CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Interpenetrating Polymer Networks (IPN)

Interpenetrating polymer network (IPN) is an intimate combination of two polymers both in network forms, at least one of which is synthesized or crosslinked in the immediate presence of the other. Unlike chemical blending, there are no induced covalent bonds between the two polymers. Since IPNs consist of mechanical blending of two different crosslinked polymer, they therefore have better combined physical and mechanical properties than the chemical or mechanical blends. A schematic representation of an ideal IPN is shown in Figure 2.1.

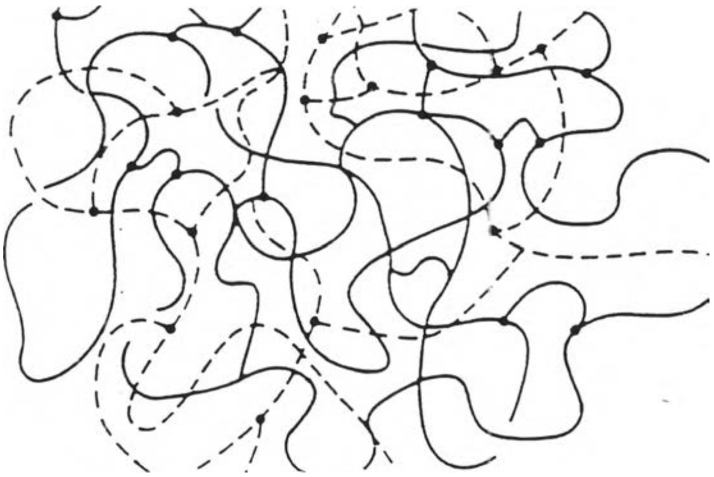


Figure 2.1 Ideal interpenetrating polymer network (IPN) :

______, polymer A ; -------- , polymer B. (Klempner, 1978)

The ways of polymers combined influence their final properties. Mechanical blending (Figure 2.2a) 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 2.2b), block (Figure 2.2c), alternative (Figure 2.2d), or graft (Figure 2.2e) copolymerization reactions.

The chemical and physical combinations of two or more structurally dissimilar polymers provide for the modification of properties to meet specific needs, e.g. flexibility, tensile and impact strength, chemical resistance, weatherability, flammability resistance, or other properties. (Klempner, 1978)

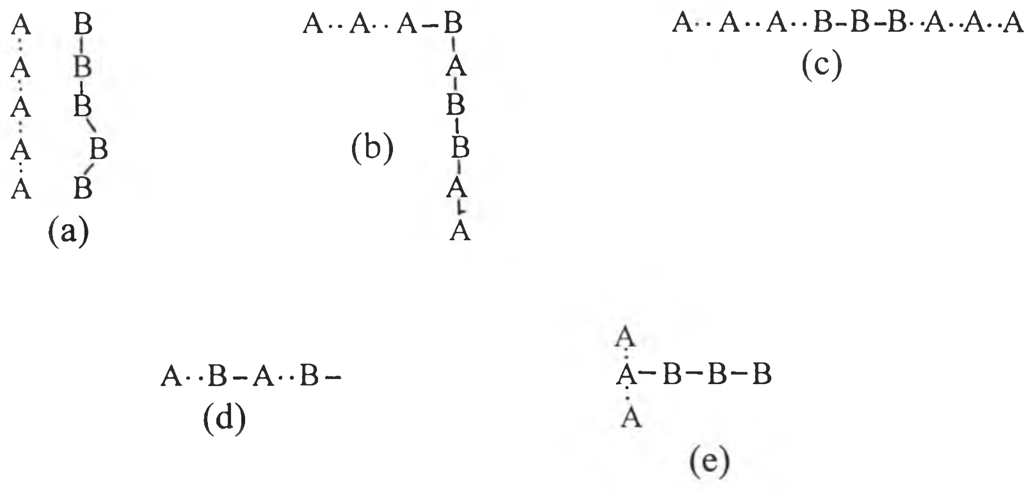


Figure 2.2 Mixed polymer structures :a)mechanical polymer blend ; b) random copolymer ; c) block copolymer ; d) alternating copolymer ; e) graft copolymer. (Herman, 1989)

IPN can be synthesised in a variety of ways, including sequential and simultaneous synthesises.

Sequential synthesis

Monomer I is combined with a cross-linking agent and an initiator to form an elastomeric network I. It is then swollen in monomer II containing also a cross-linking agent and an initiator to form a network II (Figure 2.3a).

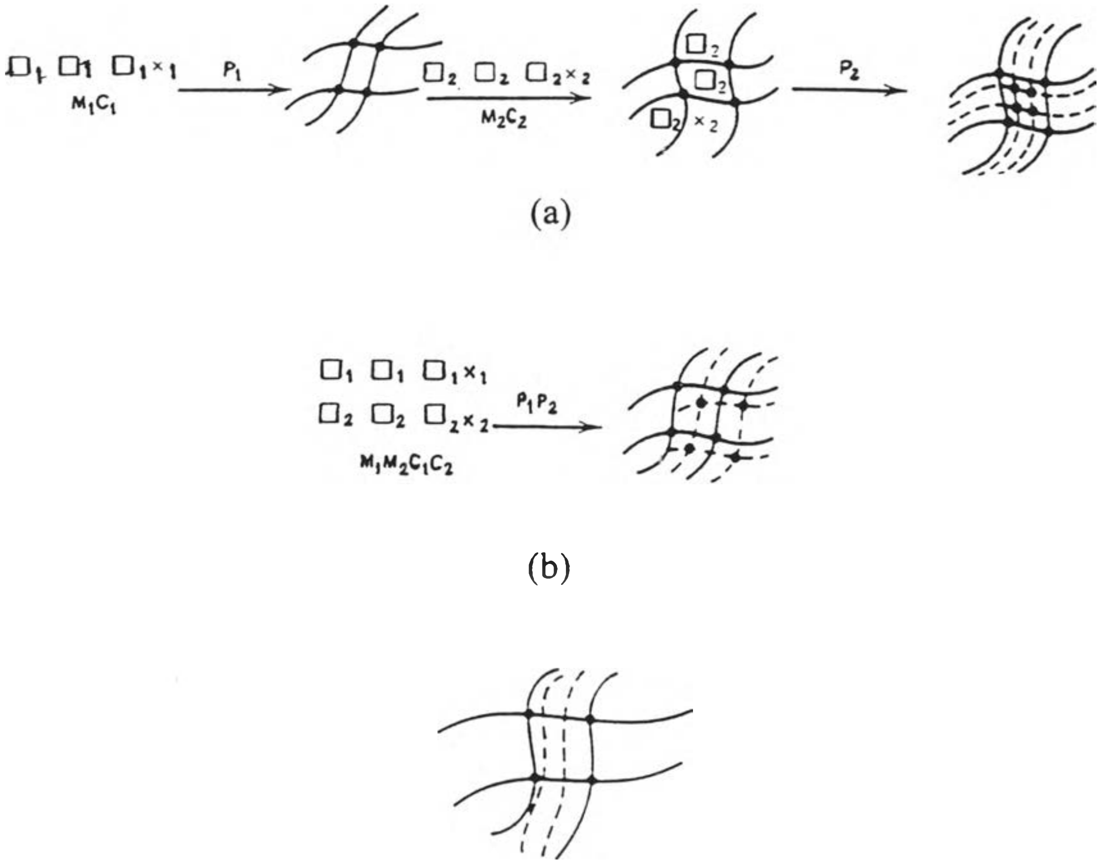
Examples of sequential IPNs are (a) poly(ethyl acrylate) with polystyrene, poly(methyl methacrylate), poly(styrene-co-methyl methacrylate), (b) poly(n-butyl acrylate) with polystyrene, (c) styrene-butadiene block copolymer with polystyrene, (d) caster oil with polystyrene, and (e) polybutadiene with polystyrene, etc.

Simultaneous synthesis

Monomers or linear prepolymers of two monomers combine together with their respective cross-linking agents and catalysts, in bulk (melt), solution, or dispersion. The individual monomers are polymerized by chain or stepwise polymerization (Figure 2.3b). In all cases, one component is a rubbery polymer and the other a glassy one. An advantage of this synthesis is that low to medium pressure reaction injection molding machine (RIM) can be employed for fabrication of products with designed shape. Examples of simultaneous IPNs are (a) PU with poly(methyl methacrylate), (b) PU with polyacrylate, (c) PU with epoxy, (d) PU with unsaturated polyester, (e) butyl rubber with poly (methyl acrylate), poly (butyl acrylate), etc. (Frisch, 1983)

Simultaneous IPNs of PU with other polymers were formed by mixing of the urethane prepolymer (either in solution or in bulk), together with its chain extender and a cross-linking agent, with either epoxy, polyacrylate, polyester, or poly (methyl methacrylate) together with their respective cross-linking agent, then to cast into film or to mould into sheet forms. They are finally thermally cured.

