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นาย ประเสริฐ เรียบร้อยเจริญ

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STUDY OF THE PROPERTIES AND STRUCTURES OF POLYURETHANE ELASTOMERS SYNTHESIZED FROM NORBORNANE DIISOCYANATE

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ประเสริฐ เรียบร้อยเจริญ : การศึกษาสมบัติ และโครงสร้างของโพลิยูรีเทนอีลาสโตเมอร์ที่สังเคราะห์จากไดไอโซไซยาเนตชนิดใหม่ (STUDY OF THE PROPERTIES AND STRUCTURES OF POLYURETHANE ELASTOMERS SYNTHESIS FROM NORBORNANE DIISOCYANATE) อาจารย์ที่ปรึกษา : ดร. ศิริพร ดำรงค์ศักดิ์กุล, 176 หน้า. ISBN 974-332-988-9.

งานวิจัยนี้ได้ทำการศึกษาโครงสร้าง และสมบัติของโพลิยูรีเทนอีลาสโตเมอร์สองชนิดที่แตกต่างกัน (โพลิยูรีเทนอีลาสโตเมอร์ชนิดที่บ่มด้วยความชื้นในอากาศ (moisture cured polyurethane elastomers) และโพลิยูรีเทนอีลาสโตเมอร์ชนิดสององค์ประกอบ (two-component polyurethane elastomers)) ที่ผลิตจากไซโคลอะลิฟาติกไอโซไซยาเนตชนิดใหม่ (new cyclo-aliphatic isocyanate) (นอร์บอร์เนนไดไอโซไซยาเนต (norbornane diisocyanate)) และเปรียบเทียบกับโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซไซยาเนตชนิดทั่ว ๆ ไป สำหรับโพลิยูรีเทนอีลาสโตเมอร์ชนิดที่บ่มด้วยความชื้นในอากาศจะทำการศึกษาผลกระทบจากชนิดของไดไอโซไซยาเนต (นอร์บอร์เนนไดไอโซไซยาเนต และไอโซโฟโรนไดไอโซไซยาเนต) และผลกระทบของ NCO% จากการทดลองพบว่า โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนนไดไอโซไซยาเนตมีความว่องไวและความต้านทานต่อสภาพอากาศสูงกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนต ในขณะเดียวกันโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนต มีสมบัติทางกล และมีการแยกเฟสดีกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนไดไอโซไซยาเนต และจากการวิเคราะห์ทางโครงสร้างพบว่า โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนตมีหมู่ยูเรียคาร์บอนิลที่มีพันธะไฮโดรเจนมากกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนไดไอโซไซยาเนต ซึ่งเป็นการบอกโดยนัยถึงความแข็งแรงที่สูงกว่าในโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนต ซึ่งสอดคล้องกับผลการทดลองในเรื่องความแข็งแรงทางแรงดึง การเพิ่ม NCO% จาก 6% เป็น 8% เป็นการเพิ่มความแข็งแรงทางแรงดึงของโพลิยูรีเทนอีลาสโตเมอร์ซึ่งสอดคล้องกับจำนวนหมู่ N-H ที่มีพันธะไฮโดรเจน หมู่ยูรีเทนที่มีพันธะไฮโดรเจน และหมู่ยูเรียที่มีพันธะไฮโดรเจน ของโพลิยูรีเทนอีลาสโตเมอร์ที่ NCO% = 8% ซึ่งพบว่ามีมากกว่า ที่ NCO% = 6%

