

CHAPTER I

INTRODUCTION



The urethane-producing reaction was well known in the nineteenth century. In the late 1930s, the commercial potential of polyurethanes as fiber, adhesive, coating and foam began to be recognized by Otto Bayer. Most polyurethanes' application have been developed during the past 30 years[1].

A urethane group is formed by the chemical reaction between an alcohol and an isocyanate. Polyurethane results from the addition polymerization between polyisocyanates and diols or polyols (eq.1.1).



Since the functionality of the polyol or the isocyanate can be adjusted, a wide variety of branched or crosslinked polymers can be formed. Examples of polyol component are polyester and polyether polyols, which cover a wide range of molecular weights. The structure of polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic, or polycyclic. The variety of reactants lead to various kinds of polyurethane products with a wide range of physical and mechanical properties as shown in Figure 1.1. A wide variety of additives may be added in order to control and modify both the polyurethane reaction itself and the properties of the final polymer. These additives include catalysts, crosslinking agents, chain extending agents, blowing agents, surfactants, coloring materials, fillers, smoke suppressants and flame retardants.[2-3]

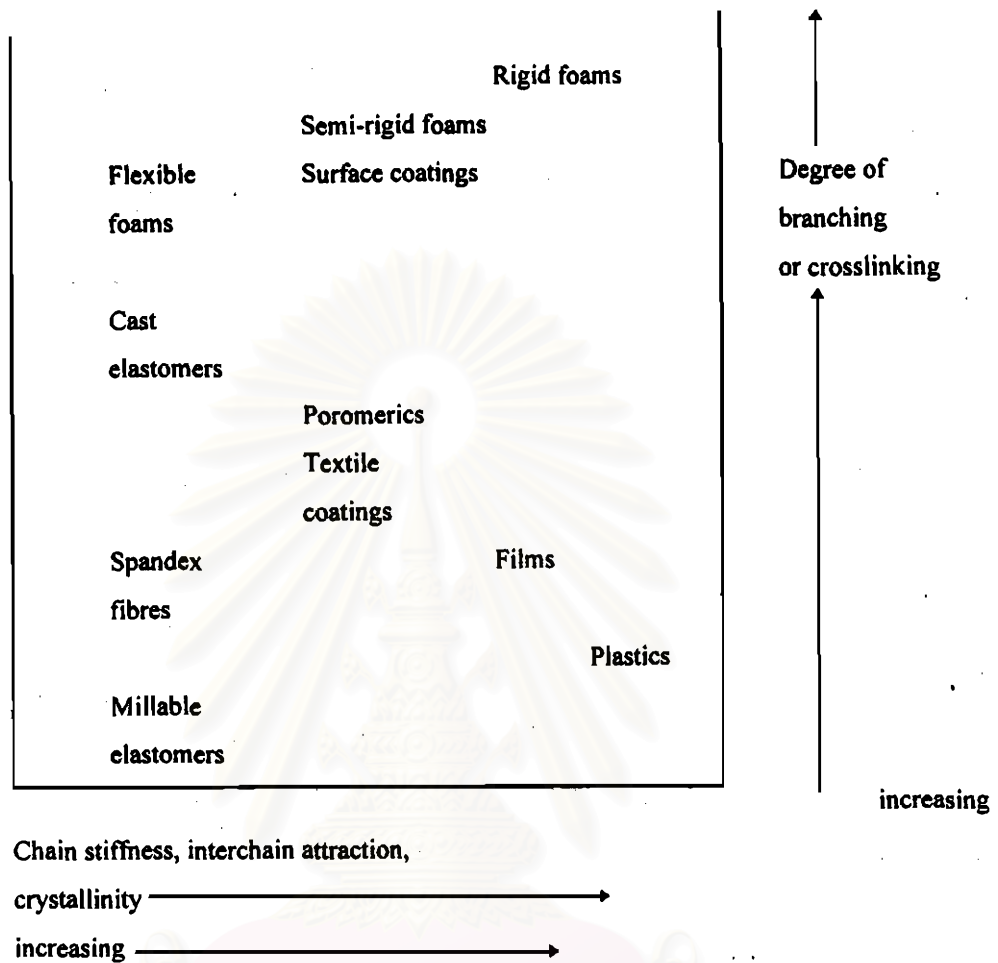


Figure 1.1 Structure-property relationships in polyurethanes (Hepburn, 1991)

1.1 Raw Materials for Polyurethane [1-4]

1.1.1 Isocyanates

Isocyanates are major polyurethane components. Many isocyanates are available, but about 95% of all polyurethanes are based on toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI) and its derivatives (Figure 1.2).