If one of the two polymers is in network form (cross-linked) and the other is a linear non-crosslinked polymer, i.e., a semi-IPN results (Figure 2.3c). The different categories of IPNs are shown in Table 2.1.



(a)

(b)

(c)

Figure 2.3 Synthesis of IPNs : a) sequential IPN ; b) simultaneous IPN ; c) semi-IPN. Network I = solid lines ; Network II = dot lines ; = crosslink sites ; M = monomer ; C = catalyst ; x = cross-linking agent ; P = polymerization. (Herman, 1989)

Table 2.1 Classification of IPNs. (Herman, 1989)

Category	Definition
Full IPN	Any material containing two or more polymers in which there are no induced cross-links between the individual polymers.
Sequential IPN	Polymer A is swollen in monomer B, its cross-linking agent, and initiator, polymerizing B *in situ*.
Simultaneous IPN	Monomers A and B, and their respective cross-linking 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 cross-links, 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 cross-linked and polymer II linear
Pseudo-IPN	Simultaneous IPN in which one polymer is in network form, ie, cross-linked, and the other linear.

Interpenetrating polymerization is a mode of blending of two or more polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise. It is the only way to combine cross-linked polymers together. Most of the normal blending or mixing of polymers results in a multi-phase morphology due to the well known thermodynamic incompatibility of polymers. This incompatibility arises from the relatively small gain in entropy upon mixing the polymers due to contiguity restrictions imposed by their large chain length. However, if the mixing is accomplished on a lower molecular weight level and polymerization is achieved simultaneously with cross-linking, phase separation may be kinetically controlled, since the entanglements have been made permanent by the cross-linking. In other words, phase separation cannot occur without breaking covalent bonds.

Combining polymeric networks in different compositions often results in controlled different morphologies and, in effect, produces IPNs with synergistic behavior. For example, a glassy polymer (T_g above room temperature) combined with an elastomeric polymer (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. More complete phase mixing enhances mechanical properties owing to increased physical crosslink density.

Morphology and T_g

The morphology of IPNs is related to physical properties such as modulus and T_g. In addition it is controlled by chemical compatibility (e.g. solubility parameters), interfacial tension, cross-link densities, mode and kinetics of polymerization, and polymer components. The compatibility of IPNs is enhanced because the polymers are interlocked in a three-dimensional structure during polymerization not allowing a phase separation occurred. Monomers of similar solubility parameters usually give compatible IPNs. In general, the smaller the phase domains, the more compatible the system.

Measure of T_g can be acheived using the Dynamic Mechanical Spectroscopic technique. The transitions may be broadened or shifted by more or less mixing in IPNs. In the limit of total compatibility (complete mixing), only one Tg is observed. In conjunction with other mechanical methods of analysis, e.g. electron microsccpy, a good interpretation of the molecular morphology is usually attainable.

The glass transitions of compatible IPNs can be calculated from the following equations :

$$T_g = W_1 T_{g1} + W_2 T_{g2} \tag{2.1}$$

where W_1, W_2 and T_{g1}, T_{g2} are the weight fractions and glass transitions of polymer I and II, respectively. Glass transition increases with increasing cross-link density. (Herman, 1989)

2.2 Polyurethanes

Polyurethanes were discovered by Otto Bayer and his co-workers of I.G.Farbenindustric at Leverkusen, Germany in 1937. They are usually produced by the reaction of a polyfunctional isocyanate with a polyol or other reactant containing two or more reactive groups with isocyanate, most often hydroxyls. Since the functionality of the polyol or the isocyanate can be adjusted, a wide variety of branched or crosslinked polymers can be formed. The polyol component covers a wide range of molecular weights and types of polymeric backbones, such as polyester and polyether polyols. The polyfunctional isocyanates can be aromatic, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly as produced or modified. The flexibility in the selection of reactants leads to produce various kinds of polyurethane products having a wide range of structures and, in effect, of physical and mechanical properties. Figure 2.4 illustrates the molecular structure features used to produce polyurethanes in different forms, such as fibre- or film-forming, and also different types of polymers from elastomer, thermoplastics, thermoplastic elastomers, to thermosettings.(Hepburn, 1991)

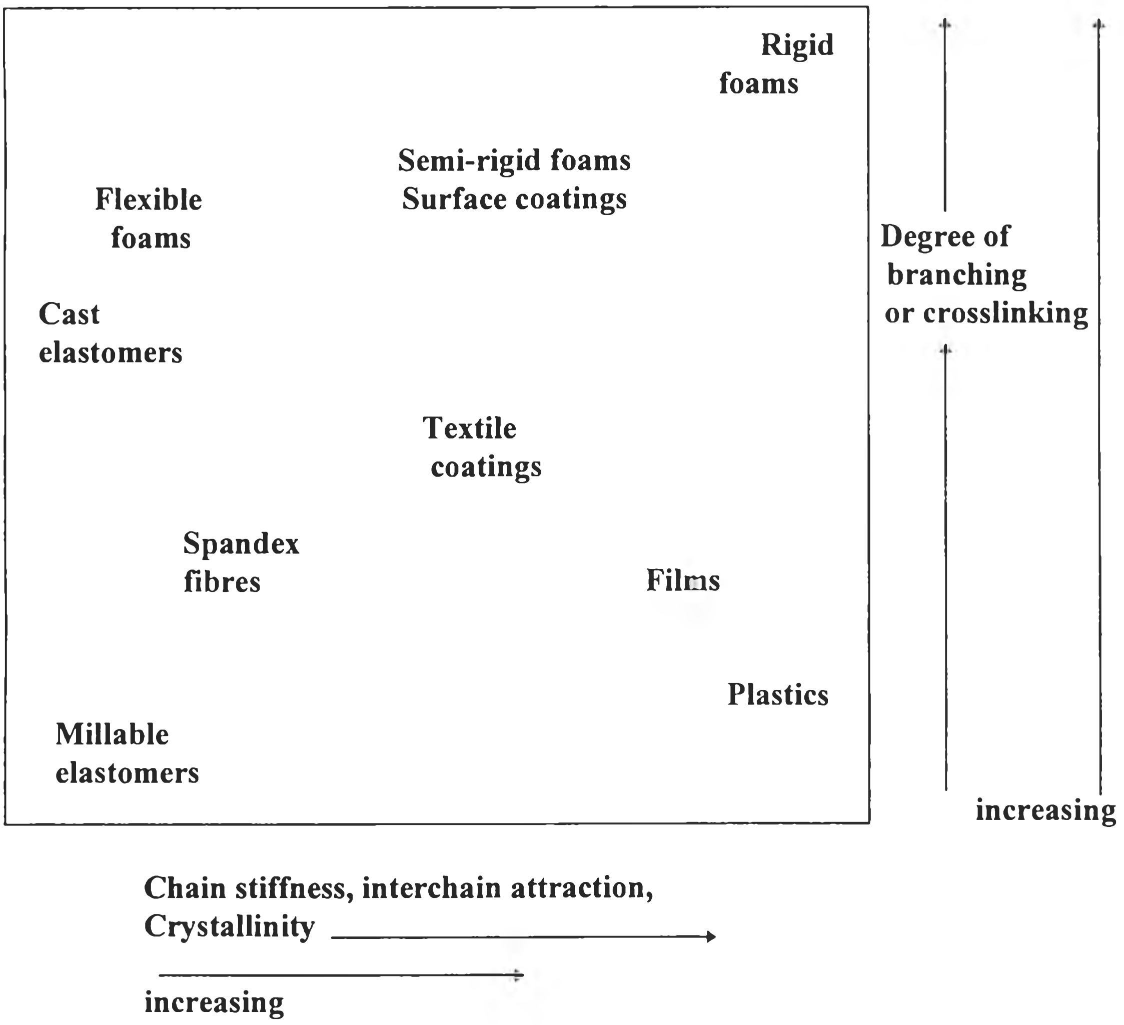


Figure 2.4 Structure-property relationships of polyurethanes.

(Hepburn, 1991)

2.2.1 Basic Chemistry of Polyurethanes

Polyurethane synthesis depends basically on the chemistry of isocyanates and compounds containing active hydrogen atoms and their chemical reactions. Since the latter has a great number such as those contain hydroxyl, amino groups, when reacting with the isocyanates gives a chemical different bonding formation.

