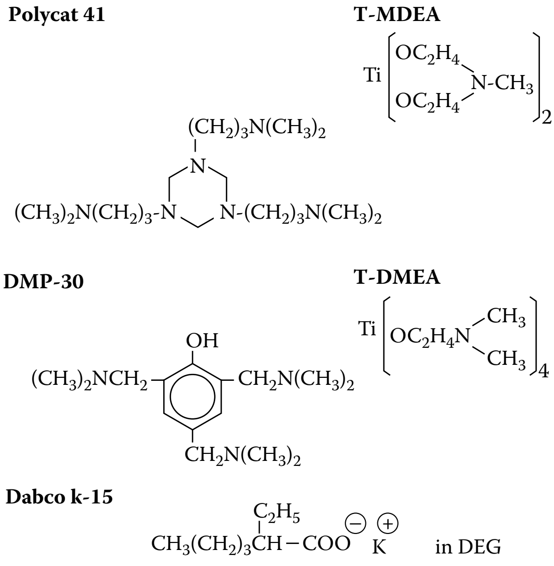


Figure 5.26 Cyclotrimerization Catalysts -1, [5.81].

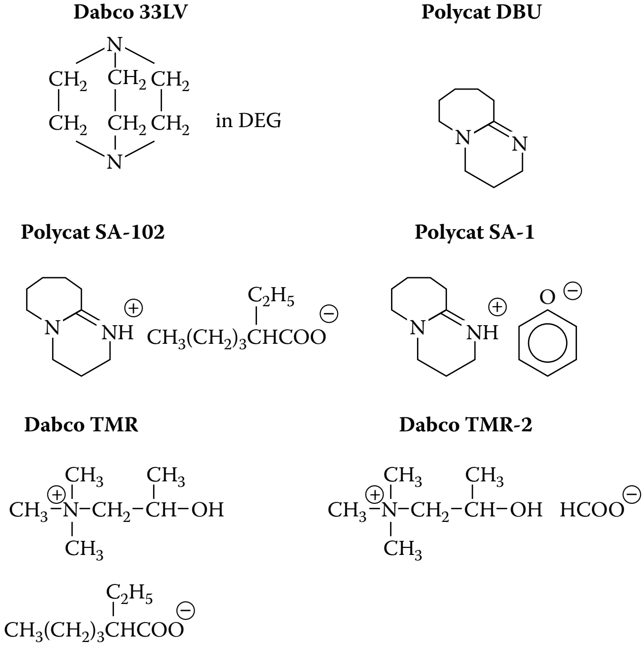


Figure 5.27 Cyclotrimerization Catalysts-2, [5.81].

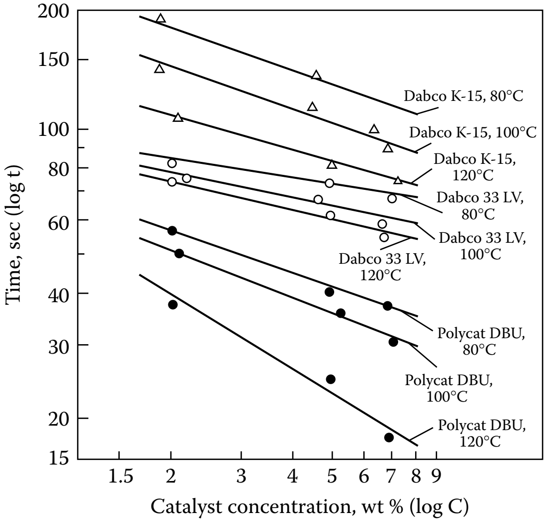


Figure 5.28 Cyclotrimerization Catalysts vs. Gel Time at 80° and 100°C, [5.81].

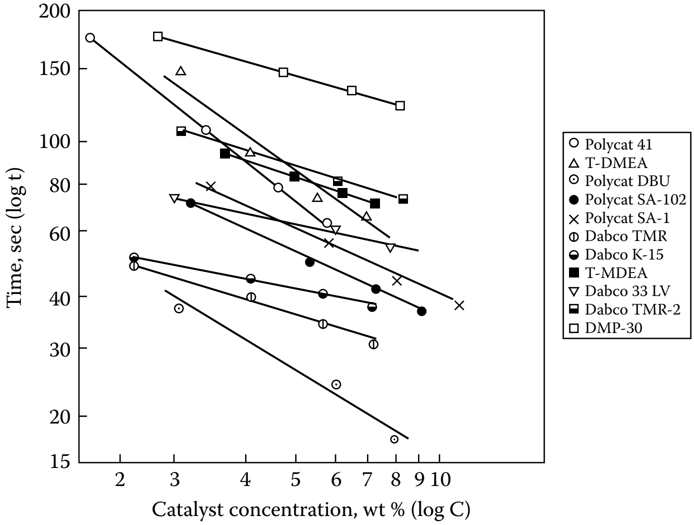


Figure 5.29 Cyclotrimerization Catalysts vs. Gel Time at 120°C, [5.81].