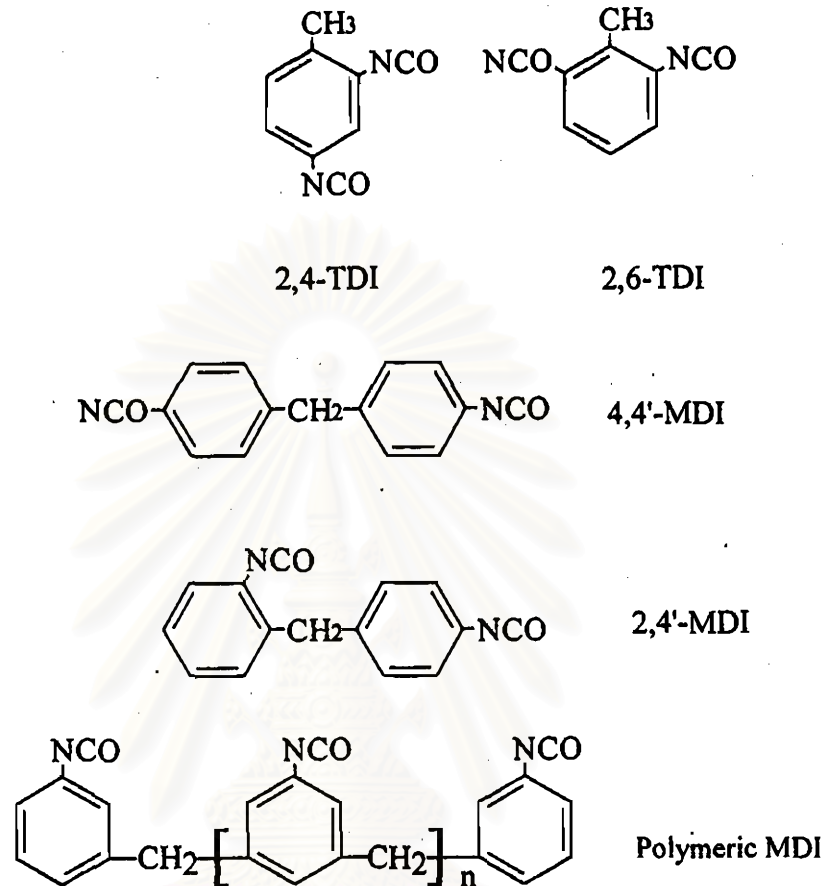


Figure 1.2 Structures of TDI , MDI isomers and Polymeric MDI

TDI is used mainly in the production of low density foams for cushioning. MDI yields polyurethanes of a much higher strength than the TDI-based polyurethane. MDI is available in two types, purified monomeric MDI and polymeric MDI (Figure 1.2). About 80% of MDI is used in the production of flexible and rigid polyurethane foam. The remaining is used in thermoplastic polyurethane.

1.1.2 Polyols

Most polyols used in making polyurethane are polyethers with terminal hydroxyl groups (Table 1.1). They are used to make flexible polyurethane foams and elastomers. Hydroxyl-terminated polyesters are also used to obtain flexible and rigid polyurethane with special properties (Table 1.2). The size and flexibility of its molecular structure and functionality of polyols control the degree of crosslinking in the polyurethane that is formed. The degree of crosslinking has a dominant effect on the stiffness of the polymer. For example a rigid foam must have stiff polymer network and a high degree of crosslinking whereas a flexible foam has a lesser degree of crosslinking.

Table 1.1 Polyethers used in polyurethane elastomer synthesis(Hepburn,1991)