Reaction with polyols : the reaction of diisocyanate with polyol is shown in reaction (1).

$$\underset{\text{Polyol}}{n\text{OH-R-OH}} + \underset{\text{Diisocyanate}}{n\text{OCN-R}'\text{-NCO}} \rightarrow \underset{\text{Polyurethane}}{[\text{-O-R-O-C(O)-NH-R}'\text{-NH-C(O)-}]_n} \quad (1)$$

The reaction is exothermic. The rate of polymerisation reaction depends on the structure of both the isocyanate and the polyol. Aliphatic polyols having primary hydroxyl end-groups are the most reactive.

Reaction with water : the reaction of isocyanates with water yields a substituted carbamic acid, which then breaks down to an amine and carbon dioxide gas, which in the manufacture is used as a blowing agent to produce low density flexible foams.

$$R\text{-}NCO + H\text{-}O\text{-}H \longrightarrow [RNHCOOH] \longrightarrow R\text{-}NH_2 + CO_2(g) \qquad (2)$$

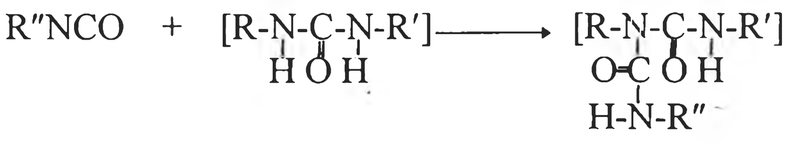
Isocyanate Water Substituted carbamic acid Amine Carbon dioxide

Reaction with amine : di-primary amine functional group compound are used as chain-extender and a curing agent in polyurethane manufactures. The reaction results polyurea having two reactive hydrogens in the urea linkage (see reaction (3)). This provides a potential for secondary reaction with isocyanates.

$$RNCO + R'NH_2 \longrightarrow RNHCONHR' \qquad (3)$$

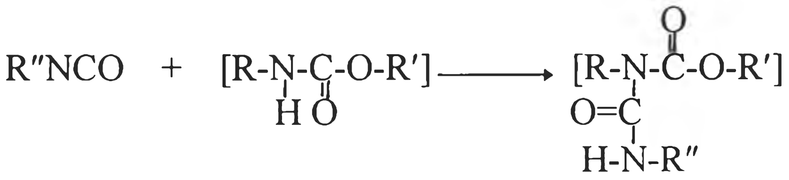
Isocyanate Amine Urea

Secondary reactions of isocyanates with urea or urethane linkage : Isocyanates may react, under suitable conditions, with the active hydrogen atoms of the urethane and urea linkages to form biuret and allophanate linkages, respectively.



$$R''NCO + [R\text{-}\underset{H}{\underset{|}{N}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{H}{\underset{|}{N}}\text{-}R'] \longrightarrow [R\text{-}\underset{\substack{O=C\\ |\\ H\text{-}N\text{-}R''}}{\underset{|}{N}}\text{-}\underset{O}{\underset{\|}{C}}\text{-}\underset{H}{\underset{|}{N}}\text{-}R'] \qquad (4)$$

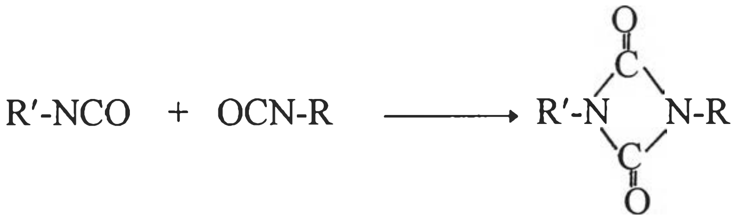
Isocyanate Urea Biuret



$$R''NCO + [R\text{-}\underset{H}{N}\text{-}\underset{O}{\overset{}{C}}\text{-}O\text{-}R'] \longrightarrow [R\text{-}\underset{\underset{H\text{-}N\text{-}R''}{O=C}}{N}\text{-}\overset{O}{C}\text{-}O\text{-}R'] \qquad (5)$$

Isocyanate Urethane Allophanate

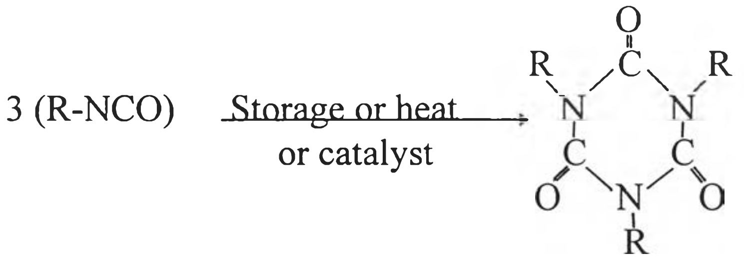
Isocyanate polymerisation reactions : Isocyanates from oligomers, especially in the presence of basic catalysts, giving uretidinediones (commonly called dimers), see reaction (6) and isocyanurates (commonly called trimers), see reaction (7). MDI (diphenylmethane diisocyanate) dimerizes slowly when left standing at room temperature, making a limited storage life of MDI.



(6)

Isocyanate Isocyanate Urethidinedione

Isocyanurate are formed on heating both aliphatic or aromatic isocyanate. Isocyanurate formation gives very stable branch point unlike the uretidinedione, biuret, allophanate or urethane linkages.

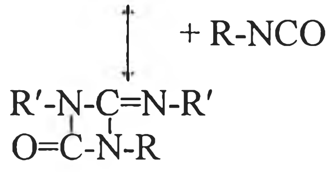

(7)

Isocyanurate

In the presence of special catalyst, isocyanate can react to form carbodiimide with elimination of carbon dioxide. It can react reversible with isocyanate to give a uretonimine as shown in reaction(8).

$$R'\text{-}NCO + OCN\text{-}R' \longrightarrow R'\text{-}N{=}C{=}N\text{-}R' + CO_2 \qquad (8)$$

Isocyanate Carbodiimide



$$\updownarrow + R\text{-}NCO$$

$$\begin{array}{l} R'\text{-}N\text{-}C{=}N\text{-}R' \\ \quad\;\; | \quad\; | \\ O{=}C\text{-}N\text{-}R \end{array}$$

Uretonimine

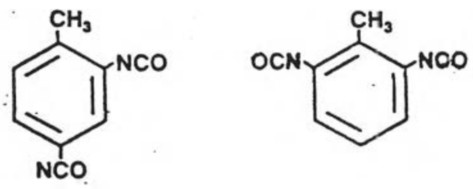
2.2.2 <u>Raw materials for polyurethanes</u>

The starting materials for producing polyurethane are the two main participants, namely isocyanate and compounds containing hydroxyl group (e.g. polyol or crosslinking agent containing diol entities). In addition to the isocyanate and polyol, additives are added to control the process of reaction and to obtain particular characteristics of final polymer.

1) Isocyanates

Variation of properties of the final polyurethane is acheived by variation of the types of isocyanate used, such as pure MDI, polymeric MDI. Several aromatic and aliphatic isocyanates are available, but about 95% of all polyurethanes are based upon the two aromatic diisocyanates, which commonly are toluene diisocyanate (TDI), and diphenylmethane diisocyanate (MDI) and its derivatives.

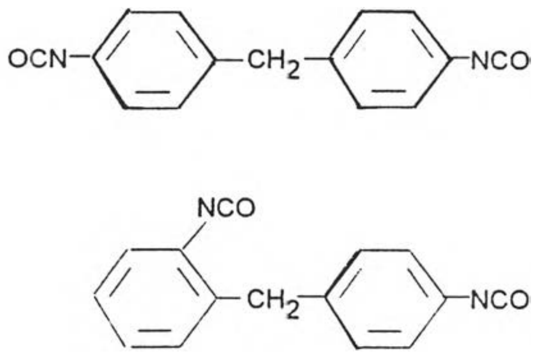
Most of the TDI used is a mixture of the 2,4- and 2,6-isomers (Figure 2.5). The 80:20 mixture of 2,4-TDI : 2,6-TDI is the most important commercial product. TDI is used mainly in the production of low density foams while the pure 2,4-TDI in some elastomer manufacture.



2,4-TDI 2,6-TDI

Figure 2.5 TDI isomers. (Woods, 1987)

MDI is available in several forms based on two types of products, purified monomeric MDI and polymeric MDI. Pure MDI is substantially 4,4′-MDI (two isocyanate groups are bonded at the para position of each phenyls), it usually contains a small amount of the 2,4′-isomer (Figure 2.6).