Constant a is a measure of relative catalyst activity at a given concentration and a given temperature. By determining gel times at different catalyst concentrations and temperatures, *b* can be calculated with the following equation:

$$b = \frac{\log(t1/t2)}{\log(C_2/C_1)}$$

where t1 and t2 are gel times at catalyst concentrations C_1 and C_2, respectively. The value can be calculated by using the value b obtained as shown in Figure 5.30.

The above technology was used to determine the relative activity of alkali metal chelates as trimerization catalysts [37]. The chelates employed are potassium chelates of 2-hydroxyacetophenone (HA-K), sodium chelates of hydroxyacetophenone (HA-Na), potassium salicylaldehyde (SA-K), sodium salicylaldehyde (SA-Na), potassium chelates of acetylacetone (AA-K), sodium chelates of acetylacetone (AA-Na), and lithium chelates of acetylacetone (AA-Li).

The catalytic activities of these chelates were found to be in the following decreasing order:

HA – K = SA – K > A – K >> Polycat 41 > Dabco TMR – 2 >> Dabco K – 15

and

HA – K > HA – Na

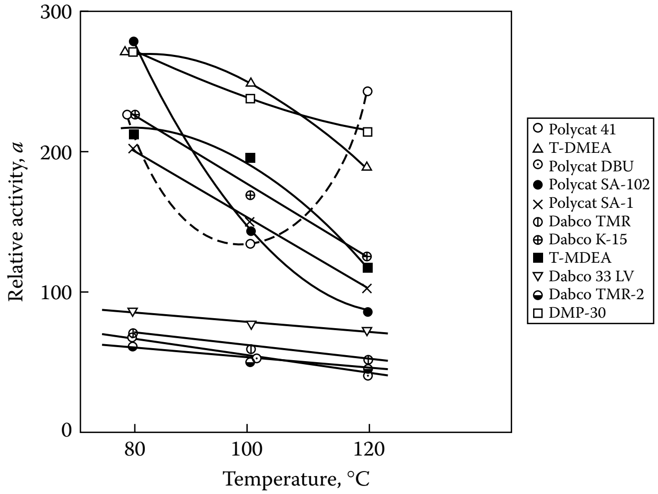


Figure 5.30 Relative Activity vs. Temperature, [5.81].

Foams were prepared using these catalysts, and HA-K resulted in the best properties for both flame retardation and friability. The advantages of the alkali metal chelates as trimerization catalysts include high catalytic activity, no odor, a simple method of preparation, and low cost.

5.4 Properties of Polyisocyanurate Foams

In general, the physical properties of isocyanate-based foams, such as polyurethane foams as well as polyisocyanurate foams have the following logarithmic relationship with the foam density [76]:

$$\log P = \log K + n \log D$$

where P is property, D is density, and K and n are constants.

The outstanding properties of polyisocyanurate foams over flame-retardant polyurethane foams are low flammability without the addition of flame retardants and higher heat and flame resistance. These properties can be obtained by the appropriate choice of modifier described in the Section 5.2 at the specified NCO/OH equivalent ratios.

5.4.1 Flammability

U.S. building codes are based on ASTM E-84 (see Appendix), which is a surface flammability test that uses a 25-foot tunnel. Polyisocyanurate foams prepared with the proper formulations can clear the rating of class 1 (flame spread of 25 feet). A laboratory-scale flammability test is the Butler Chimney test (ASTM D 3014), which is a vertical testing method. The results are expressed by percent of weight retained. Good examples of the Butler Chimney test are in a range of 96.2% to 99.0% by weight retained [15].

5.4.2 Flame and Heat Resistance

Flame and temperature resistance is also an excellent advantage of polyisocyanurate foams. The Bureau of Mines flame penetration test (or Burn-through test) [77] exhibits the superior flame and heat resistance of polyisocyanurate foam.

The test apparatus is shown in Figure 5.5 and some test results are shown in Figure 5.6 (see Section 5.2.1). Good polyisocyanurate foams have at least 30 minutes of flame penetration time for a 1-inch thick foam specimen.

It is well known that the tensile strength of iron decreases sharply at 700 C. Accordingly, in case of a steel tank fire, the heat input into steel tanks must be kept below 700°C. Therefore, the heat input requested is less than 91/MJ/hour (86,000 BU/hour) by applying heat- and flame-resistant insulation layers [9, 78].

Suitable fillers include talc and graphite. Large-scale fire tests were conducted as shown in Figure 5.31a, and fire test results are shown in Figure 5.31b.