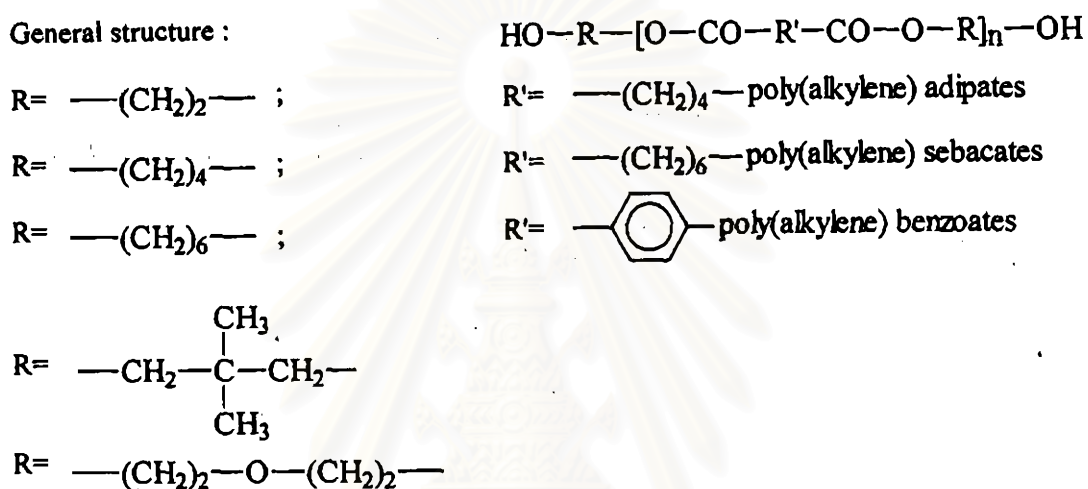
$\text{HO}-[(\text{CH}_2)_4-\text{O}]_n-\text{H}$	Poly(tetramethylene-ether) glycols used for high strength elastomers
$\text{HO}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{O}]_n-\text{H}$	Poly(oxypropylene) glycols used for lower strength elastomers

1.1.3 Chain Extending agents and Crosslinking Agents

The function of chain extending agents and crosslinking agents is to increase the size of the rigid segments and the molecular of the polyurethane. The major chain extending agents and crosslinking agents used nowadays are aromatic diamines, aliphatic and aromatic dihydroxyl compounds. Examples of

commercially important crosslinking agents are diethyl toluene diamine, diethanolamine, ethylene glycol and 1,4-butanediol.

Table 1.2 Polyesters used in polyurethane elastomer synthesis (Hepburn, 1991)



1.1.4 Catalysts

The catalysts affect both the rate and the direction of the polymerization process. The most widely used catalysts are tertiary amines and organometallic compounds such as *N,N'*-dimethylcyclohexylamine, stannous octoate and dibutyltin dilaurate.

1.1.5 Additives

In addition to isocyanate, polyols, crosslinking agents and catalysts, a wide range of additives may be added to modify the properties of the final polymer. Examples of such additives are flame retardants, coloring materials and fillers.

1.2 Castable Polyurethane Elastomers [2-5]

Polyurethane elastomer can be prepared employing two processes as follows:

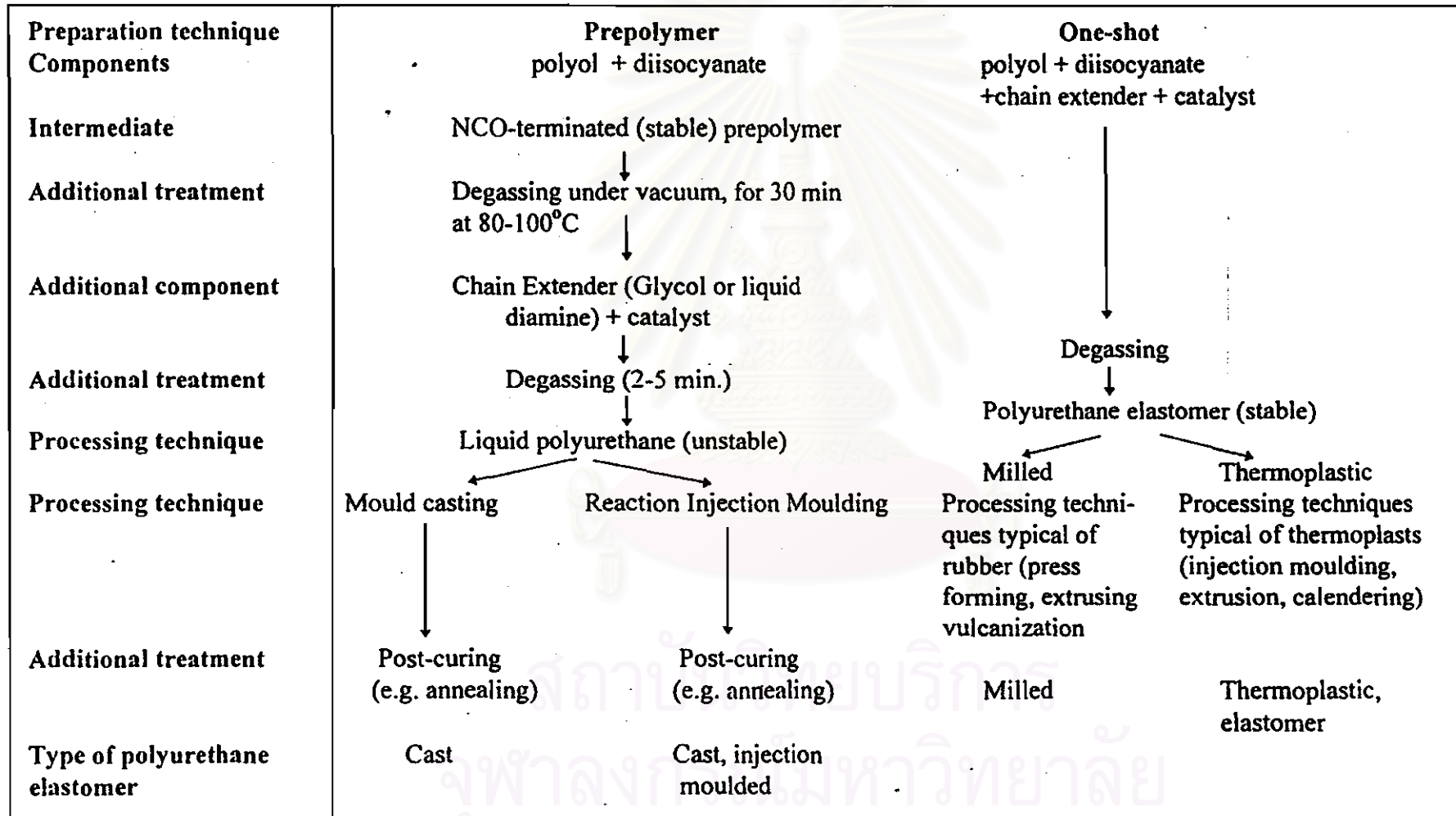
1.2.1 Prepolymer Process

An isocyanate-terminate prepolymer is initially produced from a polyol and excess diisocyanate. The prepolymer is then converted into the final high molecular weight polymer by further reaction with chain extending agents or crosslinking agents to yield high molecular weight polymer (Scheme 1.1).

1.2.2 One-shot Process

This is a one-step technique. A polyol is mixed with a chain extender and a catalyst, dried, then mixed with an isocyanate to obtain the polymer (Scheme 1.1).

Scheme 1.1 Preparation of polyurethane elastomer by prepolymer process and one-shot process (Wirpsza, 1993)



1.3 Basic Structure of a Polyurethane Elastomer [2-9]

Polyurethane elastomer is a linear block copolymer of the type shown in Figure 1.3. The properties of this polymer structure can be varied over a very wide range of strength and stiffness by modification of the polyol, diisocyanate and chain extender (Table 1.3). Properties are related to segmented flexibility, chain entanglement, interchain force and crosslinking.

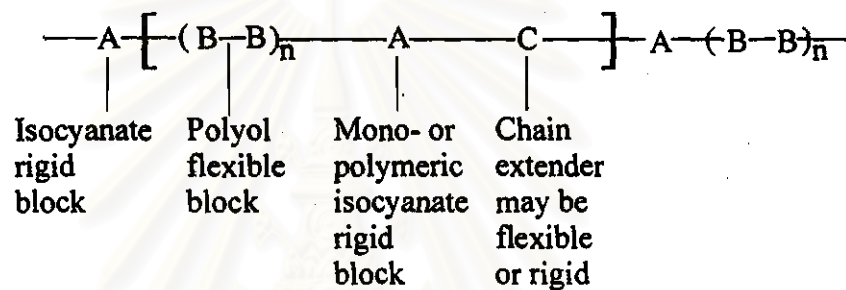


Figure 1.3 The basic unit in a urethane block copolymer (Hepburn, 1991)

Evidence from X-ray diffraction, thermal analysis, birefringence and mechanical properties strongly supports the view that these polymers can be considered in term of long (1000-2000 nm) flexible segments and much shorter (150 nm) rigid units which are chemically and hydrogen bonded together as indicated in Figure 1.4. Polyurethanes properties are the result from the combination of a number of parameters related to molecular structure.