สำหรับโพลิยูรีเทนอีลาสโตเมอร์ชนิดสององค์ประกอบ จะทำการศึกษาผลกระทบจากชนิดของไดไอโซไซยาเนต (นอร์บอร์เนนไดไอโซไซยาเนต ไอโซโฟโรนไดไอโซไซยาเนต เมทราไซลีนไดไอโซไซยาเนต และโทลูอีนไดไอโซไซยาเนต) และผลกระทบจากชนิดของสารบ่ม (อิทาเคียวหนึ่งร้อย (ethacure100) และอิทาเคียวสามร้อย (ethacure300)) โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนนไดไอโซไซยาเนตมีความว่องไว และความต้านทานต่อสภาพอากาศสูงกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนต โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนตมีสมบัติทางกล และความต้านทานต่อการเปลี่ยนสีสูงกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไดไอโซไซยาเนตชนิดอื่น ๆ (นอร์บอร์เนนไดไอโซไซยาเนต เมทราไซลีนไดไอโซไซยาเนต และโทลูอีนไดไอโซไซยาเนต) ในขณะที่โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนตมีการแยกเฟสดีกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนนไดไอโซไซยาเนต ยิ่งไปกว่านั้นยังพบว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากไอโซโฟโรนไดไอโซไซยาเนตมีความเหนียวมากกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากนอร์บอร์เนนไดไอโซไซยาเนต และโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากอะโรมาติกไดไอโซไซยาเนต (เมทราไซลีนไดไอโซไซยาเนต และโทลูอีนไดไอโซไซยาเนต) มีความแข็งมากกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากอะลิฟาติกไดไอโซไซยาเนต (นอร์บอร์เนนไดไอโซไซยาเนต และไอโซโฟโรนไดไอโซไซยาเนต) โพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากอิทาเคียวหนึ่งร้อยมีสมบัติทางกล ความต้านทานต่อการเปลี่ยนสี และความว่องไวสูง แต่มีความต้านทานต่อสภาพอากาศต่ำกว่าโพลิยูรีเทนอีลาสโตเมอร์ที่ผลิตจากอิทาเคียวสามร้อย

ภาควิชา ....วิศวกรรมเคมี........

สาขาวิชา ....วิศวกรรมเคมี........

ปีการศึกษา ....2542........

ลายมือชื่อนิสิต ....ประเสริฐ เรียบร้อยเจริญ........

ลายมือชื่ออาจารย์ที่ปรึกษา ....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....-........

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

4070333621: MAJOR CHEMICAL ENGINEERING DEPARTMENT
KEY WORD: POLYURETHANE / POLYURETHANE ELASTOMER / DIISOCYANATE / MOISTURE CURED / TWO COMPONENT / CURING AGENT

PRASERT REABROYCHAROEN : STUDY OF THE PROPERTIES AND STRUCTURES OF POLYURETHANE ELASTOMERS SYNTHESIS FROM NORBORNANE DIISOCYANATE
THESIS ADVISOR : SIRIPORN DAMRONGSAKKUL, Ph.D.
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The structures and properties of two different types of polyurethane elastomers, moisture cured polyurethane elastomers and two-component polyurethane elastomers, produced from new cyclo-aliphatic isocyanate (norbornane diisocyanate), were studied and compared with the conventional isocyanate-based polyurethane elastomers. For moisture cured polyurethane elastomers, the effects of diisocyanates (norbornane diisocyanate (NBDI) and isophorone diisocyanate (IPDI)) and the effects of NCO% were investigated. It was found that NBDI-based polyurethane elastomers have higher reactivity and weathering resistance than IPDI-based polyurethane elastomers. IPDI-based polyurethane elastomers have superior mechanical properties and better phase separation to NBDI-based polyurethane elastomers. From the structure analysis, it showed that the hydrogen-bonded urea carbonyl groups of IPDI-based polyurethane elastomers are more than those of NBDI-based polyurethane elastomers. This implies the higher strength in IPDI-based polyurethane elastomer as found in the tensile strength results. Increasing NCO% from 6% to 8% increases the tensile strength, which corresponds to the more amount of hydrogen-bonded N-H groups, hydrogen-bonded urethane and hydrogen-bonded urea groups of polyurethane elastomers at NCO% = 8% than 6%.

For two-component polyurethane elastomers, the effects of diisocyanates (norbornane diisocyanate, isophorone diisocyanate, m-xylene diisocyanate (m-XDI) and toluene diisocyanate (TDI)) and the effects of curing agents (ethacure100 and ethacure300) were examined. NBDI-based polyurethane elastomers have higher reactivity and weathering resistance than IPDI-based polyurethane elastomers. IPDI-based polyurethane elastomers have superior mechanical properties and discolouration resistance to polyurethane elastomers prepared from the other diisocyanates (NBDI, m-XDI, TDI). IPDI-based polyurethane elastomers have better phase separation than NBDI-based polyurethane elastomers. Moreover, it was found that IPDI-based polyurethane elastomer is tougher than NBDI-based polyurethane elastomer and the aromatic diisocyanate (XDI and TDI)-based polyurethane elastomers are stiffer than the aliphatic diisocyanate (NBDI and IPDI)-based polyurethane elastomers. Ethacure100-based polyurethane elastomers have superior mechanical properties, higher discolouration resistance and higher reactivity but lower weathering resistance to ethacure300-based polyurethane elastomers.

