CHAPTER II

THEORY AND LITERATURE REVIEW

Polyurethane is formed by addition polymerization between alcohols with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (a diisocyanate or polyisocyanate).

Polyol + Diisocyanate → Polyurethane

$$\text{OH-R-OH} + \text{OCN-R'-NCO} \longrightarrow \left[\underset{\substack{\| \\ \text{O}}}{\text{C}}\text{-}\underset{\substack{| \\ \text{H}}}{\text{N}}\text{-R'-}\underset{\substack{| \\ \text{H}}}{\text{N}}\text{-}\underset{\substack{\| \\ \text{O}}}{\text{C}}\text{-O-R-O} \right]_n$$

Polyurethanes can be manufactured in an extremely wide range of grades and polymer stiffness from very flexible elastomers to rigid, hard plastics because specific chemical structure can be introduced. This results in chain stiffness or flexibility, an ability to orient or crystallize and interchain attraction or chemical crosslinking, which are important in determining the ultimate physical and mechanical properties (Figure. 2.1).[1-2]

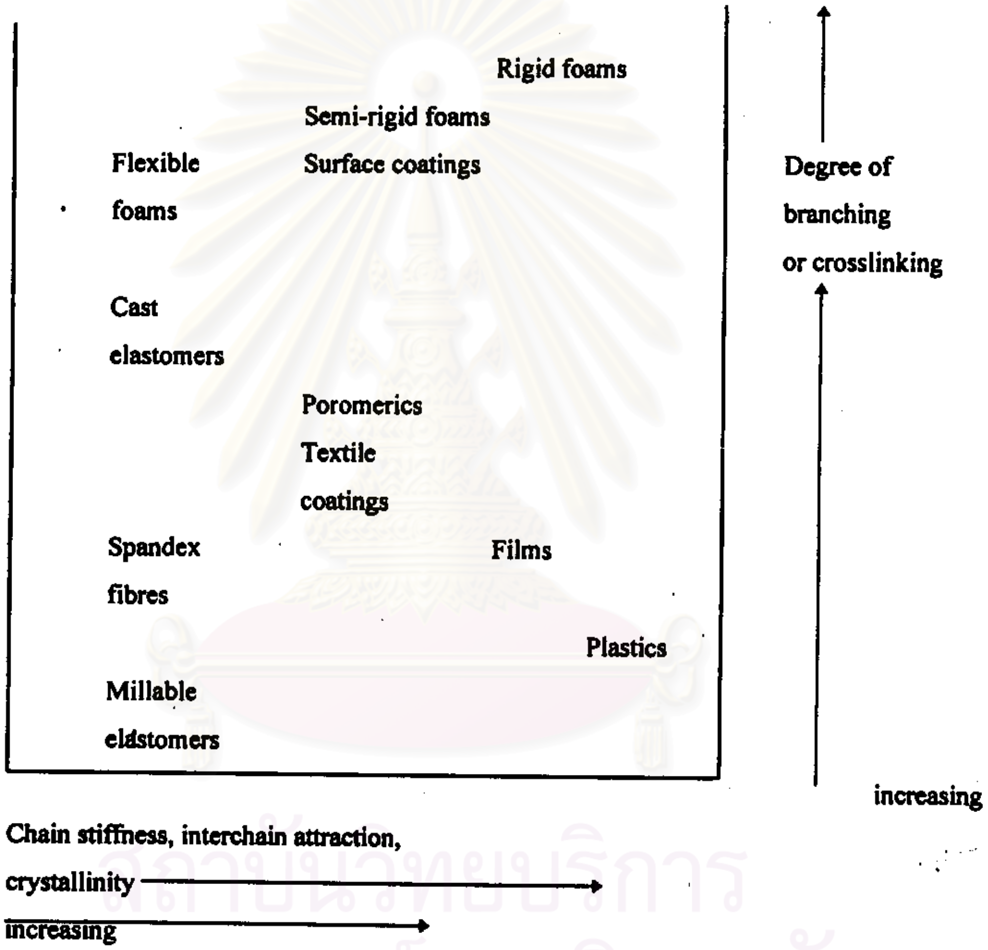


Figure 2.1 Structure-property relationships in polyurethanes.