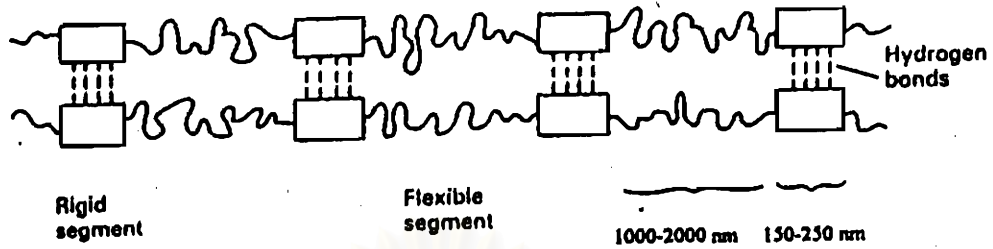


Figure 1.4 Flexible and rigid segments in a polyurethane elastomer (Wirpsza, 1993)

Table 1.3 Properties of a urethane polymer as polyol content (flexible-segments) is decreased, and diisocyanate (rigid segments) increased (Hepburn, 1991)

Weight ratio (phr)						
Polyol	100	100	100	100	100	100
1,4-Butane diol	16.2	14.24	18.89	25.04	32.86	40.69
MDI	56.2	67.78	78.89	101.42	123.49	145.72
Equivalent ratio						
Polyol	0.50	0.4168	0.3582	0.2786	0.2288	0.1939
1,4-Butane diol	0.50	0.5886	0.6447	0.6857	0.7392	0.7756
MDI	1.00	1.0000	1.0000	1.0000	1.0000	1.0000
Hardness						
IRHD	83	84	90	-	-	-
Shore D	-	-	-	53	58	59
Tensile strength (MPa)	50	45	44	38	31	27
% Elongation	575	550	600	430	300	280

1.4 Interpenetrating Polymer Networks (IPNs) [5-7,10-18]

Modification of the polymer's properties can be achieved by combination of polymers or copolymerization. The chemical and physical properties of the combined polymers depend on the properties of polymers and the way they are combined. Mechanical blending is the traditional way of physically combining of two or more polymers by mixing them in the liquid state. In chemical combination, two or more polymers or monomers are combined by covalent bonds which are formed by copolymerization reactions (Figure 1.5).

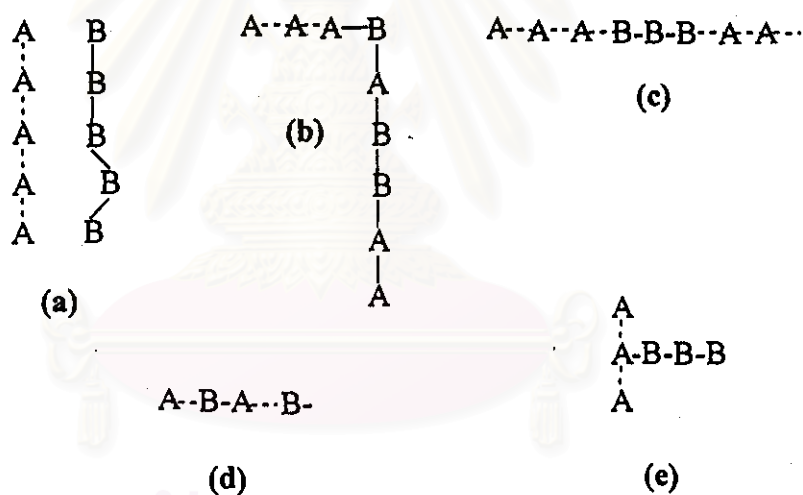


Figure 1.5 Mixed polymer structure: a) mechanical polymer blend; b) random copolymer; c) block copolymer; d) alternating copolymer; e) graft copolymer (Klempner, 1978)

The IPNs are combinations of two or more polymers that form interpenetrating rings without any chemical bond between them. Among the most interesting IPNs are those using a polyurethane as one of their component.

When the mixing is done on a low molecular weight level and polymerization is achieved simultaneously with crosslinking, phase separation may be kinetically controlled which results in better properties than the chemical or mechanical blends. For example, combination of a glassy polymer with an elastomer gives a reinforced rubber if the elastomer phase is continuous and predominant, or a high impact plastic if the glassy phase is continuous. A schematic representation of an ideal IPN is shown in Figure 1.6. The synthesis of IPN is shown in Figure 1.7. Table 1.4 shows different categories IPN.