ภาควิชา วิศวกรรมเคมี
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ลายมือชื่ออาจารย์ที่ปรึกษา
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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม -

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Finally, he wishes to convey his deep appreciation to his parents and his brother and sister who always mean so much to his mind.

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CHAPTER I

INTRODUCTION

1.1 Introduction

In 1994, an estimated 15,900 metric tons of polyurethane elastomers were consumed in Japan. Polyurethane elastomers continue to experience the fastest growth in Japan until present. The consumption of polyurethane elastomers indicates demand of polyurethane elastomers as well as raw materials such as, isocyanate, for the production of polyurethane elastomers. An estimated demand of aliphatic and cyclo-aliphatic isocyanate is approximately 10,000 metric tons. This demand continuous to grow because of the advantage of aliphatic and cyclo-aliphatic isocyanate. Aliphatic and cyclo-aliphatic isocyanate is used to produce high performance polyurethanes with outstanding optical clarity, light stability, and weathering resistance. Aliphatic and cyclo-aliphatic isocyanate is becoming important for polyurethane elastomer markets, although, the cost of these isocyanates is more expensive compared to aromatic isocyanate.

From this point, Mitsui Chemicals, Inc. has recently developed a new cyclo-aliphatic isocyanate, of which the trade name is norbornane diisocyanate (NBDI). NBDI also has high clarity, stiff norbornane structure and can be used to produce clear polyurethane elastomers. It is of interest to study systematically how the physical properties and the structure of the polyurethane elastomers produced from this new cyclo-aliphatic isocyanate (NBDI) could be developed, comparing with the conventional isocyanate-based polyurethane elastomers such as isophorone diisocyanate (IPDI)-based polyurethane elastomers and what the advantages and disadvantages of NBDI-based polyurethane elastomers are over the conventional isocyanate-based polyurethane elastomers.

Two different types of polyurethane elastomers studied in this research are moisture cured polyurethane elastomers and two-component polyurethane elastomers. This research will be carried out in order to study the effects of different isocyanate, and the effect of NCO% on the properties and structure of moisture cured polyurethane elastomers and the effect of different diisocyanate and the effect of different curing agent on the properties and structure of two-component polyurethane elastomers. The relationship between the properties and structure of polyurethane elastomers is expected to be found.

1.2 Project objectives

1. Study the properties and structure of NBDI-based polyurethane elastomers comparing to those of conventional isocyanate-based polyurethane elastomers.
2. Determine the relationship between the properties and the structure of NBDI-based polyurethane elastomers.

1.3 Scope of project

1. Synthesize the NBDI-based polyurethane elastomers and conventional isocyanate-based polyurethane elastomers, each of which is divided into 2 types:
    1) Moisture cured polyurethane elastomers
    2) Two-component polyurethane elastomers (cured by curing agent)
2. Study the effects of the NCO% (NCO% is the weight percentage of reactive -NCO groups in diisocyanate.) used in the synthesis and the effects of diisocyanate on the properties and structure of moisture cured polyurethane elastomers.
3. Study the effects of diisocyanate and the effects of curing agent on the properties and structure of two-component polyurethane elastomers.
4. Evaluate the properties and structure of moisture cured polyurethane elastomers, e.g. tensile strength, %elongation, tear strength, weathering properties, glass transition temperature, infrared absorption, and dynamic mechanical properties.
5. Evaluate the properties and structure of two-component polyurethane elastomers, e.g. tensile strength, %elongation, modulus at 100% and 300% elongation, tear strength, water immersion, heat aging, weathering properties, glass transition temperature, infrared absorption, and dynamic mechanical properties.

6. Relate the properties and structure of NBDI-based polyurethane elastomers and conventional isocyanate-based polyurethane elastomers of moisture cured polyurethane elastomers and two-component polyurethane elastomers.