(Hepburn, 1991)

2.1 Basic Chemistry [1-2]

In 1938, Otto Bayer prepared a linear polyurethane from 1,4-butanediol and hexamethylene diisocyanate (eq. 2.1).

$$\mathrm{HO(CH_2)_4OH + OCN(CH_2)_6NCO \longrightarrow \left[O(CH_2)_4OOCNH(CH_2)_6NHCOO \right]_n}$$

(2.1)

The isocyanate group can react with compounds containing active hydrogen atoms; as shown in the following equations.

$$\mathrm{RNCO + R'OH \longrightarrow RNHCOOR'} \qquad \text{Urethane} \qquad (2.2)$$

$$\mathrm{RNCO + R'NH_2 \longrightarrow RNHCONHR'} \qquad \text{Urea} \qquad (2.3)$$

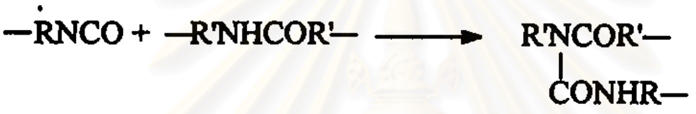
$$\mathrm{RNCO + R'COOH \longrightarrow RNHCOR' + CO_2} \qquad \text{Amide} \qquad (2.4)$$

$$\mathrm{RNCO + H_2O \longrightarrow [RNHCOOH] \longrightarrow}$$

$$\mathrm{RNH_2 + CO_2 \xrightarrow{RNCO} RNHCONHR} \qquad \text{Urea} \qquad (2.5)$$

If the reagents contain two or more function groups, polymer formation can take place. These reactions normally occur at different rate and they can be influenced and controlled by use of catalysts. Reactions (2.4) and (2.5) also give rise to carbon dioxide and can be used in forming foamed products.

Bifunctional reactants result in linear products and higher functionality leads to the formation of branched chain or crosslinked materials. Again, additional reaction of the isocyanate with the urea, urethane and amide groups already introduced during the initial polymer formation is also possible. Chain branching or crosslinking can occur by additional reactions which lead to the formation of acylurea, biuret and allophanate links onto the main chain (eqns 2.6-2.8).

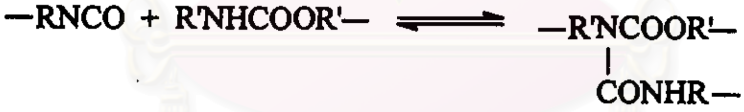


$$\text{—RNCO} + \text{—R'NHCOR'—} \longrightarrow \begin{array}{l} \text{R'NCOR'—} \\ \;| \\ \text{CONHR—} \end{array}$$

Acylurea (2.6)

$$\text{—RNCO} + \text{R'NHCONHR'—} \rightleftharpoons \begin{array}{l} \text{—R'NCONHR'—} \\ \;\;| \\ \;\;\text{CONHR—} \end{array}$$

Biuret (2.7)



$$\text{—RNCO} + \text{R'NHCOOR'—} \rightleftharpoons \begin{array}{l} \text{—R'NCOOR'—} \\ \;\;| \\ \;\;\text{CONHR—} \end{array}$$

Allophanat (2.8)

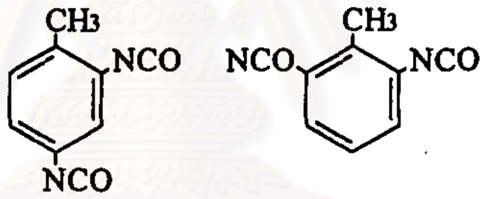
2.2 Raw Materials for Polyurethane [1-2]

Two main starting materials for producing polyurethane are isocyanate and compounds containing hydroxyl group such as polyol. In addition to the isocyanate and polyol, additives are added to obtain particular properties of final polymer.

2.2.1 Isocyanate

Several aromatic and aliphatic isocyanates are commercially available, the most common isocyanate used are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).Variation of polyurethane properties can be acheived by variation of the types of isocyanate used.

TDI is mostly used as a mixture of the 2,4- and 2,6-isomers (Figure 2.2) and the 80:20 mixture of 2,4-TDI : 2,6-TDI is the most important commercial product. A mixture of TDI is used mainly in the production of low density foams while the pure 2,4-TDI is used in some elastomer manufacture.



2,4-TDI 2,6-TDI

Figure 2.2 TDI isomers.

MDI is available in two types, purified monomeric MDI and polymeric MDI. Pure MDI contains mostly 4,4'-MDI and it a small amount of 2,4'-MDI (Figure 2.3).