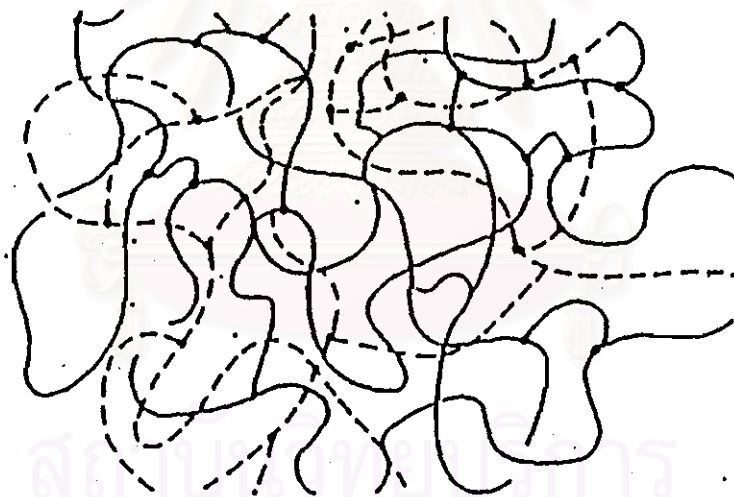


Figure 1.6 Ideal interpenetrating polymer network (IPN) : ——— polymer A,
..... polymer B (Klempner, 1987)

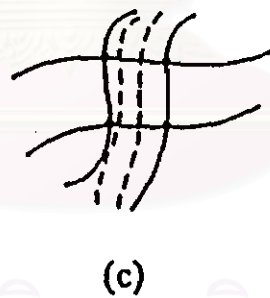
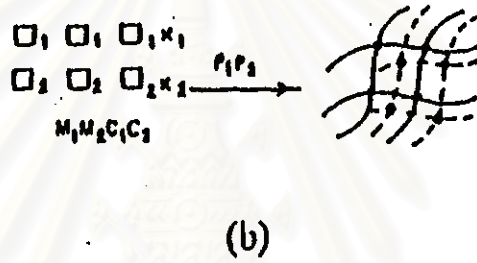
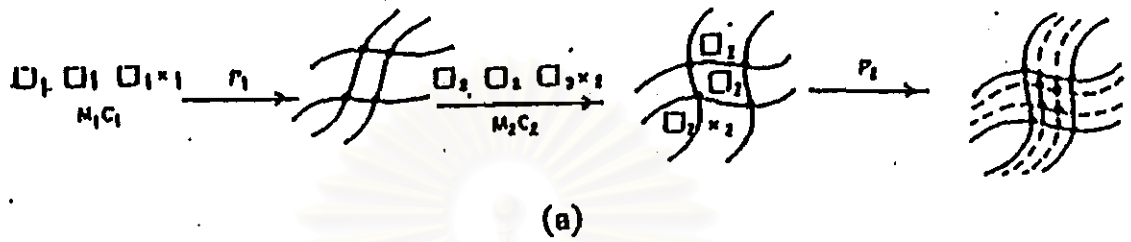


Figure 1.7 Synthesis of IPNs: (a) sequential IPN; (b) simultaneous IPN; (c) semi-IPN, Network I = solid lines; Network II = dotted lines; crosslink sites = filled circles. M = monomer; c = catalyst; X = crosslinking agent; P = polymerization (Klempner, 1987)

Table 1.4 Classification of IPNs (Klempner, 1987)

Category	Definition
Full IPN	Any material contain two or more polymers inwhich there are no induced crosslinks between the individual polymers
Sequential IPN	Polymer A is swollen in monomer B, its crosslinking agent, and initiator, polymerizing B <i>in situ</i>
Simultaneous IPN	Monomers A and B, and their respective crosslinking agents and initiators, are polymerized simultaneously by way of non-interfering modes
Thermoplastic IPN	A two-polymer IPN in which the individual polymers are thermoplastics; polymers may contain physical crosslinks, e.g. ionomers which join two or more chains together or may be phase-seperated single polymer systems
Semi-IPN	Sequential IPN in which polymer I is crosslinked and polymer II linear
Pseudo-IPN	Simultaneous IPN in which one polymer is in network form, ie, crosslinked, and the other linear

Literature Review

V. G. Kumar, M. R. Rao, T. R. Guruprasad and K. V. C. Rao (1987) synthesized simultaneous IPNs of castor oil polyurethane (COPUN) and polystyrene divinyl benzene (PSN) under conditions where the free radical polymerization of styrene and the crosslinking reaction of castor oil and toluene diiscyanate progress at comparable rates. Comparison of the mechanical properties and crosslink density of the COPUN and COPUN/PSN-IPNs indicates a marginal increase in tensile strength and crosslink density [19].

P. Zhou and H. L. Frish (1992) synthesized and characterized simultaneous IPNs, pseudo IPNs, and linear blends of urethane-containing aliphatic polycarbonate (PCU) and polystyrene (PS). The simultaneous IPNs of

PCU and PS had one T_g only at compositions above 50 wt% PCU. The pseudo IPNs and linear blends of PCU and PS exhibited multiple melting and glass transition and phase separation was observed. The full IPNs exhibit a maximum in ultimate mechanical properties at an intermediate composition.[20]

H. Chen and J.-M. Chen (1993) prepared polyurethane-polystyrene grafted IPNs in the presence of a soluble microgel to understand the effect of the microgel on the physical and mechanical properties of the IPN systems. Different types of microgels were prepared by the condensation reaction between toluene diisocyanate (TDI) and linear polystyrene containing hydroxyl groups. It was found that higher tensile strength and elongation at break were obtained for the IPNs when the proper structure of the microgel was used[21].

