

CHAPTER I

INTRODUCTION

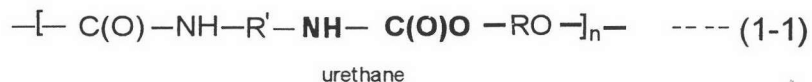


Polyurethane (PU) sometimes called urethane is polymeric material, discovered by O.Bayer and his colleagues at I G. Farbenindustrie in 1937 [1]. Since then many development and improvement of PU have been carried out worldwide in many laboratories rendering it as one of a resounding commercial polymeric materials in the world market. It is well-known that controlled physical and mechanical properties of solid PU can be made according to particular chemical formulation of starting polymeric materials (or called precursors) used.

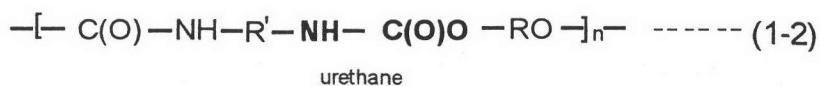
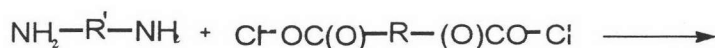
In this Chapter, basic chemistry of PU is discussed in Section 1.1. Structure and property relationship is in Section 1.2. In Section 1.3 description of preparation of PU is given prior to details of crosslinking agent used for preparation of PU elastomer in Section 1.4. Objectives and scope of the research are given in Section 1.5.

1.1 Basic Chemistry of Polyurethane

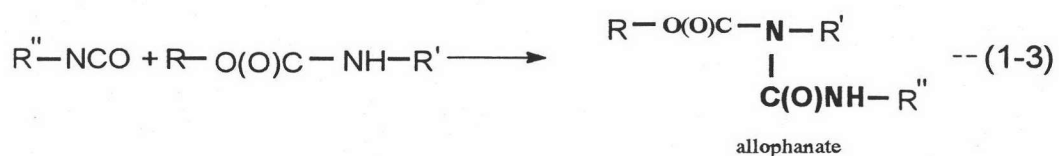
PU is commonly made in the reaction of essentially equivalent amounts of polyols and diisocyanates according to the reaction 1-1. The reaction of hydroxy with isocyanate results in urethane or carbamate group (-OC(O)NH-). Therefore, it is generally known that PU contains many urethane linkages along the polymeric backbone.



Many other alternative reactions to prepare PU have been described [2]; one of interesting reactions involves the reaction of a dichlorocarbonate with a primary or secondary diamine [3].



The isocyanate can react with other compounds having an active hydrogen bonding to a highly electron donating atom such as N, O. One significant reaction to be mentioned is the reaction of isocyanate with urethane resulting allophanate linkage (reaction (1-3)). This reaction is thermally reversible at 106 °C [4]. The linkage influences on property of solid PU by which a number of crosslinking increase resulting in polymers having better mechanical property [5].



1.2 Structure-Property Relationship of Polyurethane

It is well recognized that PU is a $(AB)_n$ -type block copolymer consisting of physically different **soft** and **hard segments**. The hard segment contributes from the urethane linkage, while the soft segment from the polyol precursor. In the case that a crosslinking agent or curative for PU, generally organic glycol compounds, is used, either physical or chemical crosslinked PU is obtained. The hard segment of elastomer is derived from the reaction of diisocyanate with the curative in addition to that described earlier.

Recent studies on the morphology of various PU show that the hard segments tend to associate with each other through hydrogen bonding due to the polar nature of the urethane moieties. As a result the hard segments cluster or aggregate into hard domains dispersing within the rubbery matrix of the soft segments, and reinforcing the matrix by functioning as pseudo crosslinkers. Other intermolecular interactions such as attraction of π -electron of aromatic diisocyanate may also contribute to aggregation of the hard segments [6]. The soft segments therefore show elastic property, while glassy property is obtained from the hard segment. Therefore, the property of PU is the combination of those of soft and hard segments, which their number could be varied by variation of stoichiometric ratio of diisocyanate to diol precursors.

The hydrogen bonding in the soft segment may be possible, e.g., between ether groups of the polyol precursor with the-NH-groups of the hard segments. This provides to increase the glass transition temperature (T_g) of soft segment and reduces T_g of the hard segment, in turn leading to

improvement in hardness and tensile strength of PU.