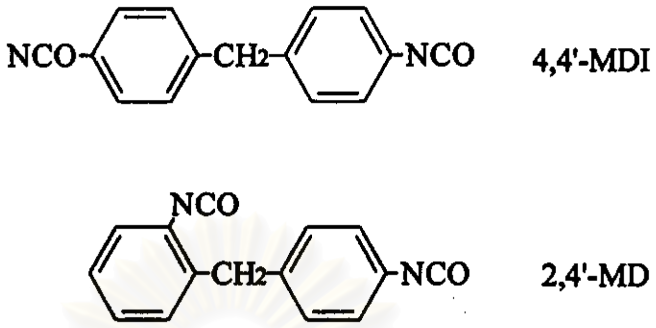


Figure 2.3 Structures of 4,4'-MDI and 2,4'-MDI.

Polymeric MDIs are undistilled MDI compositions made by phosgenation of polyamine mixtures. Polymeric MDI compositions have functionalities from about 2.5 to 3.0 . The viscosity of polymeric MDI increases with increaseing molecular weight and polymeric isocyanate content.

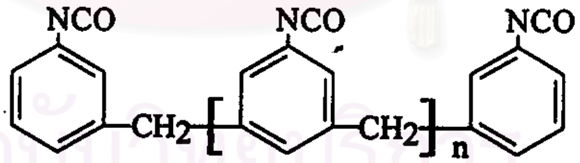


Figure 2.4 Structure of Polymeric MDI

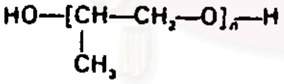
Because of different range of functionality, structure and compositions, the selection of MDI may obtain the different kinds of polyurethanes.

2.2.2 Polyols

Most of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers and hydroxyl-terminated polyesters. The molecular weight and functionality is the main factor of polyol in determining the properties of the final polyurethane. However, the structure of the polyol chain is also important.

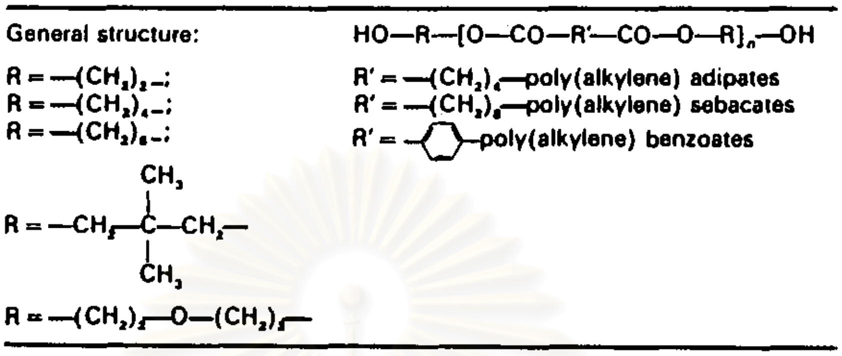
About 90% of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers (Table 2.1). They are used to make flexible polyurethane foams and elastomers.

Table 2.1 Polyethers used in Polyurethane Elastomer Synthesis. (Hepburn,1991)

$HO—[(CH_2)_4—O]_n—H$	Poly(tetramethylene-ether) glycols used for high strength elastomers; expensive
 $HO—[\underset{CH_3}{CH}—CH_2—O]_n—H$	Poly(oxypropylene) glycols used for lower strength elastomers; lower cost

Saturated polyesters with terminal hydroxyl-groups are used to make both flexible and rigid polyurethane (Table 2.2). Polyester polyols are more expensive than polyether polyols and they are more difficult to handle. Polyester polyols have certain property advantages over polyether polyols such as strength and oil resistance, however, they have less hydrolytic stability than polyether polyols.

Table 2.2 Polyesters used in Polyurethane Elastomer Synthesis. (Hepburn,1991)

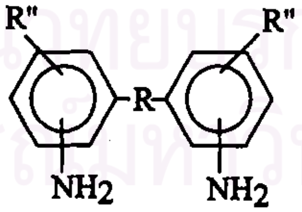


General structure:	$HO-R-[O-CO-R'-CO-O-R]_n-OH$
$R = -(CH_2)_2-;$	$R' = -(CH_2)_4-$poly(alkylene) adipates
$R = -(CH_2)_4-;$	$R' = -(CH_2)_8-$poly(alkylene) sebacates
$R = -(CH_2)_6-;$	R' = —⌬—poly(alkylene) benzoates
$R = -CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-$	
$R = -(CH_2)_2-O-(CH_2)_2-$	

(Also some copolyesters have been commercialized'—as shown in the technical literature of BASF.)