The testing conditions employed were as follows: The polyisocyanurate foams were foamed in place at 80 mm thickness with a seamless layer on outside of an iron tube with 200-mm diameter, 6-mm thickness, and 2,500-mm length. A sheet of asbestos cloth was wrapped around the tube, and a mortar coating was made over the wire mesh. The insulated tube was kept over a set of burner heads with 60-mm nozzles that were arranged cylindrically. Propane gas was burned at a rate of 10 m^3 per hour. The temperature inside the tube was measured during the test, and the results are shown in Figure 5.32.

The heat- and flame-resistant insulation layers were prepared as follows: Two layers of 50-mm perlite board covered with a mortar layer was not

Table 5.9 Fire Resistance of Filled Polyurethane and Polyisocyanurate Foams [9]

Foam	Inorganic Powder	Flame Penetration Time* (minutes)
PUR	Zero	1
PUR	Graphite 30%	8
PUR	Talc 30%	15
PIR**	Graphite 40%	180
PIR**	Talc 40%	220

* Bureau of Mines, Report of Investigation #6366, (1964);
** NCD/OH equivalent ratio: 5.0000000

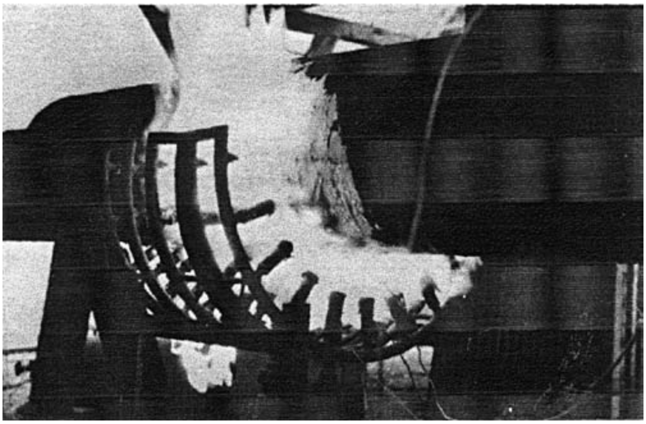


Figure 5.31a Large Fire Test Apparatus, [5.44].

flame resistant, and the inside temperature reached to 700°C in 45 minutes. In contrast, the curve #1 (foam 80 mm + asbestos cloth + wire netting + mortar) showed excellent flame resistance since the inside temperatures after 10 hours reached only 300°C. Therefore, no decrease of tensile strength of the iron tube was detected.

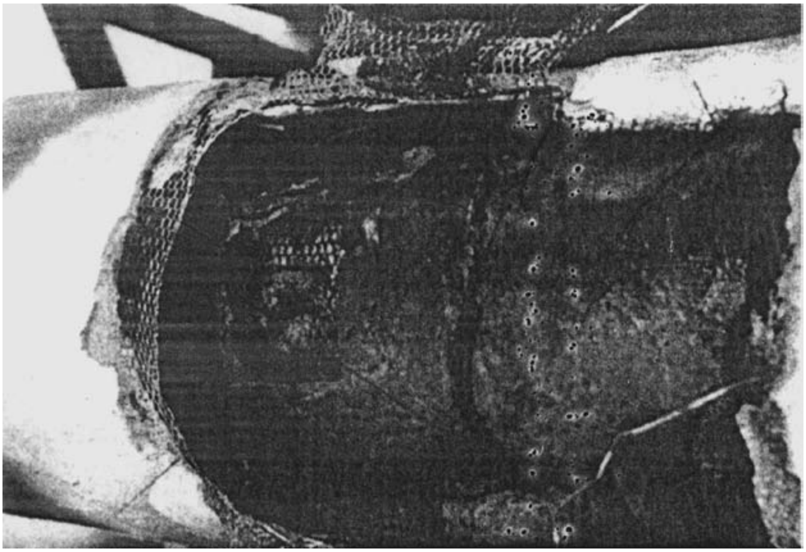


Figure 5.31b Large Fire Test Results—Carbonized PIR Foam, [6.44].

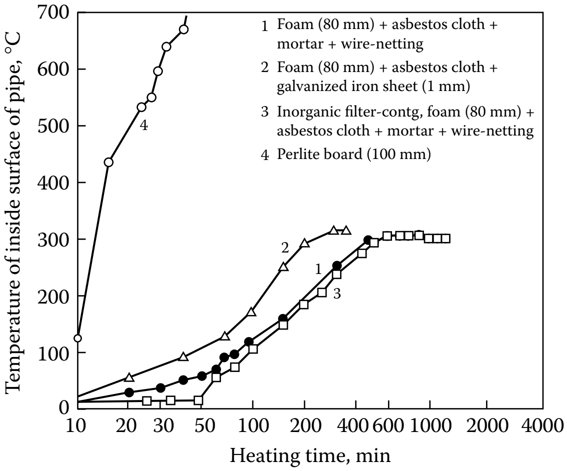


Figure 5.32 Inside Temperature of Large Fire Test, [5.44].