CHAPTER II

THEORY

In 1937, Professor Otto Bayer and his co-workers of I.G. Farbenindustrie at Leverkusen, Germany, discovered the diisocyanate addition polymerization that resulted in the preparation of many different types of polyurethanes and polyureas. After the World War II, the German chemical industry quickly recovered from the effect of war. Bayer again became active in the polyurethane field and developed elastomers and flexible foams. In fact, most polyurethane applications have been developed during the part 30 years as illustrated in Table 2.1. The range of end-products derived from polyurethanes is shown in Fig. 2.1, which illustrates the molecular structure features used to produce such diverse polymer forms, some fibre- or film-forming, some thermoplastic or thermosetting and other elastomers.

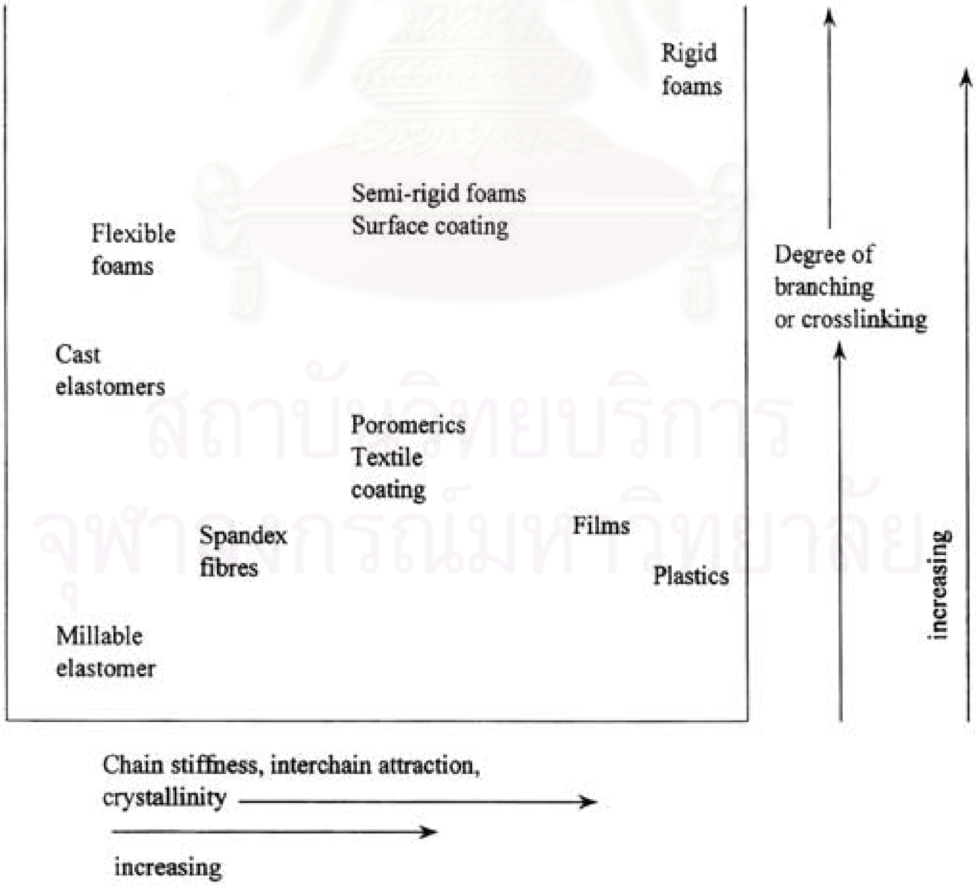


Fig. 2.1 Structure-property relationships in polyurethanes. [HEPBURN C., 1992]

Table 2.1 Some highlights in the development of polyurethanes. [WOOD G., 1987]