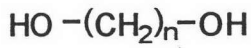
Many investigations have been carried out to study the structure-property relationships of urethane elastomers as related to the nature of the soft and hard segments. Results show that the hard segments control the hardness, modulus, and tear strength while the soft segments provide flexibility of the elastomers. In conclusion, the overall structure-property relationship of urethane elastomers is basically governed by five factors including molecular weight of solid polymers, degree of crosslinking, degree of crystallinity of hard segment, amount of hydrogen bonding in the hard and soft segments, molecular weight and molecular weight distribution and chemical structure of precursors.

1.3 Preparation of Polyurethane

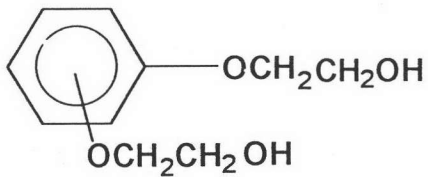
PU can be prepared either by solution or bulk step-wise polymerization reactions. However, the former is more popular due to exotherm of polymerization can be controlled. For the latter, the preparation techniques can be of two methods, i.e., casting and reactive processing techniques. The casting technique is rather simple and mostly used for preparation of slow gellation-time PU or for preliminary studies of structure-property relationship in most laboratories. The reactive processing technique such as Reaction Injection Moulding (RIM) is widely employed in industries. From small to large size, and from simple to complicated shape of products can be prepared using a RIM machine. The precursors are mixed at the machine mixed head; the polymerisation occurs suddenly and proceeds continuously in situ in a mould cavity. More details on RIM technology can be

1.4 Crosslinking Agent for Polyurethane Elastomer

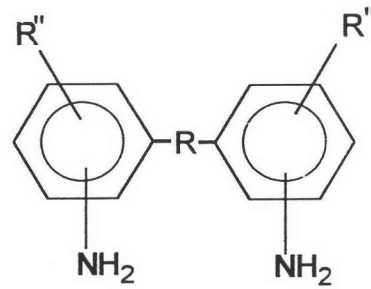
Crosslinking agents (chain extenders or curatives) are the necessary precursors for the preparation of PU elastomers as mentioned earlier. Aromatic diamines (3), aliphatic (1) and aromatic dihydroxy compounds (2) constitute the majority of curatives used today.



(1)



(2)



(3)

1.4.1 Hydroxy Crosslinking Agent

In general dihydroxy (glycol) curatives should have molecular weight less than 400. Their chemical structures may be aliphatic straight or branched compounds, cycloaliphatics or aromatics [8]. A list of various hydroxy crosslinking agent generally used are shown in Table 1.1.

Table 1.1 Hydroxy crosslinking agent

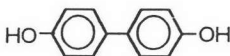

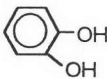
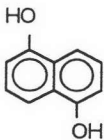
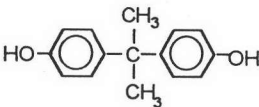
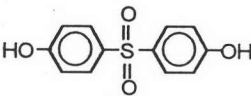
Additive	Structure	Functionality	Molecular Weight	Ref.
Ethylene glycol	HO-C ₂ H ₄ -OH	2	62.07	9
1,4-Butane diol	C ₄ H ₈ (OH) ₂	2	90.12	5
4,4'-biphenol		2	186.21	2
Quinol		2	110.11	2
Catechol		2	110.11	2
1,5-naphthalene diol		2	160.17	2
Bisphenol A		2	228.29	2
Di(4-hydroxyphenyl)sulphone		2	250.27	2

Table 1.1 Hydroxy crosslinking agent (cont.)

Additive	Structure	Functionality	Molecular Weight	Ref.
Triisopropanol amine		3	191	10
Trimethylolpropane		3	120	9
1,4-Di(2-hydroxy ethyl)hydroquinone (HQEE)		2	198	11
1,3-Di(2-hydroxy ethyl)resorcinol (HER)		2	198	11

In general, minor changes in the chemical structure of the analogous dihydroxy crosslinking agents have little effect on elastomer properties. However gross changes in dihydroxy crosslinking agents such as the introduction of an aromatic ring does have a large effect due to increase in rigidity of aromatic content. The aromatic dihydroxy tend to yield thermal

resistance and a better retention of properties at elevated temperature[5]. Additionally, they contribute to improve processibility and/or shorter demolding times [12].