5.4.3 Smoke Suppression

Polyurethane and polyisocyanurate foams have been used in commercial and household applications in recent years. The demand in the building market is especially growing. However, the hazards of smoke generated from building materials have become one of the most serious problems.

The smoke hazards include smoke hindering the escape of occupants, smoke interfering with fire fighting efforts, and the accompanying toxic hot gases being lethal even in areas remote from the flame front. Accordingly, the smoke suppression problem of polyurethane and polyisocyanurate foams has become one of the most important problems to be solved.

So-called flame retardants are based on halogen-containing compounds that generate dense black smoke and increase smoke density. Ashida et al. [30, 79] proposed two methods of smoke suppression. One method is the smoke scavenger method, and the other method is the specific silicone-modification method. The smoke density of the foam obtained was measured by a Rohm and Haas Smoke Chamber.

5.4.3.1 Smoke Scavenger Method

The principle of the smoke scavenger process [30] is that a smoke scavenger is added (10 parts per 100 parts of polyol) to the polyisocyanurate foaming system, so that black smoke can be removed. The scavengers are aromatic aldehydes including benzaldehyde, furfural, p-hydroxybenzaldehyde, and cinnamaldehyde. Benzaldehyde was found to be the best smoke scavenger. Figure 5.33a and 5.33b show comparative data of smoke densities. The addition

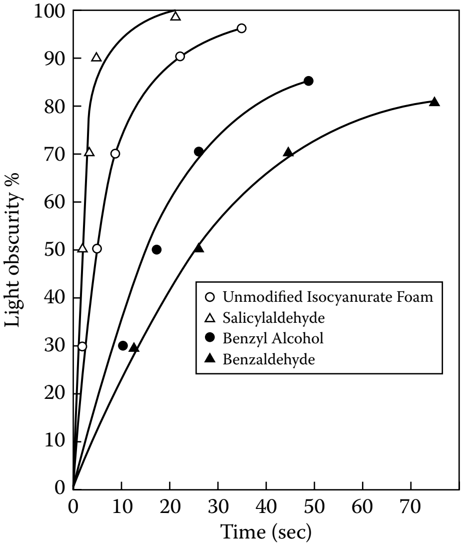


Figure 5.33a Effect of Aromatic Aldehyde on Smoke Suppression, [5.84].

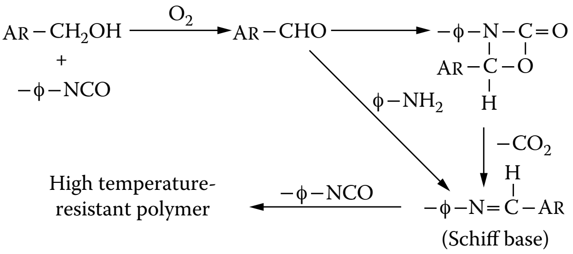
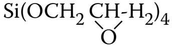


Figure 5.33b Formation of Schiff Base as Smoke Scavenger, [5.84].

of aromatic aldehyde resulted in remarkable improvements in smoke suppression, higher flame resistance by flame penetration tests, and a lower flame-spread rating by the Butler Chimney test, but the resultant foams had the disadvantage of unsatisfactory friability as measured by Tumbling friability tests.

5.4.3.2 Smoke Suppression by Silicon-Containing Compounds

Polyisocyanurate foams were prepared utilizing silicon-containing compounds as smoke suppressants [79]. Poly (siloxane-oxyalkylene) block copolymers with a high ratio of ethylene oxide (EO)/Si and a low ratio of propylene oxide (PO)/Si produced a foam with very low friability, a remarkable reduction in smoke generation, and lower surface flammability. Unfortunately such foam is not cost-effective.

Compound added	Foam	Density KG/M^3	Si %	Max. %	Light obs. sec.	Butler %	Btt. min.	C-421 %
None	IC*	35	0	96	30		(Bursting)	
$Si(OC_2H_5)_4$	IC	43	1.05	95	52	79	50	32
 $Si(OCH_2\underset{O}{CH\text{-}H_2})_4$	IC	33	0.52	73	55	83	92	60
$Si(OC_6H_5)_4$	IC	38	0.46	95	42	83	NA	92
$C_6H_5Si(OC_2H_5)_3$	IC	31	0.85	96	42	82	70	78
$CH_3Si(OC_2H_5)_3$	IC	33	1.13	97	46	67	63	45
 $\underset{O}{CH\text{-}CH}CH_2O(CH_2)_3Si(OCH_3)_3$	IC	33	0.99	96	52	82	97	65
$CH_2{=}CHSi(OC_2H_4OCH_3)_3$	IC	33	0.85	94	61	82	145	65
$CH_3Si(OC_2H_5)_3$	OX**	43	1.15	94	50	78	49	28
$Si(OC_2H_4OH)_4$	OX	31	0.75	90	45	75	70	67

Note: (a) IC:

Unmodified polyisocyanurate foam

(b) OX:

Oxazolione-modified polyisocyanurate foam

(c) Light obscuration:

Test method : ASTM D-2843-70, data is recorded as % and time (sec).