2.2.3 Crosslinking Agents

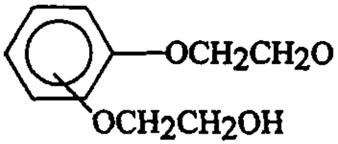
Crosslinking agents (chain extender or curatives) are another important starting materials for the preparation of polyurethanes. The major crosslinking agents used nowadays are aromatic diamines (7), aliphatic and aromatic dihydroxyl compounds (8 and 9). Examples of commercially important crosslinking agents are diethyl toluene diamine, diethanolamine, ethylene glycol, and 1,4-butanediol.



(7)

$HO-(CH_2)_n-OH$

(8)



(9)

2.2.4 Catalysts

The catalysts affect both the rate and the direction of the polymerization process. The most widely used catalysts are tertiary amines and organotin compounds such as N,N-dimethylcyclohexylamine and dibutyltin dilaurate, respectively.

2.2.5 Additives

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

2.3 Methods for Preparation of Polyurethane Elastomers [1-5]

The process for the preparation of polyurethane elastomer are classified to two process : prepolymer process and one-shot process.

2.3.1 Prepolymer Process

The prepolymer route for the preparation of polyurethane is shown in Figure 2.5 . This route employs two separate steps. Initially the diiscyanate and polyol are reacted together to form an intermediate polymer which is called a 'prepolymer', which is a thick viscous liquid or low-melting-point solid. Then the prepolymer is converted into the final high molecular weight polymer. Further reaction of the prepolymer with a diol or diamine chain-extender or crosslinker yields high molecular weight polymer. Catalyst may also be used in this step.

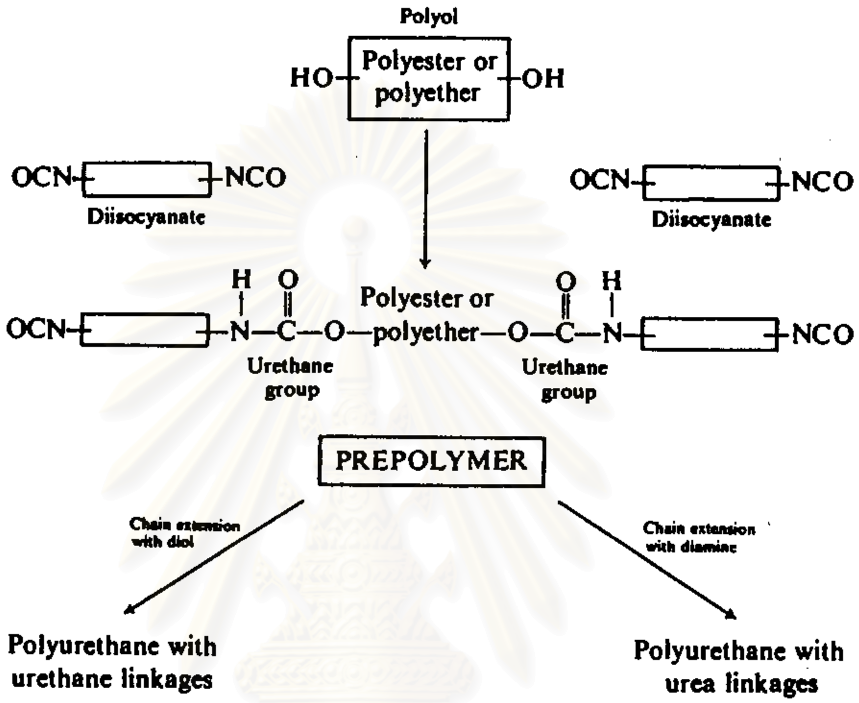


Figure 2.5 Prepolymer route for the preparation of a polyurethane elastomer. (Hepburn,1991)

2.3.2 One-shot Process

The polyurethane formation can also be achieved by simultaneously mixing of polyol, diisocyanate and crosslinking agent in the presence or absence of catalysts as shown in Figure 2.6.