4,4′-MDI

2,4′-MDI

Figure 2.6 Structures of 4,4′-MDI and 2,4′-MDI. (Woods, 1987)

Pure MDI is a white to pale yellow solid with a melting point of 38°C. The difficultly of handling pure solid MDI is because of its tendency to form dimer which leads to the development of modified MDI. It is a liquid at room temperature and has a reduced tendency to dimerize.

The melting point of pure 4,4′-MDI is also reduced by increasing the 2,4′-MDI content, but it is not suitable for the production of polyurethane elastomers having a high modulus.

There common methods used for preparation of modified MDI include

(1) To react some of the isocyanate groups with an aliphatic diol having a low molecular weight or with a mixture of such diols yields a solution of diurethanes having isocyanate end-groups (e.g. Figure 2.7) in 4,4′-MDI.

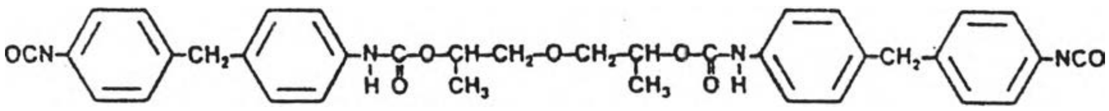


Figure 2.7 Modified pure MDI. (Woods, 1987)

(2) To convert part of the diisocyanate to uretonimine-linked trifunctional and higher isocyanates, (e.g. Figure 2.8).

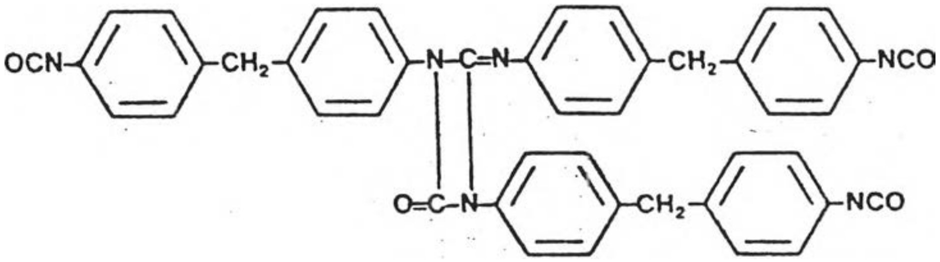


Figure 2.8 Modified pure MDI. (Woods, 1987)

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

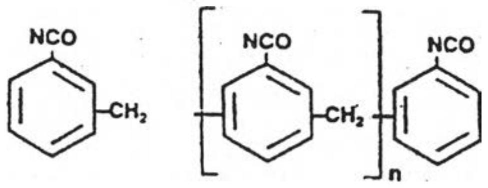


Figure 2.9 Structure of polymeric MDI. (Woods, 1987)

Because of different range of functionality, structure and compositions, the selection of MDI may obtain the different kinds of polyurethanes. Table 2.2 shown main applications of polyurethane which are affected from different types of MDI.

2) Polyols

Most of the polyols used in polyurethane manufacture are classified into two classes : hydroxyl-terminated polyethers and hydroxyl-terminated polyesters. The structure of polyol plays a large part in determining the properties of the final urethane polymer. The molecular weight and funtionality of the polyol are the main factors; however the structure of the polyol chains is also important.

Table 2.2 Range of MDI variants. (Woods, 1987)

Average functionality	Product description	Polyurethane type	Main applications
2.0	Pure MDI	High performance elastomers	Shoe-soling. Spandex fibres. Flexible coatings. Thermoplastics.
2.01-2.1	Modified, liquid pure MDI	High performance elastomers. Microcellular elastomers.	Shoe-soling. Flexible coatings. RIM and RRIM. Cast elastomers.
2.1-2.3	Liquid, low functionality polyisocyanates.	Flexible, semi-rigid and rigid foams.	Automotive parts. Insulating sealants. Cast elastomers.
2.5	Low viscosity liquid polyisocyanates.	High density flexible foams. Structural foams.	Foam-backs for carpets/vinyls. Computer cabinets.
2.7	Low viscosity polymeric MDI.	Low density rigid foams. Semi-rigid foams.Isocyanurate foams. Particle binders.	Insulating foams. Energy absorbing foams. Chipboard and foundry sand binders.
2.8-3.1	High functionality polymeric MDI.	Rigid polyurethane and isocyanurate foams.	Continuous lamination of rigid foam and rigid foam slabstock.

Polyether polyols

About 90% of the polyols used in polyurethane manufacture are hydroxy-terminated polyethers. These are made by the addition of alkylene oxides, usually propylene oxide, onto alcohols or amines which are initiators. The commercial polyol production is usually by base catalysis.

The epoxide ring of propylene oxide may theoretically open at either of two positions on reaction but, in practice, the ring opens preferentially at the less sterically-hindered position with the base catalysis. Polyethers based on propylene oxide thus contain predominantly secondary hydroxyl end-groups, which are several times less reactive with isocyanates than the primary groups. For some applications polyether polyols based only on propylene oxide may have inconveniently low reactivity.

Initiator +	**Alkylene oxide** →	**Polyether polyol**
Polyfunctional alcohol or amine	Propylene oxide alone or copolymerised with ethylene oxide	Polyether polyol with both primary and secondary hydroxyl end-groups

The polymerization of propylene oxide and ethylene oxide

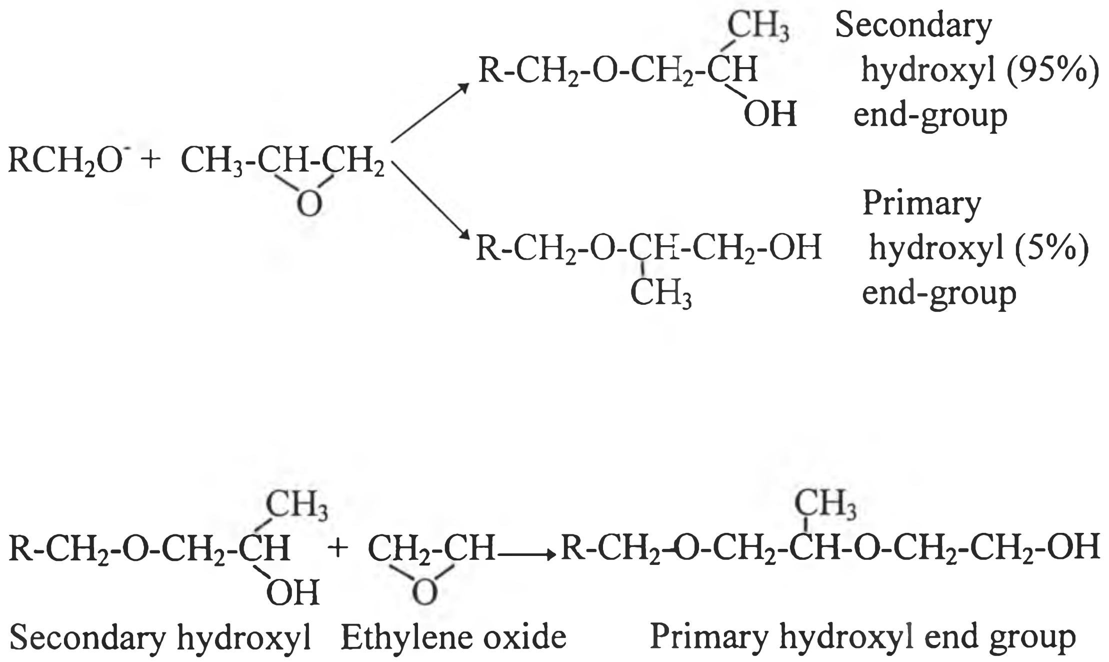


Figure 2.10 The manufacture of polyether polyols. (Woods, 1987)

Polyester polyols

Saturated polyesters with terminal hydroxyl-groups are used to make both flexible and rigid polyurethane polymers. Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. Polyester polyols have certain property advantages over polyether polyols with respect to strength, oil resistance, etc., but they have less hydrolytic stability than polyether polyols.

Preparation of polyester polyols, is to use conventional methods of polyesterification, i.e. reaction between acid and diol or polyol. The water of condensation being removed by distillation and the reaction assisted by the usage of vacuum or azeotrope. The molecular weight can be controlled from the molar ratio of the reactants and the reaction conditions. It is essential that the terminal groups should be hydroxyl group so as to ensure for ultimated reaction with isocyanates.