Chamber : Rohm & Hass XP-2 smoke chamber is used.

(d) Butler:

Butler chimney flammability test, ASTM D-3014

Data is recorded as % weight retained.

(e) C-421:

Tumbling friability test, ASTM C-421

Data is recorded as % weight loss.

Figure 5.34 Silicone Compounds as Smoke Suppressants, {5.85].

Other evaluated silicon-compounds were organosilicates, as shown in Figure 5.34 [79]. Tetrahydroxyethyl orthosilicate (Si $[OC_2H_4\text{-}OH]_4$) and tetraethylorthosilicate (Si $[OC_2H_5]_4$) have been found to be cost-effective and powerful smoke suppressants for modified polyisocyanurate.

5.4.4 HCN Generation

In connection with black smoke generation, accompanying hydrogen cyanide (HCN) gas generation is a serious fire problem. Toxic hazards can occur in areas far from flame front. Some of the literature discusses HCN generation from urethane foams in nitrogen or air atmospheres [80–84]. Ashida et al. studied HCN generation from isocyanate-based foams and N-containing

Table 5.10 Effect of Atmospheric Gas on HCN Generation [85]

	HCN, mg/g	
Foam	In Air	In Nitrogen
Rigid urethane foam (PAP 1-135)	11.5	0.23
Rigid urethane foam (TDI)	0.48	0.45
Flexible urethane foam (TDI)	0.50	0.45
Modified isocyanurate foam	19.4	0.66
Polyacrylonitrile yarn	20.4	18.1

polymers in a hot air atmosphere [85]. The apparatus employed was a combustion tube, and the pyridine-pyrazolone method was used to analyze the results [86].

5.4.4.1 Effect of Atmospheric Gas on HCN Generation

Table 5.10 [85] compares HCN generation in nitrogen and in air. HCN generation in nitrogen from polyurethane and polyisocyanurate foams is only a trace amount. In contrast, HCN generation in air is significantly high. These data suggest that the mechanism that produces CN-compounds is the same as the ammono-oxidation mechanism that produces acrylonitrile.

5.4.4.2 Effect of Temperature on HCN Generation

Figure 5.35 [85] shows the relationship between HCN generation and temperature. It is important to note that the maximum generation of HCN in air was found to be at 500°C, and at higher temperatures, at HCN generation decreased sharply due to oxidation. Accordingly, the decomposition temperature of 500°C was used throughout the study.

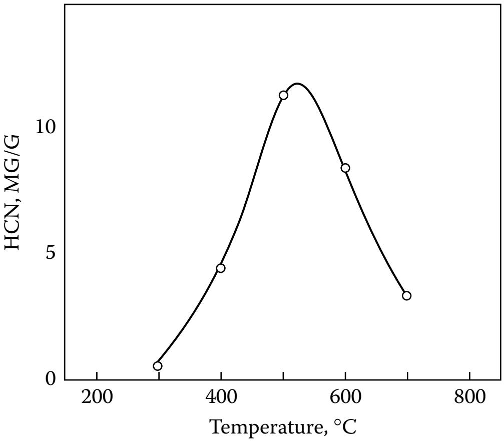


Figure 5.35 Decomposition Temperature vs. Amount of HCN Generation, [5.86].

Table 5.11 HCN Emitted from Foams at °C in Air [85]

	Foam	Isocyanate	Blowing Agent	HCN. mg/g
1	R-U	PPI	R-11	14.1
2	R-U	PPI	CO_2	17.1
3	R-U	PPI	R-11	11.5
4	R-U	PPI	CO_2	14.6
5	R-U	PPI	R-11	12.8
6	R-U(FR)	PPI	R-11	4.33
7	R-U(FR)	PPI	R 11	8.01
8	R-U	p-TDI	R-11	0.48
9	R-U	p-TDI	CO_2	0.52
10	R-U	c-TDI	R-11	9.01
11	F-U	p-TDI	CO_2	0.11
12	F-U	p-TDI	$CO_{2+R\text{-}11}$	0.50
13	F-U(FR)	PPI	CO_2	1.70
14	F-U	PPI	CO_2	9.13
15	I-M	PPI	R-11	19.4
16	I-M	PPI	R-11	20.7
17	I-M	PPI	R-11	16.6
18	I-M(Kode 25)	PPI	R-11	30.3

R-U: rigid urethane foam; F-U; flexible urethane foam; I-M: modified isocyanurate foam; FR: flame retardant foam; PPI: polymeric isocyanate; p-TDI: 80/20 isomer TDI; c-TDI: undistilled TDI.