H. L. Frish and P. Zhou (1993) synthesized pseudo-IPN's of Polycarbonate-urethane and polystyrene with different M_n and narrow MWD of the linear PS. The pseudo-IPNs with ultra-high M_n of the linear PS possess a single T_g . This may reflect the result of a high extent of entanglement of linear PS chains with the PCU network and the limited molecular mobility of the linear PS chains with high M_n . [22]

X. W. He, J-M Widmaier and G. C. Meyer (1993) studied kinetics of phase separation in polyurethane/polystyrene semi-interpenetrating polymer networks. The phase separation process of in-situ polyurethane/polystyrene semi-interpenetrating polymer networks has been followed by optical microscopy. The final morphology has been examined by scanning electron microscopy, and its relation to the phase separation process has been

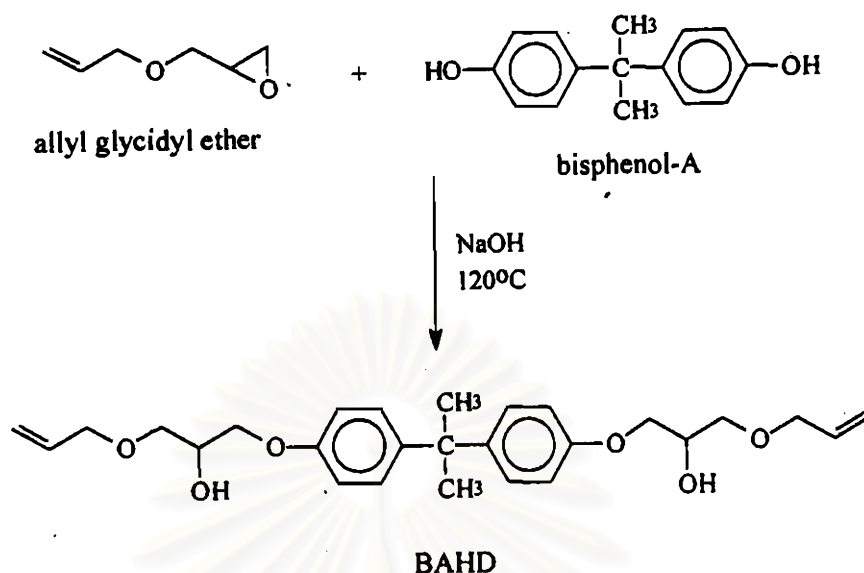
established. The thermodynamic of the phase separation process has also been examined.[23]

K. H. Hsieh, W. Y. Hung, D. C. Liao and S. C. Kao (1995) prepared graft-interpenetrating polymer networks (graft-IPNs) of polyurethane (PU) and bismaleimide (BMI) by using a simultaneous polymerization technique. The effects of the PU molecular weight and the amounts of the PU on the mechanical properties, thermal stability, dynamic mechanical properties, density, and morphology of the IPNs were studied. The graft-IPNs exhibited superior ultimate tensile strength and large improvement in flexural strength when the short soft segments of the PU were introduced. Better thermal stability of the IPNs was obtained by increasing the BMI content [24].

Y. C. Chou and L. J. Lee (1995) prepared IPNs based on a polyurethane (PU) and two unsaturated polyester (UPE) resin. Methyl ethyl ketone peroxide (MEKP) and 2,5-Dimethyl-2,5 bis(2-ethylhexanoylperoxy) hexane (DMB) were used as initiators. Cobalt naphthanate (Co) was used as a promoter for MEKP. It was found that simultaneous reaction of the two reacting systems resulted in a co-continuous structure that provided enhanced tensile properties and impact strength.[25]

Objectives and Scope of the Research

1. Synthesis of bis-(3-allyloxy-2-propanol) diphenylolpropane (BAPD) from the reaction between bisphenol-A and allyl glycidyl ether (Scheme 1.2).