As the polyesters are required to be hydroxyl-terminated it is usual to react in an excess of the stoichiometric amount of the difunctional glycol with the dibasic acid:

$$(n+1)R(OH)_2 + nR'(COOH)_2 \rightarrow H[OROOCR'CO]_nOROH + 2n\,H_2O \quad (9)$$

Caprolactone polyester : another type of polyester which is of interest in polyurethanes is that obtained by the addition polymerization of caprolactone in the presence of an initiator :

$$2nCH_2(CH_2)_4CO{+}HORO \rightarrow HO[(CH_2)_5COO]_mR[OOC(CH_2)_5]_nOH \quad (10)$$

A typical series of commercial polycaprolactone polyesters for PU synthesis is given in Table 2.3.

Table 2.3Conventional and high molecular weight polycaprolactone polyesters for PU synthesis, where f is an average-functionality. (Hepburn, 1991)

Molecular weight	OH value	Structure	Form	Approximate melting point (°C)
550	204	Linear	Liquid	20
830	135	Linear	Liquid-solid	25
1000	112	Linear	Paste	38
1250	90	Linear	Wax-like	40
2000	56	Linear	Wax-like	47
3000	36	Linear	Wax-like	55
4000	28	Linear	Wax-like	58
250	540	Branched, f=2.4	Liquid	-
540	310	Branched, f=2.3	Liquid	-
25000	5	Linear	Tough polymer	60
45000	2	Linear	Tough polymer	

3) Additives

In addition to isocyanates and polyols, the basic materials for making polyurethanes, a wide range of auxiliary chemicals may be added to control and modify both the polyurethane reaction and the properties of the final polymer.

These additives include catalyst, chain extenders, crosslinking agents, flame retardants, colouring material and fillers which are shown in Table 2.4.

Table 2.4 Reasons for using additive. (Woods, 1987)

Additives	Type of material	Purpose
Catalyst	Tertiary amines Organometallic compounds	To speed up the reaction of isocyanate and polyol
Crosslinking agent Chain extender	Polyols Polyamines	To give polymer crosslinks or introduce specialised polymer segments
Blowing agents	Water (reacts with isocyanate giving CO_2 gas). Chlorofluoromethanes	To produce foamed structures
Surfactants	Silicone fluids	To aid and help foam-forming processes
Colours	Various pigments Carbon black	To identify different foam grades and for aesthetic reasons
Fillers	Particulate inorganic materials Fibres (chopped, milled or continuous fibres,nets)	To modify properties (stiffness, fire performance etc.)
Flame retardants	Phosphorus or halogen-containing molecules	To reduce flammability

(a) Chain-extenders and crosslinking agents

These are low molecular weight polyols or polyamines. They react with diisocyanate to form a polyurethane or polyurea segment in the urethane polymer. They are usually added in sufficient amount to permit hard-segment segregation that results in an increase in modulus and the hard-segment glass transition temperature (T_g) of the polymer.

When diamines are used as additives, instead of glycols of similar molecular weight, they give faster reaction with isocyanates. They resulting polyurea hard-segment has a higher density of secondary bonding so that the Tg and the thermal stability of the polymer are both increased.

Some chain-extending agents and crosslinking agents are shown in Table 2.5.

Table 2.5 Chain-extending agents, crosslinking agents and their diisocyanate equivalents. (Woods, 1987)

Additive	Functionality	MW.	OH value (mgKOH/g) or NH value	Weight of diisocyanate (g / 100g of required additive)	
				TDI	MDI
Ethylene glycol	2	62.07	1801	280	401
Diethylene glycol	2	106.12	1057	164	235
Propylene glycol	2	76.11	1474	229	329
Dipropylene	2	134.18	836	130	186
glycol	2	90.12	1245	193	278
1,4-Butane diol	2	400	280	43.5	62
Polypropylene glycol 400	2	108.15	1037	161	231
m-Phenylene diamine	2	178.27	629	97.7	140
Diethyl toluene diamine	2	18.01	6230	968	1389
Water	3	105.14	1601	248	357
Diethanolamine	3	149.19	1128	175	252
Triethanolamine	3	92.11	1827	284	407
Glycerol					

(b) Catalysts

The catalysts affects both the rate and the direction of the polymer-forming process. The catalysts most widely used commercially in polyurethane processes are tertiary amines and organotin compounds.

1. Tertiary amines are the catalysts most widely used in making polyurethane foams. The mechanism of catalysis by a tertiary amine involves the donation of electrons by the tertiary nitrogen to the carbonyl carbon of the isocyanate group thus forming a complex intermediate. The efficiency of tertiary amine increase with the basicity of the amine, but decreases with steric hindrance of the aminic nitrogen.

Some tertiary-amine catalysts are N,N-Dimethylaminoethanol, N,N-Dimethylcyclohexylamine, Diaminibicyclooctane(DABCO), N-Ethylmorpholine

2. Organometallic compounds are used to accelerate the urethane reaction. The most popular are stannous octoate and dibutyltin dilaurate. The former is used in most flexible foam systems, while the latter in RIM and cast elastomers systems. Organometallic catalysts form an

intermediate complex with the isocyanate and a the hydroxyl groups of the polyol. This complex formation inhibited by steric hindrance of the Sn atom.(Woods, 1987)

2.2.3 Methods for preparation of polyurethanes

In the preparation of flexible foams, rigid foams and elastomer polyurethanes are classified to two processes : prepolymer process and one-shot process. (Oertel, 1985)

a) Prepolymer process

The prepolymer route for the formation of polyurethane and the prepolymer reaction are illustrated in Figure 2.11. The final polymer is formed due to two separate steps. Initially the diisocyanate and polyol are reacted together to form an intermediate polymer which is called a 'prepolymer', and is normally a thick viscous liquid or low-melting-point solid of low or no strength. Then the prepolymer is converted into the final high molecular weight polymer by further reaction with a diol or diamine chain-extender or crosslinker, also catalyst may be used in this step.

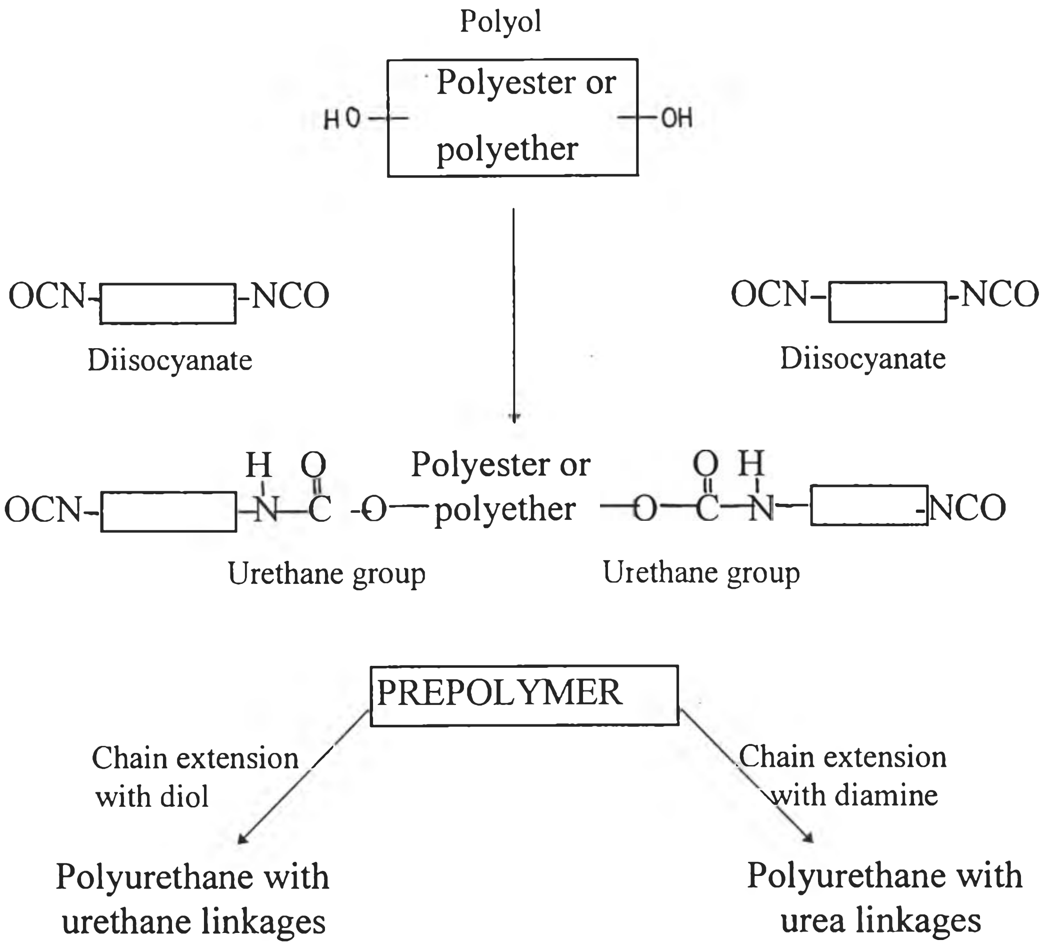


Figure 2.11 Prepolymer route for the formation of a polyurethane. (Hepburn, 1991)

b) One-shot process

The polyurethane formation can be acheived by simultaneously mixing of polyol, diisocyanate and chain-extender in the presence or absence of catalysts, schematic representation given in Figure 2.12.