5.4.4.3 HCN Generated from Various Polymeric Foams

Table 5.11 [85] lists HCN amounts generated from various polymeric foams including polyurethane and polyisocyanurate foams at 500°C in air.

5.4.4.4 HCN Generation vs. Percent Nitrogen in Foams

Figure 5.36 [85] shows the relationship of HCN generation and percent nitrogen content percent. A remarkable difference can be seen between TDI-based foams and polymeric isocyanate-based foams. TDI-based foams, both flexible and rigid, generated smaller quantities of HCN than did polymeric isocyanate-based flexible and rigid foams. Urethane-modified and oxazolidone-modified polyisocyanurate foams generated larger quantities of HCN than did conventional rigid foams. However, it could be estimated that the foams generate very small quantities of HCN when exposed to flame, because rigid char formed on the foam surface hinders the decomposition of the inside of the foams.

5.4.4.5 HCN from Nitrogen-Containing Polymers

The HCN generation of N-containing polymers were compared at 500°C in air. Table 5.12 [85] shows the results. It is interesting to note that the N-containing polymers in the table generate significant quantities of HCN, but urethane foams generate only small quantities. HCN from polyisocyanurate foams cannot be ignored.

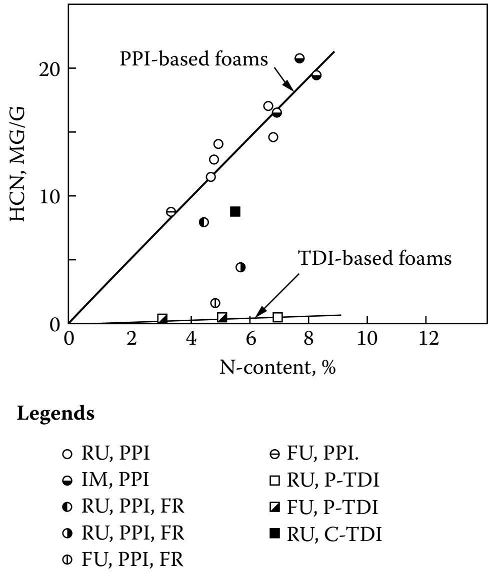


Figure 5.36 % Nitrogen in Foams vs. Amount of HCN Generation, {5.86].

Table 5.12 HCN Generated from N-Containing Polymers [85]

Polymer	HCN (mg/g)
Wool yarn	67.7
Polyacrylonitrile yarn	20.4
Nylon yarn	1.63
Dried sardine	5.33
Rigid urethane foam (PAPI 135)	11.5
Rigid urethane foam (TDI)	0.48
Flexible urethane foam (TDI)	0.11

5.5 Applications of Polyisocyanurate Foam

The application areas of polyisocyanurate foams are based on the low flammability of foams without the addition of flame retardants, high flame resistance, and high heat resistance. These polyisocyanurate foams include urethane-modified polyisocyanurate foams, amide-modified PIR foams, and urea-modified polyisocyanurate foams. However, imide-modified polyisocyanurate foams and carbodiimide-modified polyisocyanurate foams are, in general, open-cell foams, so their thermal insulation property is as low as that of inorganic fibers such as glass fiber and mineral fiber.

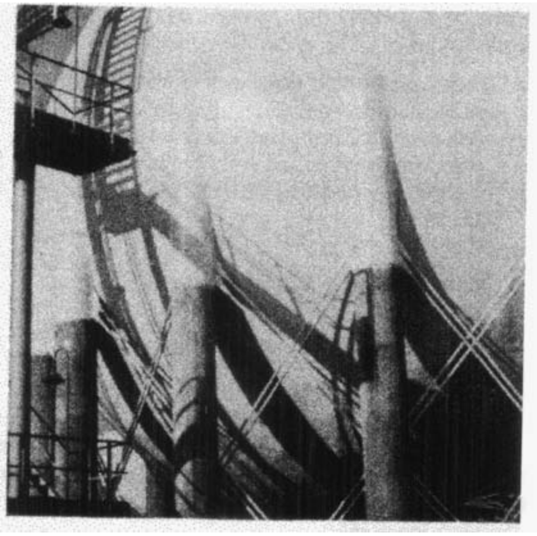


Figure 5.37 Spherical LPG Tank by Frothing-in-Place, [5.44].

Glass fibers have the advantages of noncombustibility and being less expensive, but have disadvantages of low melting points and low flame resistance.