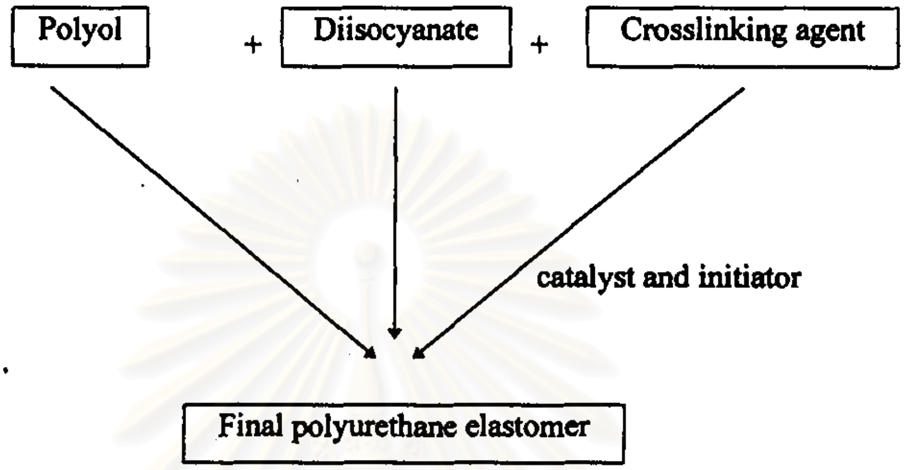


Figure 2.6 One-shot process for polyurethane elastomer preparation.

(Hepburn,1991)

2.4 Basic Structure of a Polyurethane Elastomer [1-2]

Polyurethane elastomer is a linear block copolymer of the type shown in Figure 2.7. The properties of this segmented polymer structure can be varied over a very wide range of strength and stiffness by modification of its three basic building blocks: the polyol, diisocyanate and chain extender (Table 2.3). Properties are related to segmented flexibility, chain entanglement, interchain forces and crosslinking.

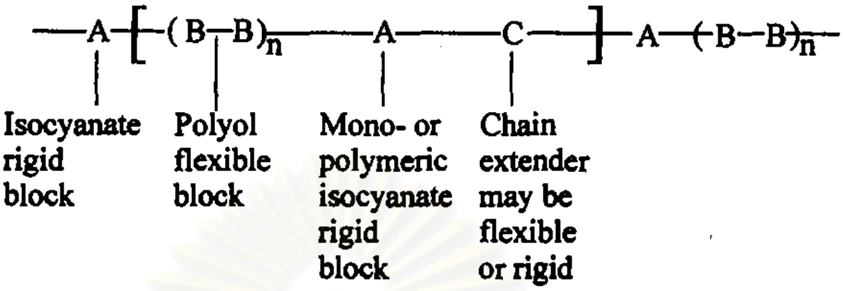


Figure 2.7 The basic unit in a urethane block copolymer.

Table 2.3 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

These polymers consist of long (1,000 - 2,000 nm) flexible segments and much shorter (150 nm) rigid units which are chemically and hydrogen bonded together, the flexible and rigid segments undergo orientation on extension as shown in Figure 2.8. Urethane elastomer are now generally accepted to have a two-phase structure in which rigid segments separate to form discrete domains in a matrix of soft segments. The rigid domains are seen both to form physical crosslink sites and to function as reinforcing filler particles in the soft-segment matrix. Modulus-temperature data usually show at least two transitions, one below room temperature which relates to the motion of the flexible polyol segment and one above 100 °C which is due to the interchain forces in the rigid units. Multiple transitions may also be observed when mixed polyols are employed.

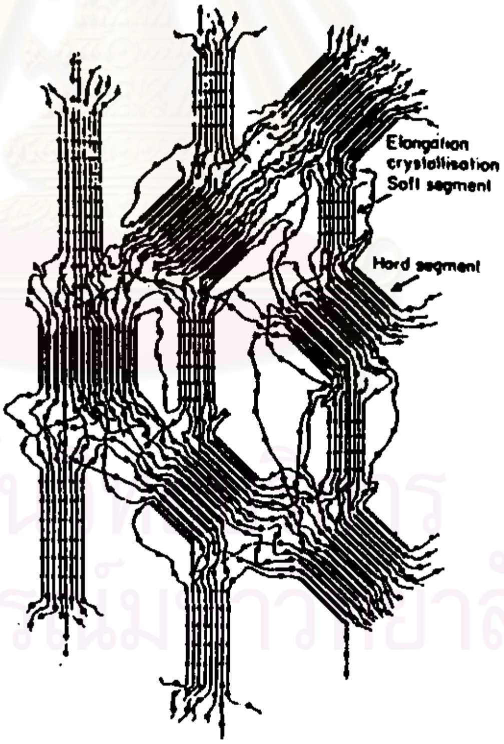


Figure 2.8 Strain-induced elongation crystallization of polyether soft segments in a segmented polyurethane elastomer by elongation it to 200% extension. (Hepburn,1991)