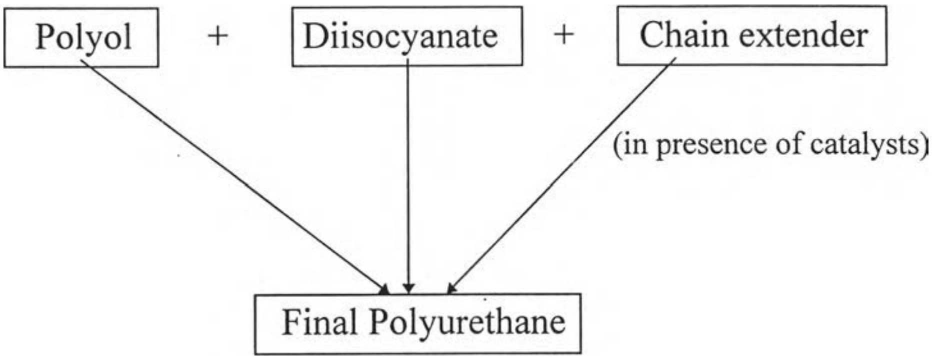


Figure 2.12 One-shot process for polyurethane preparation. (Hepburn, 1991)

2.2.3 Basic structure of Polyurethanes

The urethane elastomer can be regarded as a linear block copolymer (Figure 2.13). This segmented polymer can vary a wide range of properties by modification of its three basic chemicals, the polyol, diisocyanate and chain extender, which are building blocks.

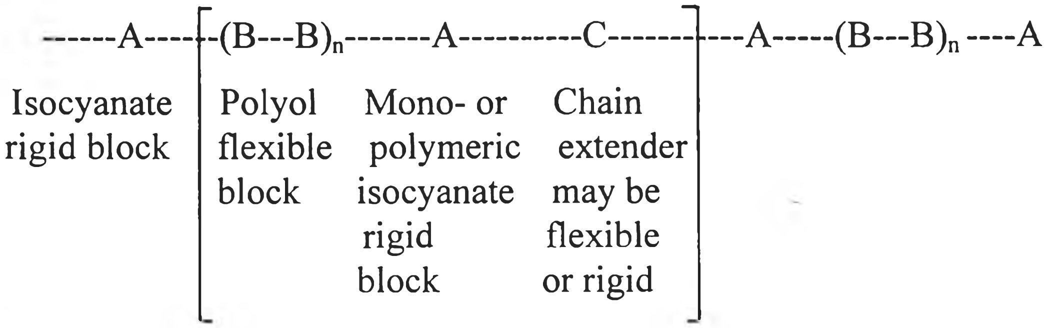


Figure 2.13 The basic unit in a urethane block copolymer. (Hepburn,1991)

Evidence from x-ray diffraction, thermal analysis, birefringence and mehanical properties supports that these polymers have a two-phase structure, long (1000-2000 mm.) flexible segments (also known as soft segment) and much shorter (150 nm.) rigid segment(also known as hard segment), the whole undergoing orientation on extention as indicated in Figure 2.14.

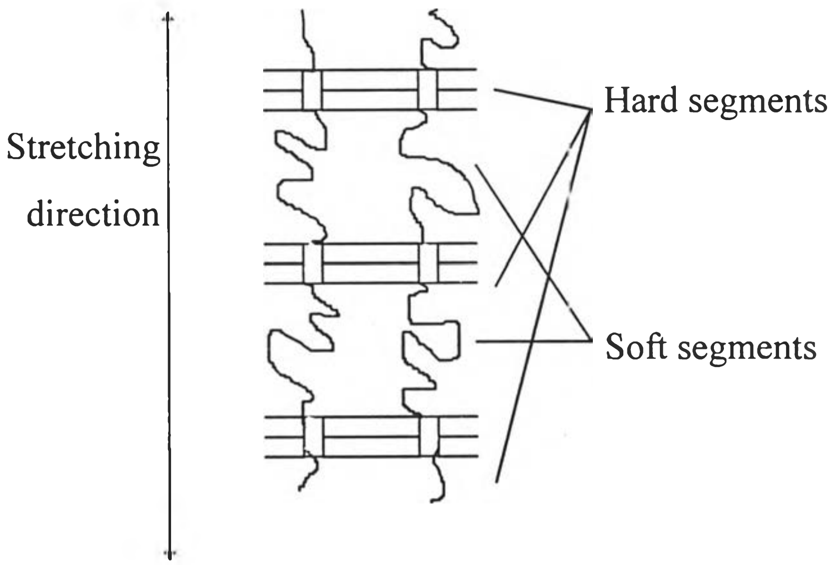
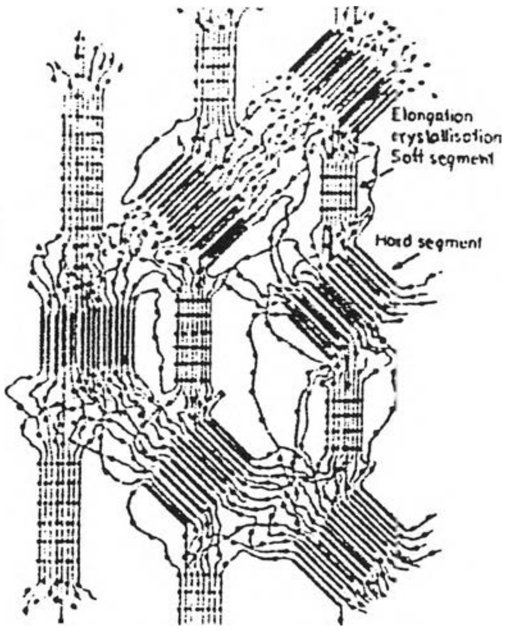


Figure 2.14 Flexible and rigid segments in a polyurethane elastomer. (Hepburn, 1991)

The rigid segments separate to form domains in a matrix of soft segments. They function as physical crosslink sites and as reinforcing filler particles in the soft segment matrix. This concept is illustrated in

Figure 2.15. Strain-induced crystallization occurs in the soft segments due to stretching and disentanglement, the rigid domains then lie in a disorientated manner transverse to the direction of stretching.

Hydrogen bonding occurs between the NH-groups (proton donor) and the carbonyl groups (electron donor) of the urethane and urea linkage in the rigid domains, and also formed between the NH-group of the urethane and urea linkages and the carbonyl oxygen atoms of polyester chains in the soft segments. They also tend to align by weaker hydrogen-bonding with the NH-groups; which are more labile than those formed with carbonyl oxygen atoms.



<u>Figure 2.15</u> Strain-induced elongation crystallization of polyether soft segments in segmented polyurethane elastomer by elongating it to 200% extension. (Hepburn, 1991)

Flexible segments

Amorphous aliphatic polyether or aliphatic polyester polyols are the usual materials used as flexible segments in commercial elastomeric polyurethanes. These have glass transition temperature (T_g) below room temperature and are low-melting-point solids or liquids with molecular weight ranging from about 600 to about 3000.

Those having higher molecular weights give the final polyurethanes with better tensile properties but with an increasing tendency to cold-harden, and this is a phenomenon which is due to slow crystallization of the flexible blocks during storage. Therefore an increase in the molecular weight of the flexible blocks for a given overall molar ratio of polyol block to isocyanate plus chain extender are a fall in modulus and an increase in the elongation at break.

Phase mixing is greater in polyester based polyurethanes than polyether based ones because the NH-ester carbonyl hydrogen bonds are stronger than the urethane NH-ether oxygen bonds. Because of these weaker interchain forces, the latters have somewhat inferior physical properties; they do however possess a superior hydrolytic stability.

Polycaprolactone polyol are considered to be a good compromise since they allow for elastomers to be synthesized with both excellent physical properties and hydrolytic stability.

Rigid segments

The reaction of diisocyanate with a glycol or a diamine is to form respectively the urethane or the urea linkages, which provides the property of hard segments, which determine the interchain interactions in the elastomers to a large extent and so determine the network structure in these materials.