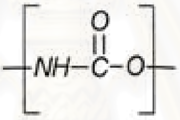
1937-40	Otto Bayer and co-workers made polymers by polyaddition processes from various diisocyanates with glycol and/or diamines.
1940-45	Development of millable polyurethane elastomers and adhesives in Germany (I.G. Farben), U.K. (ICI) and the U.S.A. (du Pont). Polyurethane coatings for barrage balloons (ICI), synthetic polyurethane bristles (I.G. Farben).
1945-47	Manufacture of millable polyurethane elastomers, coatings and adhesives.
1950	Cast elastomers from polyester diols, diisocyanate prepolymers and chain-extenders.
1953	First flexible polyurethane foam manufacture with a Bayer system using a high pressure machine, a polyester polyol and TDI.
1956	First manufacture of polyether-based flexible polyurethane foam in the U.S.A. using a two stage or 'pre-polymer' process.
1957	ICI introduces the first commercially available polymeric MDI composition for rigid polyurethane foam manufacture.
1959	ICI introduces the first rigid foam system based on polymeric MDI and a polyether polyol.
1959	'One-shot' system for flexible polyether-based foam introduced in the U.S.A.
1960	ICI introduces the first polymeric MDI-based semi-rigid energy absorbing foam for vehicles.
1960-65	Rigid foam blowing by chlorofluoromethanes.
1962	First production line moulded 'deep seat' flexible polyurethane car cushions at Austin-Morris (U.K.).
1963	ICI demonstrates production line manufacture of refrigerators using MDI-based polyurethane foam.
1963	First cold-store built entirely from metal-faced polyurethane rigid foam laminate made continuously (Australia).
1964	ICI inverse- and floating-platen systems for the continuous manufacture of rigid polyurethane foam-cored building boards in production.
1965	First commercial production of self-skinning flexible foam (Soc. Quillery, France).
1968	ICI introduces isocyanurate rigid foam.
1968	General Motors make the first polyurethane microcellular bumper for the Pontiac G.T.O.
1973	MDI-based 'soft-face' bumpers made by RIM system for Chevrolet taxis.
1979	ICI introduces wholly-MDI-based systems for flexible foam moulding.
1983	ICI introduces system to make dual-hardness, moulded seating from MDI-based, flexible foam.

2.1 Raw Materials

Polyurethanes are defined as polymers which contain urethane groups (Fig. 2.2) in the main polymer chain. The urethane group results from the interaction of an isocyanate and a hydroxyl compound :

$$R{-}NCO \;+\; HO{-}R' \longrightarrow R{-}NH{-}CO{-}O{-}R' \qquad (1)$$

When a diisocyanate and a diol react together a linear polyurethane is obtained whilst a diisocyanate and a polyhydric compound (polyol) lead to a cross-linked polymer. Thus diisocyanates and diols (and polyols) are the principal raw materials used in the manufacture of polyurethanes.



$$\left[-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O- \right]$$

Fig. 2.2 The urethane link. [HEPBURN C., 1992]

2.1.1 Isocyanates

While the chemistry and technology of polyurethanes are of relatively recent origin, the chemistry of organic isocyanates dates back over hundred years. Wurtz, in 1849, was the first to synthesize aliphatic isocyanates by reacting organic sulfates with cyanates :

$$R_2SO_4 \;+\; 2KCNCO \longrightarrow 2RNCO \;+\; K_2SO_4 \qquad (2)$$

The structure of the isocyanates obtained by Wurtz was later confirmed by Gautier (1869), who oxidized aliphatic isocyanides with mercuric oxide to the corresponding isocyanates :

$$R{-}N{=}C \;+\; HgO \longrightarrow R{-}N{=}C{=}O \;+\; Hg \qquad (3)$$

The first aromatic isocyanate and phenyl isocyanate, was prepared by Hofmann (1850), by pyrolysis of symmetrical diphenyl oxide :

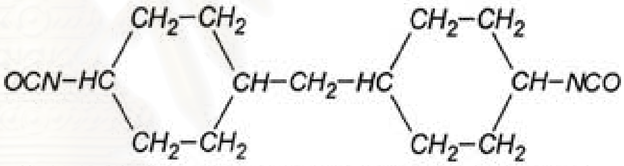
$$C_6H_5{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \longrightarrow 2C_6H_5NCO \;+\; H_2 \qquad (4)$$

Several aromatics and aliphatic diisocyanates are available but 95% of all polyurethanes are based upon the two aromatic diisocyanates, toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) and its derivatives. TDI is usually obtained as a mixture of 2,4- and 2,6 isomers. The symbol of TDI is followed by a number that refers to the percentage of the 2,4-isomer contained in the product, for example 80:20-TDI contains 80% 2,4-isomer and 20% 2,6-isomer.