2.5 Interpenetrating Polymer Networks (IPNs) [3-4,6]

The chemical and physical combinations of two or more structurally different polymers provide for the modification of properties to meet specific needs such as flexibility, tensile and impact strength, chemical resistance, weatherability, flammability resistance, or other properties.

The ways of polymer combination influence their final properties. Mechanical blending (Figure 2.9a) is the traditional way of physically combining of two or more polymers by mixing them in the liquid state, i.e., melt, solution, or dispersion; there are no covalent bonds between the polymers. In chemical combination, i.e., two or more polymers or monomers, are combined by covalent bonds which are formed by random (Figure 2.9b), block (Figure 2.9c), alternative (Figure 2.9d), or graft (Figure 2.9e) copolymerization reactions.

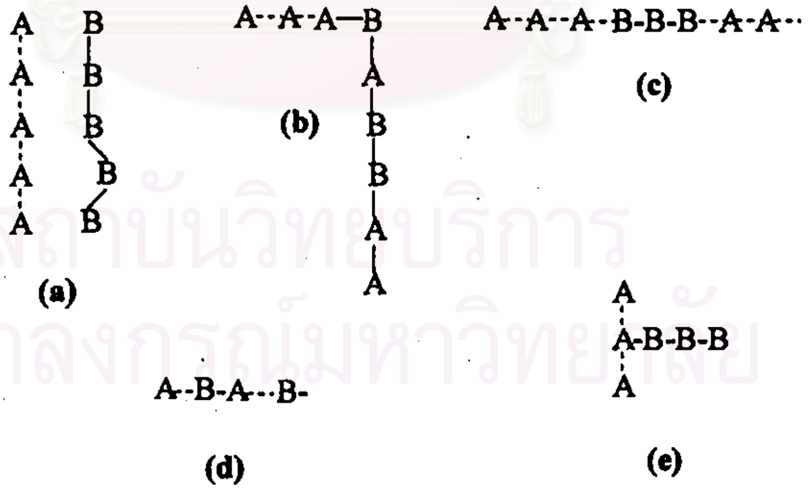


Figure 2.9 Mixed polymer structure : a) mechanical polymer blend ; b) random copolymer ; c) block copolymer ; d) alternating copolymer ; e) graft copolymer. (Klempner, 1978)

Interpenetrating polymerization is a blending of two or more polymers to produce a mixture in which phase seperation is not extensive. It is the only way to combine crosslinked polymers together. Most of the normal blending or mixing of polymers result in a multi-phase morphology due to the well known thermodynamic incompatibility of polymers. However, if the mixing is accomplished on a low molecular weight level and polymerization is achieved simultaneously with crosslinking, phase seperation may be kinetically controlled. Therefore, they have better combined physical and mechanical properties than the chemical or mechanical blends. For example, combination of a glassy polymer (T_g above room temperature) with an elastomer (T_g below room temperature) 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 2.10.

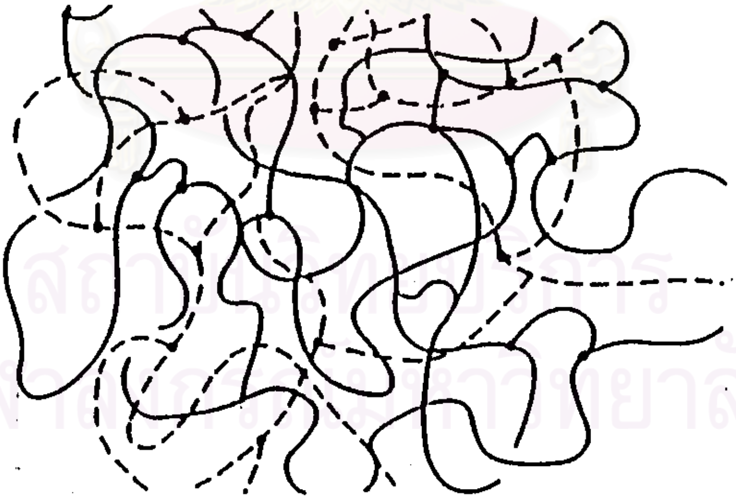


Figure 2.10 Ideal interpenetrating polymer network (IPN) :
——— polymer A , ………… polymer B. (Klempner, 1987)