Hydroxy curatives having hydroxy functionality more than two are used for preparation of chemical crosslinked PU, i.e., three dimension network structure, while dihydroxy ones could only prepare physical crosslinking, i.e., two-dimension network. The physical crosslinking can be destroyed easily at elevated temperature and recovered again when temperature is reduced. While the chemical crosslinking cannot be easily destroyed, and once destroyed it cannot be recovered.

An investigation of the effect of a series of aliphatic glycols provides evidence that glycol chain extenders affect final physical properties even though they are relatively minor components in the formulations. Increasing molecular weight of the extender improves low-temperature properties to some extent.

Mixed glycol systems are employed to produce transparent polyurethanes [8]. The system must be capable of preventing crystallization of PU over time to ensure stable optical property. The mixed glycols system are employed to broaden the processing range of thermoplastic polyurethane elastomers.

1.5.2 Amine Crosslinking Agent

Amino compounds are also very important to be used as crosslinking agents for the preparation of PU. Amino reacts with isocyanate, which is faster than the reaction of glycol with diisocyanate, to give urea linkage (-NH-C(O)-NH-). Therefore, the solid polymer obtained when using amine curatives will have PU and polyurea hard segments. This polymer is usually called polyurethaneurea. Commercially important diamine curatives are given in Table 1.2.

Unsubstituted aromatic amines such as methylene dianiline and *m*-phenylene diamine are too reactive to have sufficient pot life for hand batch mixing. Therefore, use of a dispensing machine such as RIM machine, is required. Substituent such as chloride atoms and methyl or alkyl carboxylate groups in the aromatic rings of the amine curatives reduces the chemical reactivity of the amino groups through the electron withdrawing effect and /or steric hindrance of the substituents. A reasonable pot life can therefore be obtained.

In an earlier study of the diamine curatives, it is indicated that 4,4'-methylenebis-(2-chloroaniline), MOCA, imparts a better balance of tensile, tear, modulus, and hardness properties to the resulting the elastomers [Ref]. It also show that chloride substituents in these diamines did not cause reduction in elastomer properties as were observed with diisocyanates having methyl substituents.

Table 1.2 Amine crosslinking agents for Castable Urethane Elastomer

Common or trade name	Chemical name	Equivalent weight	Ref.
MOCA, Curene	4,4'-Methylene bis(2-chloroaniline)	133.5	12
MDA	4,4'-Methylene dianiline	63.5	12
Cyanacure	1,2-Bis(2'-aminophenylthio)ethane	138	11
Polacure	Trimethyleneglycol-di- <i>p</i> -aminobenzoate	157	5
Ethacure 300	3,5-dimethylthio-2,4- and 2,6-toluenedi-amine	107	5
Caytur 21	Methylene dianiline sodium chloride complex dispersed in dioctyl phthalate	217	5
Baytec 1604	3,5-diamine-4-chloro-isobutylbenzoate	121	5

Search for a MOCA replacement in recent years has intensified because of concerns over its potential health hazards to human [13]. Due to the toxicity of the most used of MOCA, it is no longer manufactured in the United States. As a result, during the past few years several new curatives have become available commercially.

1.5 Objective and Scope of the Research

1.5.1. Objective

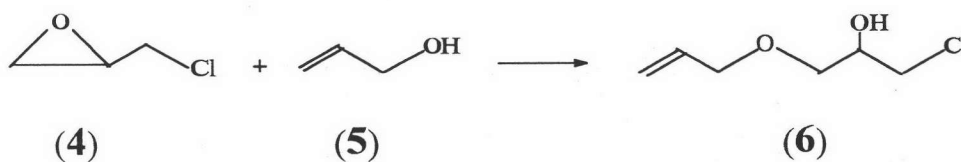
The principle objective of this study was to synthesize new crosslinking agents suitable for preparation of chemical crosslinked polyurethane, which is suitable for engineering applications.

1.5.2 Scope of the Research

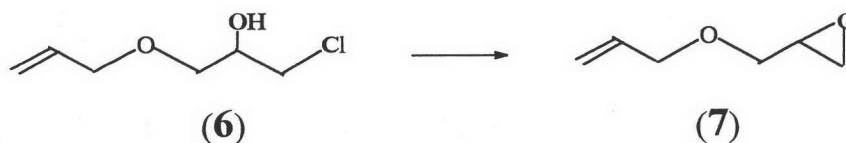
1.5.2.1 To synthesize crosslinking agents containing multifunctional groups in particular hydroxy and vinyl pendants in the molecule. Basic raw materials and synthetic routes are simple and wellknown. It may be therefore expected that the synthesis of new curatives may be feasible to scale up to industrial scale.