5.5.1 Seamless Insulation for Petrochemical Tanks and Pipelines

For fire safety in petrochemical plants, very strict fire regulations have been issued. In February 1966 the first product in the world of urethane-modified polyisocyanurate foam, Airlite Foam SNB (trademark of Nisshinbo Ind.), was applied by a frothing-in-place process to a petrochemical plant in the Chiba Prefecture Petrochemical Complex in Japan. Application areas included spherical tanks, on-ground tanks, and pipelines [78]. Figure 5.37 shows a spherical LPG tank, and Figure 5.38 shows LPG pipelines.

Figure 5.38 LPG Pipelines by Frothing-in-Place, [5.44].

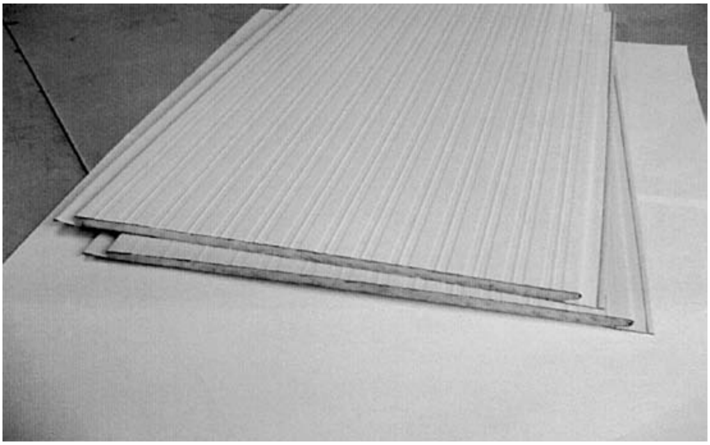


Figure 5.39 Wall Siding by Resol-Modified PIR Foam, [5.18 -c]. (Courtesy of Hodogaya Chemical Co. Ltd).

5.5.2 *Wall Panels*

Exterior walls of high-rise buildings require light-weight, highly thermal insulation. Flame resistance and sufficient physical strength are also required. Polyisocyanurate foam-cored, metal-faced sandwich panels can meet these requirements. Therefore, high-rise building are promising application area for polyisocyanurate foams. Continuous production of metal-faced sandwich panels has been reported [36, 43, 64].

5.5.3 *Residential Wall Sidings*

Metal-faced wall sidings have the advantages of being cheap and light weight, and they are easy to transport and install. They are also used as exterior walls of less-expensive houses. Some of the literature [10, 19, 27, 36, 40] discusses polyisocyanurate foam-cored wall sidings. Figure 5.39 shows an example of wall sidings.

5.5.4 *Cryogenic Applications*

LNG is a mixture of methane, ethane, propane, and butane. Methane has a boiling point of −146°C. LNG is required to be stored and carried as liquid at −162°C.

Komada et al. [16] reported the success of a mesh-lined (ML) system for cryogenic insulation with rigid urethane foams. The use of mesh is very effective for preventing foam cracks. Nadeau et al. discussed the use of polyisocyanurate foams for cryogenic applications [87].

5.5.5 Gashol Tank Floats

Gasoline–alcohol blends (gashol) are increasingly used as automotive fuel. In order to prevent vaporization in storage tanks, rigid polyurethane foam floats are used. A storage problem is that rigid urethane foams are not resistant to gashol, and the foam float swells. Modified polyisocyanurate foam, however, is swelling-resistant to gashol and is used as floats. Currently, gasoline is blended with 10% ethyl alcohol in the United States and 25% ethyl alcohol in Brazil.

References

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Appendix

A.1 Analyses

A.1.1 Analyses of Raw Materials

Polyisocyanate: ASTM D-1638
Polyether oolyol: ASTM D-2849
Rapid method of OH determination: Reference: 3.130
OH determination by phenyl isocyanate: Reference: 3.134

A.1.2 Analyses of Foams

From Reference 3.127 to Reference 3.133

A.1.3 Isocyanates in Air

The International Institute, Inc., Analysis of Isocyanates in Air (1982).