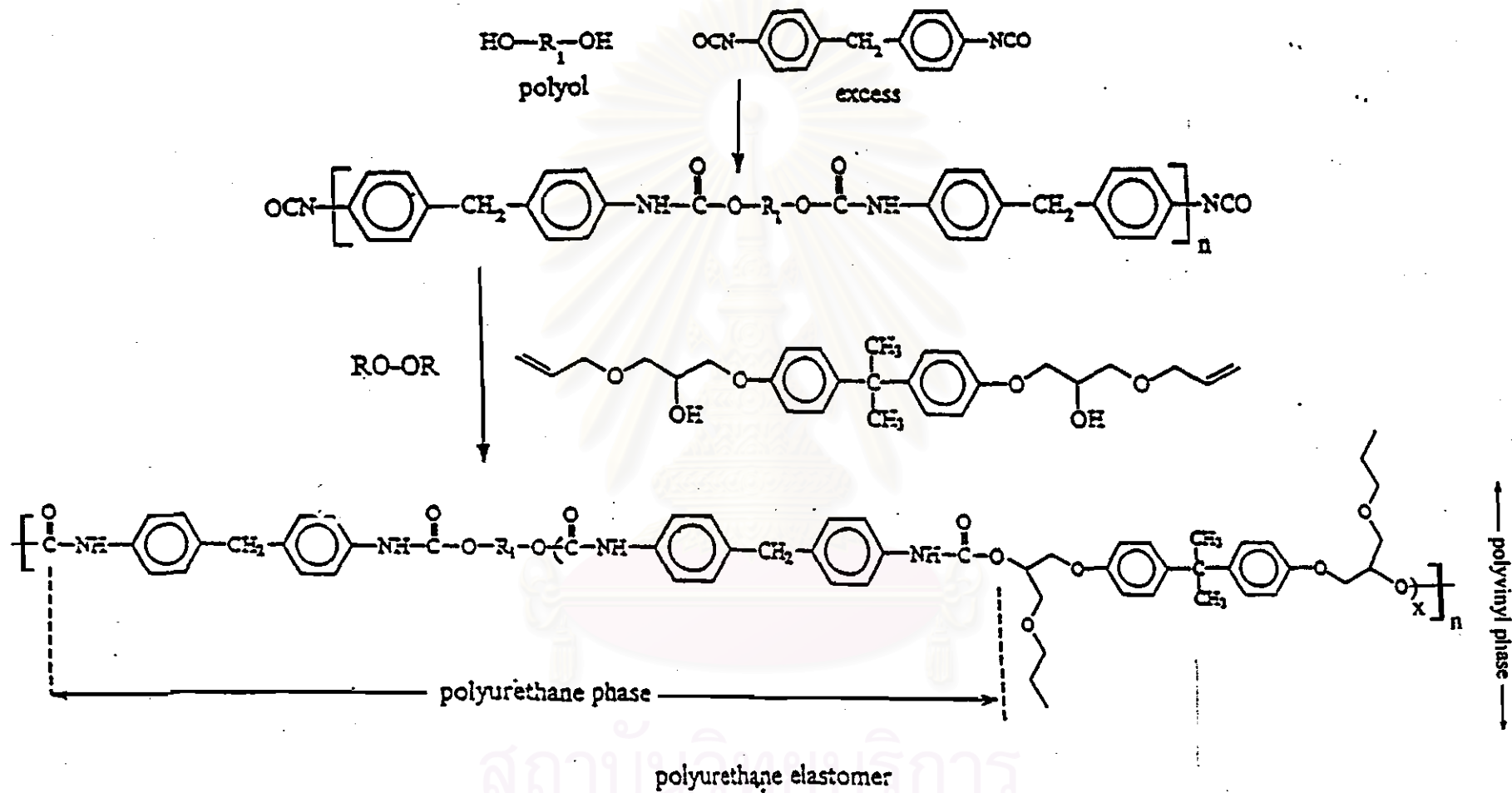
Scheme 1.2 Preparation of BAPD

2. Preparation of PU and PU/PS elastomers by use of BAPD as a crosslinking agent

When BAPD is used in the preparation of polyurethane elastomers, the hydroxyl groups in BAPD should react with the isocyanate groups in MDI to give urethane linkages, while the vinyl groups are expected to undergo free radical polymerization in the presence of a free radical initiator to give polyurethane elastomer as shown in Scheme 1.3.

3. Determination of the suitable compositions for the preparation of PU and PU/PS elastomers by one-shot process using hand-casting procedure by variation of the equivalent weight ratio of MDI:polyol:BAPD, amount of initiator and styrene monomer.

4. Investigation of the mechanical properties and thermal properties of the elastomers.



Scheme 1.3 Reaction sequence for the preparation of polyurethane elastomer