Examples of important isocyanate used in polyurethanes manufacturing are the 2,4- and 2,6- toluene diisocyanates (TDI); 4,4′-diphenylmethane diisocyanates (MDI); and its aliphatic analogue; 4,4′-dicyclohexylmathane diisocyanate ($H_{12}MDI$); 1,5-naphthalene diisocyanate (NDI); 1,6-hexamethylene diisocyanate (HDI); xylene diisocyanate (XDI); isophorone diisocyanate (IPDI); paraphenylene diisocyanate (PPDI); and 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (TMDI). The structure formula of diisocyanate is given in Fig. 2.3a and 2.3b.

$OCN(CH_2)_6NCO$

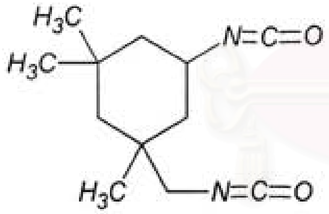
1, 6 -Hexamethylene diisocyanate (HDI)



4, 4′-Dicyclohexylmethane diisocyanate ($H_{12}MDI$)

(isomeric mixture)

(Desmodur W-Bayer)

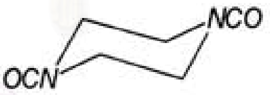


3-Isocyanatomethyl-

3, 5, 5-trimethylcyclohexyl isocyanate.

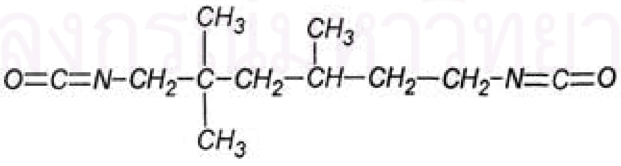
(Isophorone diisocyanate) (IPDI)

(Huls)



1, 4-Cyclohexyl diisocyanate (CHDI)

(Elate 166, Akzo Chemic)



$$O{=}C{=}N{-}CH_2{-}C(CH_3)_2{-}CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}N{=}C{=}O$$

2, 2, 4-(2, 4, 4-) Trimethylhexamethylene diisocyanate (TMDI)

(an isomeric mixture of 2,2, 4- and 2, 4, 4-) (Veba Chemic)

Fig. 2.3a Aliphatic diisocyanates used in polyurethane elastomer synthesis.

[HEPBURN C., 1992]