Morphological structure in urethane elastomers can be correlated with stress-strain behavior as modulus decreases and extensibility increases with decreasing rigid segment content. Increases in modulus and tensile strength with increasing rigid segment content are well-established property trends in urethane elastomers. In low rigid segment content, poor domain formation results, and strain crystallization of the flexible segment is used to account for the high modulus observed.

2.3 Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is low cost and compatible with many additives and other polymers. The additives, such as plasticizers, heat stabilizers, fillers, help PVC be processed easily and produce products with a variety of properties (see Table 2.6) . The products may be rigid, such as pipes, rain gutters and window frames, or flexible such as in cable insulation, medical tubing and plastic gloves.(Totsch, 1990)

Table 2.6 Effect of PVC additives on product properties. (Totsch, 1990)

Auxiliary	**Affected property of the PVC article**
Stabilizer	Prevents decomposition during processing, imparts light and weathering resistance
Colorant	Colour, weathering resistance
Plasticizer	Mechanical properties, burning behaviour
Impact modifier	Impact strength and other mechanicalproperties
Lubricants	Rheology of the PVC melt, also affects transparency, gloss, surface finish and printability
Fillers	Mechanical properties
Flame retardants	Burning behaviour
Antistatic agents	Electrical properties
Blowing agents	Processing to expanded products

2.3.1 Polymerization Process

The three processes to manufacture PVC are the suspension process, the mass or bulk process and the emulsion process. All are based on free radical-initiated polymerization of vinyl chloride monomer (VCM). The process differ in the form in which the VCM enters into the reaction. The manufacturing process affects the properties of the PVC and its applications.

The suspension process is the most important one. It accounts for approximately 75% of PVC produced around the world. VCM is stirred in water to produce a fine dispersion. The initiator, which most frequently is an organic peroxide, dissolves in the VCM droplets. The suspending agent prevents the agglomeration of the newly formed particles. The reaction parameters can be controlled and product properties such as molecular weight can be also controlled with variation within a wide ranges.

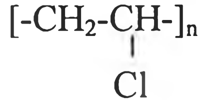
In the emulsion process, an emulsifier is used to form a fine dispersion of VCM in water. The initiator is dissolved in the water.

Polymerization results is precipitated and spray dried. Emulsion PVC is the preferred product for the manufacture of pastes.

The mass or bulk process is very simple, it involves the polymerization of pure VCM. As no emulsifiers or suspending agents are used, the resultant product is very pure. A disadvantage is the inflexibility of the process, which is different to controll heat of reaction. (Herman, 1989)

2.3.2 Structure and Property of PVC

The repeating unit of the PVC chain is



$$[-CH_2-\underset{Cl}{\underset{|}{C}}H-]_n$$

Where n (the degree of polymerization) has values between about 500 and 2000, i.e. the molecular weight range is about 30000 - 100000. The molecular weight of PVC affects both the processability and the physical properties. In general, the higher the molecular weight, the greater the difficulty in processing and the higher the physical properties.

The physical properties of PVC are dependent on the nature and type of plasticisers, also on other compounding ingredients.

For chemical properties, pure PVC is resistant to most acids and alkalis, although it is decomposed by concentrated sulphuric, nitric and chromic acids. It is dissolved by tetrahydrofuran and isophorone, swollen to varying extents by ketones, esters and aromatic and chlorinated hydrocarbons, but is resistant to aliphatic hydrocarbons and oils.

The glass transition temperature (T_g) of conventional PVC is about 80°C, and crystalline PVC is up to about 110°C, depending on temperature of polymerization. The plasticisation lowers the T_g and the softening point. The melting point of crystalline PVC may be as high as 273°C. It starts to decompose at about 100°C, and has a low softening point, between 70 and 80°C.(Penn, 1971)

2.3.3 Miscibility of PVC

Because of its low cost and versatility, PVC was used in blending with other polymers to improve processability and properties, such as heat distortion temperature, impact strength, and service life.

Usually, melt mixing and blending of solutions is used. If blending is achieved on intimate scale, a type of interpenetrating polymer network (IPN) may be obtained.

The miscibility of PVC with other polymers was controlled by specific interactions [e.g., hydrogen-bonding or more generalized electron donor/ electron acceptor(Lewis acid-base) interactions]. Such interactions dominate in the mixing of two polar species. PVC behaves generally as an electron acceptor, and thus interact strongly with electron donors such as carbonyl, ether, nitrile, and sulfonyl groups in the second polymer.

The most obvious specific interactions is the ability of the α-hydrogen in PVC to form a hydrogen-bond with a carbonyl unit in an ester or amide group.

$$C{=}O\text{------}H\text{-}C\text{-}Cl$$

PVC is the most miscible with different homopolymers and copolymers. Table 2.7 lists some of the typical modifier polymers for PVC of current technological interest.(Leonard, 1986)

Table 2.7 Typical Modifiers for PVC. (Leonard, 1986)

Purpose	**%**	**Modifier**
Impact strength or toughness	5-10	Ethylene/vinyl acetate copolymer (EVA) Polybutyl acrylate (PBA)
	5-15	Acrylonitrile-butadiene-styrene (ABS) Methacrylate-butadiene-styrene (MBS)
	10-20	Chlorinated polyethylene (CPE) Acrylonitrile-butadiene copolymer (NBR)
	-	Ethylene-propylene-diene terpolymer (EPDM) Ethylene-propylene rubber (EPR)
Permanent plasticization	often 40-50%	EVA, NBR, poly-ε-caprolactone (PCL), Polyurethane (PU), polyester (PES), PCL graft with polystyrene (PCL-g-PS)
Processability	1-10	PMMA, acrylate-methacrylate (AMA), MMA/ethyl acrylate copolymer (MMA/EA), Styrene-acrylonitrile copolymer (SAN)
	To 30	Vinyl chloride/vinyl acetate copolymer (VC/VA)
	7-12	SAN (foam extrusion)
To raise heat distortion temperature	To 50	SAN, styrene-acrylonitrile-methacrylate-butadiene copolymer (SAMB)
Chemical resistance	30-50	NBR
Weathering	5-20	EVA (sometimes grafted), CPE

2.4 Polymers in Automotive Industry

Polymer are an important material used in automotive industry because of its unique properties such as lower costs, lighter weight, stronger and more durable than metals materials. The plastic usage of the United States in automotive industry in 1983 through 1993 is shown in Table 2.8, it can be used to represent the world's plastic usage in automotive (Herman, 1989).

Table 2.8 U.S. Plastics usage in the automotive industry 1983-1993. (Herman, 1989)

	1000 t		
Material	1983	1988	1993
thermoset polyester	52.4	81.9	123.7
polyurethane	105.1	122.7	127.5
polypropylene	108.5	112.7	103.9
polyethylene	21.8	27.4	31.3
ABS	27.9	24.6	22.9
styrene-maleic anhydride	17.7	19.3	7.7
modified poly(propylene oxide)	5.9	8.0	8.9
polystyrene	2.4	3.6	1.4
nylon	39.1	46.2	48.5
thermoplastic polyester	8.9	12.4	17.3
polycarbonate	5.1	11.1	22.9
acetal resins	7.5	8.6	8.8
acrylics	9.5	10.9	10.8
PVC	58.4	59.0	58.4
phenolic resins	6.4	8.3	23.9
other	15.3	18.6	23.9
Total	*491.9*	*556.7*	*636.9*

Since these studied were aimed to develop a material for automotive industry, some polymers which are frequently used are discussed in details.

Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is used in many forms, e.g., plasticized, calendered sheet, injection-molded parts, and extruded sheet. It is often combined with other polymers to improve specific properties. Example of PVC applications as a materials in automobiles are upholstery and trim, rubber strips, welting, crash pad and arm rest, gasketing, streering wheels, insulation and harness, battery separator.

Polypropylene

Polypropylene has become the most widely used thermoplastic in automobiles because of its versatility and low cost. Example of its applications are trim, climate-control ducts, steering wheels, fan shrouds, electric box connectors, battery cases.

Acrylonitrile Butadiene Styrene (ABS)

ABS is also the most widely used as instrument panels, interior trim, plated part, crash pads, skins (in combination with PVC), etc. The other styrenic based polymer, such as poly(styrene-acrylonitrile) (SAN), styrene maleic anhydride(SMA) are also used for instrument panels.

Nylon

Unfilled nylon-6, nylon-6/6, and nylons 11 and 12 are used as electrical, fuel system, and mechanical parts, e.g. gears, door handle, brake-fluid reservoir and electrical parts, e.g. cable jacketing, lamp sockets and plugs.

Nylon filled with glass has been used for structural applications such as headlamp housings, keylock housings, fender extensions, and window louvers.