IPN can be synthesised by employing sequential and simultaneous synthesis which will be discussed as follows:

2.5.1 Sequential Synthesis

This synthesis is a two-step process. First, monomer I is combined with a crosslinking agent and an initiator to form an elastomeric network I. It is then swollen in monomer II containing also a crosslinking agent and an initiator to form a network II (Figure 2.11a).

Example of sequential IPNs are poly(ethyl acrylate) with polystyrene, poly(n-butyl acrylate) with polystyrene, styrene-butadiene block copolymer with polystyrene, caster oil with polystyrene, and polybutadiene with polystyrene, etc.

2.5.2 Simultaneous Synthesis

In this method, monomers or linear prepolymer of two monomers are combined together with their crosslinking agents and catalysts. Then, the individual monomers are polymerized simultaneously by chain or stepwise polymerization (Figure 2.11b). In all cases, one component is a rubbery polymer and the other a glassy one. Examples of simultaneous IPNs are polyurethane with polymethyl methacrylate, polyurethane with polyacrylate, polyurethane with epoxy polymer, polyurethane with unsaturated polyester, butyl rubber with poly(methyl acrylate), etc.

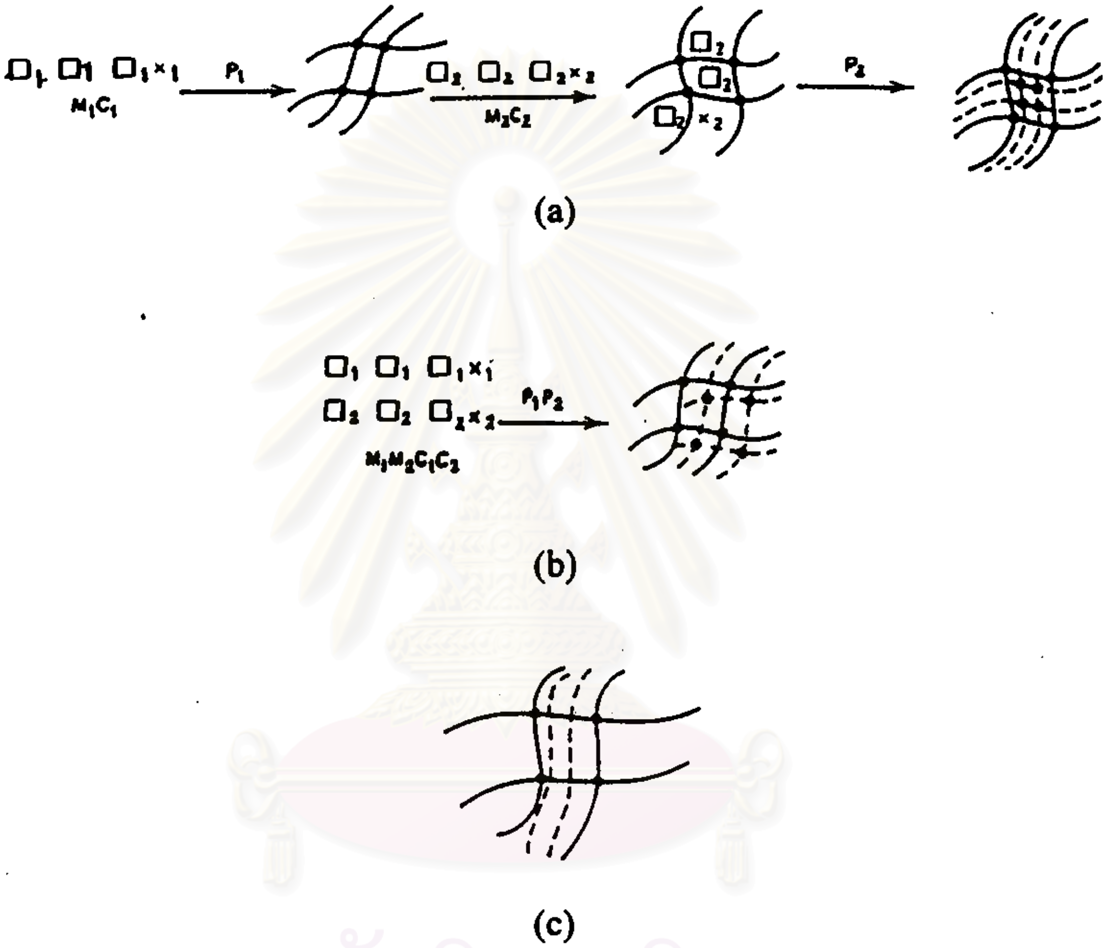


Figure 2.11 Synthesis of IPNs : (a) sequential IPN ; (b) simultaneous IPN ; (c) semi-IPN. Network I = solid lines ; Network II = dotted lines ; cross-link sites = filled circles. M = monomer ; c = catalyst ; X = crosslinking agent ; P = polymerization. (Klempner,1987)

Combination of a crosslinked polymer and a linear polymer results in a semi-IPN (Figure 2.11). Table 2.4 shows different catagories of IPN.

Table 2.4 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 *in situ*
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

2.6 Literature Review

V. G. Kumar, M. Rama Rao, T. R. Guruprasad, and K. V. C. Rao (1987) synthesized simultaneous interpenetrating networks (IPN) 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 from COPUN to 60COPUN/40PSN IPN. IPN samples prepared with further increased PSN content show steady decrease in the above properties. This several of the expected trend was attributed to the possible greater molecular interpenetration achieved due to similar gelation times with resulltant extension of chains and increase in free volume between crosslinks. This was further confirmed from thermogravimetric data on the initial stages of decomposition of the IPNs.[7]