A.2 Testing Methods of Foams

A.2.1 Flexible Urethane Foams: Physical Properties

Air flow: ASTM D-3574, Test G
Aging-steam autoclave: ASTM D-3574, Test K
Aging-steam autoclave: ASTM D-3574, Test J
Bonded foams: ASTM D-3490
Compression force deflection (CFD): ASTM D-3574, Test C
Compression set-constant deflection: ASTM D-3574, Test D
Elongation: ASTM D-3574, Test E
Foam density: ASTMD-3574, Test A
Foam specification-cushioning: ASTMD-3453
HR foam specification: ASTM D-3770
Indentation force deflection (IFD): ASTM D-3574, Test B
Resilience (ball rebound): ASTM D-3574, Test H
Roller shear: ASTMD-3574, Test I-2
Sound absorption: ASTM C-384
Static force loss: ASTM D3574, Test I-1

Tensile strength: ASTM D-3574, Test E
Tear strength: ASTM D-3574, Test E
Yellowness index: ASTM D-1925

A.2.2 Flexible Foams: Flammability

Aircraft seats: FAR # 25.853(c)
Butler chimney: ASTM D-3014
Corner test (small): ASTM D-3894
Furniture seat cushion: California 133
Horizontal flammability (for autos): FMVSS 302
Ignition test: ASTM D-1929
Mattress cigarette test: U.S. Department of Commerce
Mattress and cushion flammability: DOC FF4-72
NBS corn calorimeter-heat release: ASTM E-1354, NFPA-264A
Radiant heat flammability: ASTM D-3675 (similar to E–162)
Vertical flammability: California 117, ASTM F-501

Abbreviations:

FMVSS: Federal Motor Vehicle Safety Standard
ISO: International Organization for Standardization
ASTM: American Society for Testing and Materials
UL: Underwriters Laboratories Inc., USA
FMC: Factory Mutual Corporation
DOC: U.S. Department of Commerce
FAR: The American Federal Aviation Administration

A.2.3 Microcellular Foams

Flexural recovery: ASTM D-3768
Microcellular urethanes—high temperature sag: ASTM D-3769
Specification—shoe soles: ASTM D-3851
Test methods: ASTM D-3489

A.2.4 Rigid Urethane Foams: Physical Properties

Aging: ASTM D-2126
Cell size: ASTM D-3576
Compressive strength: ASTM D-1621 & D-695
Dimensional stability: ASTM D-2126

Foam density: ASTM D-1622
Flexural strength: ASTM D-790
Friability: ASTM C-421
Fungi resistance: Based on ASTM G-21
General properties: ASTM D-2341
Heat distortion: ASTM D-648
Open cell content: (Porosity) ASTM D-2856
Rate of rise: ASTM D-2237
Solvent resistance: Based on ASTM D-543
Specific heat: ASTM C-351
Shear strength: ASTM C-273
Specific heat: ASTM C-351
Tensile strength: ASTM D-638 & D-1623
Thermal conductivity: ASTM C-177, C-518, & D-2326
Water vapor transmission: ASTM E-96
Water absorption: ASTM D-2842

A.2.5 Rigid Foams: Flammability

Burn-through test: U.S. Bureau of Mines, Report of Investigation, No. 6366 (1964) and No. 6837
Butler chimney flammability: ASTM D-3014
Heat and smoke release (Ohio State Univ.): ASTM E-906
Horizontal flammability: ASTM D-1692 (discontinued), UL-94
Monsanto 2-foot tunnel test: *J. Paint Technology*, 39, 494, 1967
NBS smoke density: ASTM E-662 = ISO Dev. Test 5659 (similar to UL-723, NFPA 255)
Oxygen index: ASTM D-2863, (ISO 4589) Vertical
Radiant heat test: ASTM D-3675
Radiant heat test: ISO/DP 5658; ASTM E-162
8-foot tunnel test: ASTM E-286
Tunnel test of building materials: ASTM E-84
30/30 tunnel test: *J. Cell. Plastics*, April, 309, 1967
4-foot tunnel test: *J. Fire Flammability*, (1972), p.154.
XP-2 smoke density: ASTM D-2843

A.2.6 Rigid Foams: Electrical Properties

Dielectric constant and dissipation factor: Based on ASTM D-1673
Dielectric breakdown and dielectric strength: ASTM D-149
Electrical resistance: ASTM D-257

A.3 Unit Conversion

The standard units of ASTM have been switched from the English units to the SI units.

ASTM designation: E-380-89a: "Standard Practice for Use of International System of Units (SI)" (the modernized metric system) lists the unit conversion factors from the English units to the SI units.

Unit Conversion: From English Units to SI Units

English Unit × Multiplier = SI Unit			
Density	lb/ft^3	16.018	kg/m^3
	lb/ft^3	0.0160	g/cm^3
	lb/in^3	7440	g/cm^3
Stress or pressure	lb / in^2	0.006895	MPa
Drop impact	ft-lb	1.356	J
Notched izod impact	ft-lb/in	53.38	J/m
Tensile impact	ft-lb/in^2	2.103	KJ/m^2
Thermal conductivity	Btu/in/h/ft^2/°F	0.1445	W/in/°C
Specific heat	Btu/lb/°F	4.187	kJ/kg/°C
Linear thermal expansion	in/in/°F	1.8	m/m/°C
Viscosity	Centipoise	1	mPa. s
Tear strength	lb/in	0.175	kN/m

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