The proposed synthetic pathways for the new multi-hydroxy and vinyl crosslinking agents have three step as follows:

step 1) Preparation of chlorohydrin compound (6).

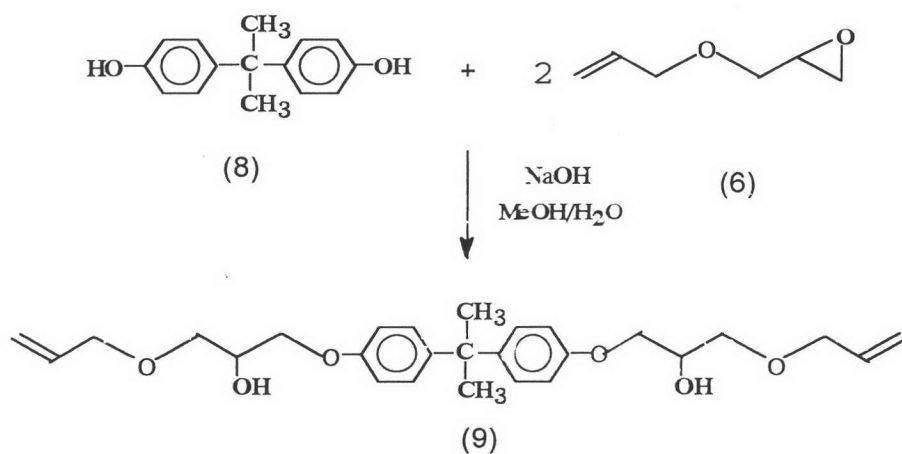


2) Formation of epoxide (7).

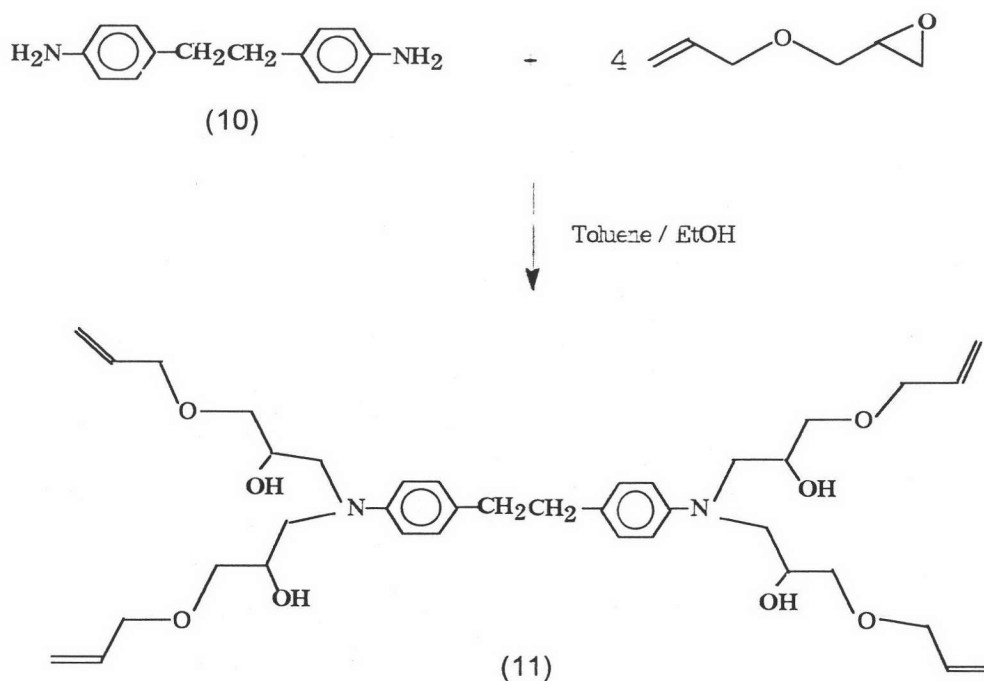


3) The reaction of epoxide with nucleophiles.

a) Hydroxy nucleophiles (8)



b) Amine nucleophiles



1.5.2.2 The crosslinking agents synthesized will be purified and characterized using chromatographic and spectroscopic methods.