Peiguang Zhou and H. L. Frish (1992) synthesized and characterized simultaneous two component interpenetrating polymer networks (IPNs), pseudo IPNs, and linear blends of urethane-containing aliphatic polycarbonate (PCU) and polystyrene (PS). The simultaneous full IPN's of PCU and PS had one T_g only at compositions above 50 wt% PCU, as determined by DSC and DMA. The single phase morphology in the one T_g region was comfirmed by transmission electron microscopy (TEM). The pseudo IPN's and linear blends of PCU and PS exhibited multiple (melting and glass) transition by DSC measurements and phase seperation was observed by TEM over the whole composition range. The full IPN's exhibit a maximum in ultimate mechanical properties at an intermediate composition. Superior solvent resistance as well as beter thermal stability was shown by the IPN's as compared to the pseudo IPN 's, linear blends, and pure crosslinked components.[8]

H. L. Frish and Peiguang Zhou (1993) studied phase behavior of pseudo-IPN's of Polycarbonate-urethane and Polystyrene. The pseudo-IPN's PCU/PS with different $\overline{M_n}$ and narrow MWD of the linear PS have been synthesized and characterized. The effect of $\overline{M_n}$ and composition on the phase morphology of the pseudo-IPN's of PCU/PS has been studied by DSC and SEM. The pseudo-IPN's with ultra-high $\overline{M_n}$ of the linear PS appeared to possess a single T_g and no SEM-resolvable domains at 35 wt% PS and below. This metastable state 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 $\overline{M_n}$.[9]

X. W. He, J-M Widmaier and G. C. Meyer (1993) studied kinetics of phase seperation in polyurethane/polystyrene semi interpenetrating polymer networks. The phase seperation 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 it relation to the phase seperation process has been established. The thermodynamic of the phase seperation process has also been examined. [10]

Y. C. Chou and L. J. Lee (1995) prepared interpenetrating polymer networks based on a polyurethane (PU) and two unsaturated polyester (UPE) resin. Two initiators, 2,5-dimethyl-2, 5 bis (2-ethylhaxanoylperoxy) hexane (DMB) and methyl ether ketone peroxide (MEKP) were used. Cobalt naphthanate (Co) was used as a promoter for MEKP, and the content of Co was 25 wt% of MEKP. The amount of MEKP/Co used was 1% by weight of the UPE resin. The mechanical properties, such as tensile strength, elongation at break, impact strength, and dynamic mechanical properties of IPNs were studied by changing reaction temperature, PU reaction rate, and UPE reaction rate. It was found that simultaneous reaction of the two reacting system resulted in a co-continuous structure that provided enhanced tensile properties and impact strength.[11]