Polyurethane

Polyurethane (PU) is also commonly used in automobile. Applications include seating, interior padding, exterior body panels, complete soft front ends, components mounted in the engine space and accessories such as mirror surrounds and spoilers.

Other polymers

Other polymers and their applications used in automobile are less common such as

- acetal : fuel system parts, seat-belt release mechanism
- polycarbonate : bumper fascia
- glass reinforced poly(ethylene terephthalate) (PET) : side roof rail
- polysulfone (PSF) : climate-control panel
- glass reinforced polyphenylene oxide (PPO) : instrument panel
- acrylic : lenses
- polyethylene : gas tanks, valence panel
- cellulosic : steering wheel cover
- glass reinforced phenolic : Transmission reactor
- thermoplastic elastomers : fascia, piston seal, vacuum-driven diaphragm motor
- glass and graphite fibers reinforced vinyl ester : composite-driveshaft (Klein, 1988 and Wigotsky, 1992)

Example of the car which used plastic materials is showed in Figure 2.16.

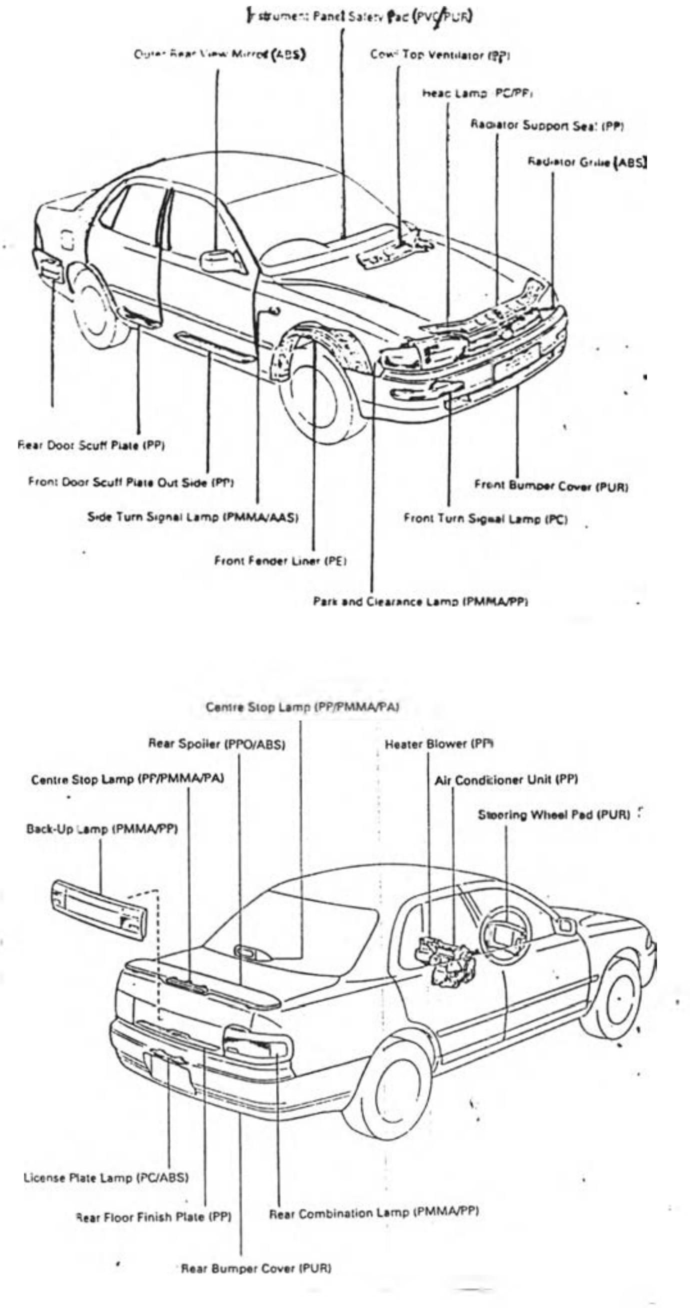


Figure 2.16 Location of plastic parts in Toyota Camry car.
(Toyota Co.,Ltd)

Relevant literature review

M.Omoto, J.Kusters, D.Sophiea, D.Klempner and K.C.Frisch (1988) prepared a pseudo-interpenetrating polymer network (pseudo-IPN) of polyurethane (PU) and poly(vinyl chloride) (PVC). The polyurethane used is based on a mixture of polycaprolactone glycol (PCL), miscible with PVC, and poly(oxypropylene glycol) (PPG), immiscible with PVC. Experimental data from dynamic mechanical spectroscopy indicated that increasing the content of PPG-based PU decreased the compatibility of the resulting PU with PVC. Tensile strength increases at lower PU content due to increasing PVC content and an interpenetrating effect.

P.K.Bandyopadhyay and M.T.Shaw (1982) investigated the plasticization of poly(vinyl chloride) (PVC) by polyurethanes (PU) made from polycaprolactone (PCL) diol and *p,p'*-diphenylmethane diisocyanate (MDI). By varying the PCL chain length, the miscibility of PU in PVC increased by increasing the PCL chain length, i.e., decreasing the MDI content. PU containing high molecular weight PCL slowly crystallize from the 50:50 blend. The rate of crystallization depends on PVC/PU ratio. The replacement of PCL-2000 segment by polyether glycol produced PU with decreased miscibility in PVC. This evidence revealed by a broadened glass transitions and high damping properties over wide ranges of temperature.

N.Natchimuthu, P.Rajalingam and G.Ranhakrishnan (1992) synthesized ternary semi-IPN of nitrocellulose (NC), poly(vinyl chloride-co-vinyl acetate) (Vc-Vac copolymer) and polypropylene glycol-based polyurethane (PU). The resulting polymers were characterized using FT-IR, SEM and DSC. The semi-IPN of NC/PU was found to be incompatible whereas ternary semi-IPN of NC/Vc-VAc copolymer/PU was partially compatible. FT-IR indicated hydrogen bonding between the urethane groups and the carbonyl groups of the copolymer. SEM and DSC results indicated improved compatibility for the ternary system.Tensile strength increased when the proportion of NC to Vc-VAc copolymer increased, and NCO/OH ratio increased.

S.J.Kim, B.K.Kim and H.M.Jeong (1994) studied the miscibility of thermoplastic elastomeric polyurethane (TPU) with poly(vinyl chloride) (PVC). The former were prepared from 4,4′-diphenylmethane diisocyanate (MDI), hydroxy-terminated poly(butylene adipate) (PBA) and dimethylolpropionic acid (DMPA). The resulting polymer showed a single Tg, irrespective of neutralization of carboxylic acid groups of the DMPA unit in TPU by TEA. When hydroxy-terminated poly(propylene glycol) (PPG) was used as the soft segment instead of hydroxy-terminated PBA, two separate Tg's of PVC and TPU were observed, irrespective of neutralization.

H.X.Xiao, K.C.Frisch, H.L.Frisch (1983) investigated the effect of variation of the NCO/OH ratio of the polyurethane(PU) prepolymer, and the molecular weight (MW) of the polyols in the PU component on the mechanical properties and morphology of PU-Poly(methyl methacrylate) IPNs. PU prepolymers were prepared from the reaction of poly (oxytetramethylene)glycol and 4,4′-diphenylmethane diisocyanate. The mechanical properties increased with increasing NCO/OH ratio and decreased with increasing MW of the polyol in PU. The morphology was studied using DSC and SEM. Improved phase compatibility was observed when NCO/OH ratio increased and MW of the polyol decreased.

D.S.Lee and S.C.Kim (1984) synthesized a simultaneous interpenetrating polymer networks of polyurethane (PU) - poly(methyl methacrylate) (PMMA) under high pressure. The morphology was studied using TEM, and the Tg behavior using DMA and DSC. The composition of the PU and PMMA was fixed at 50/50% by weight. The domain sizes of PU phase decreased from about 300 to 30^{o} with increasing synthesis pressure from 1250 to 20000 kg/cm^{2}. A broad Tg was observed when IPN's were synthesized under high pressure which showed the increased degree of interpenetration of the component networks.

G.B.Guise and G.C.Smith investigated the influence of composition on the properties of cast polyurethanes prepared in a one-step stoichiometric reaction of diisocyanate with polycaprolactone(PCL) diol, and PCL triol crosslinking agent with 1:1 hydroxyl-isocyanate. In some formulations the elastomeric properties were lost due to the crystallization of PCL soft segments, which tended to crystallize more readily than harder ones. These materials showed the melting and glass transitions when examined by DSC and TMA. The molecular weight of the PCL diol had a greater influence on the Tg than the diol concentration.