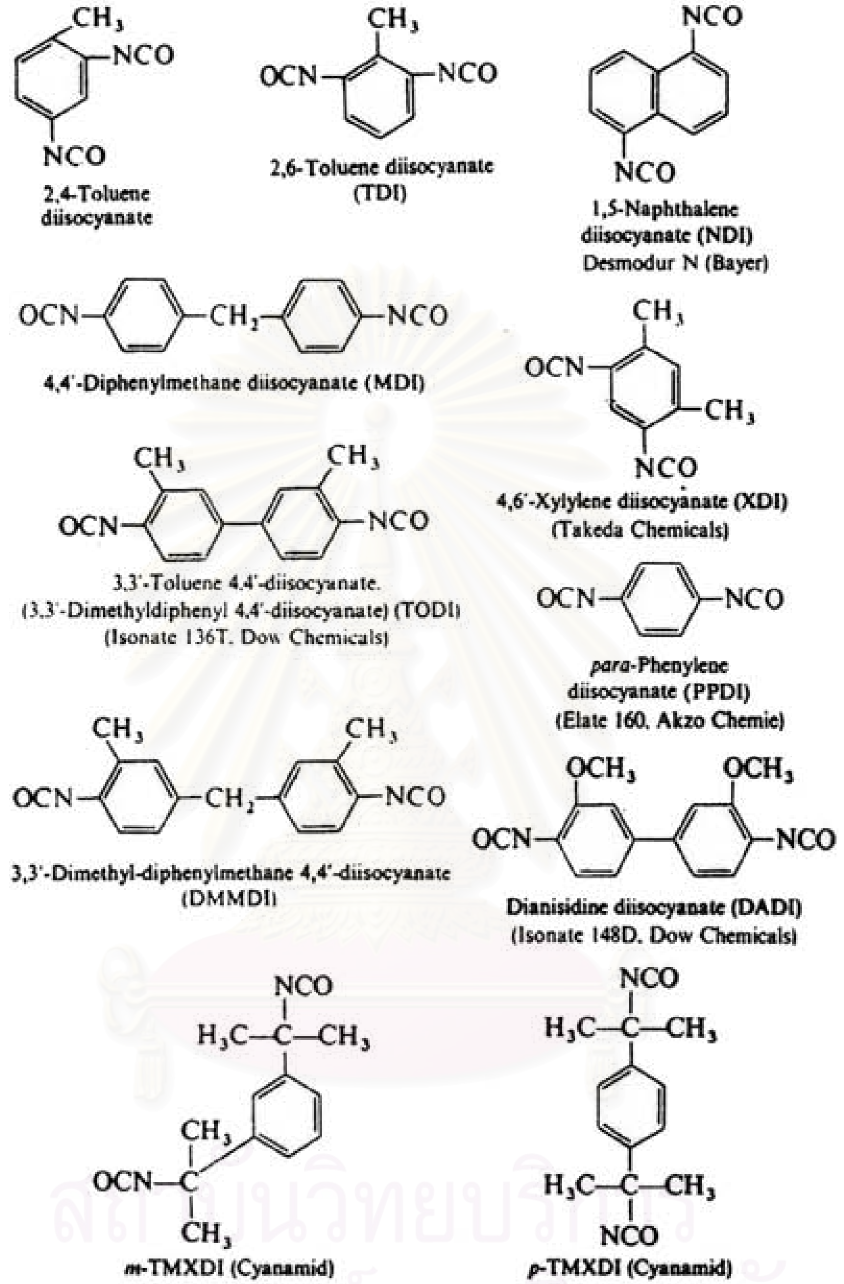


Fig. 2.3b Aromatic diisocyanates used in polyurethane elastomer synthesis.

[HEPBURN C., 1992]

Isocyanate value is the weight percentage of reactive -NCO groups.

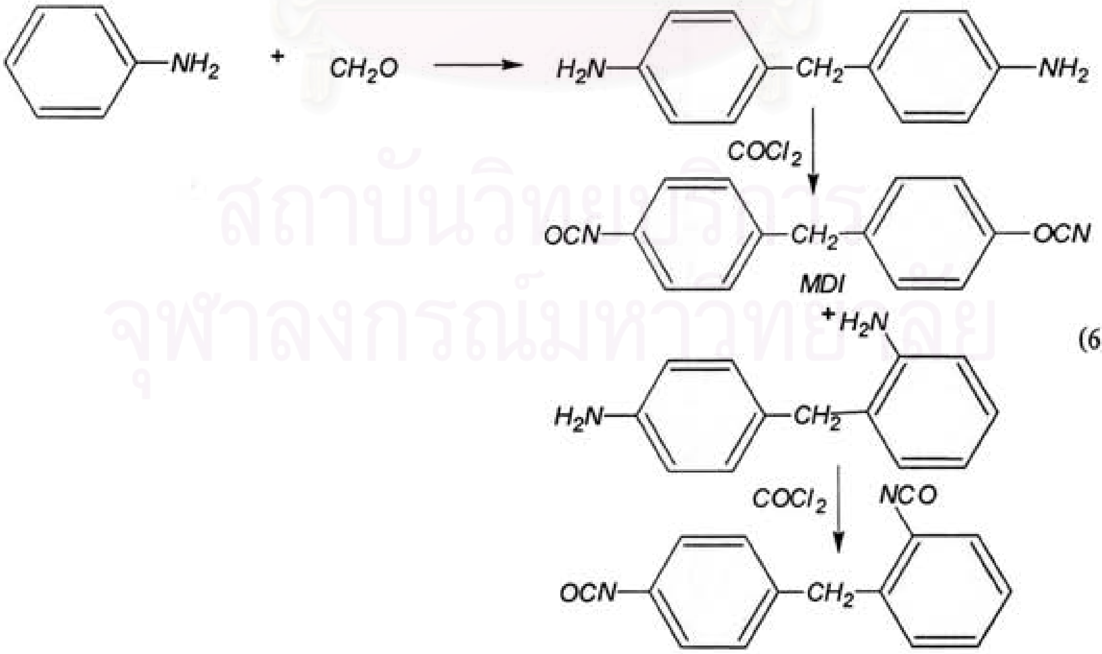
$$Isocyanate\ \ value = \% - NCO\ \ groups = \frac{42 \times functionality \times 100}{Molecular\ \ Weight} \qquad (5)$$

Toluene diisocyanates (TDI)

Toluene diisocyanates are prepared by direct nitration of toluene. The TDI isomer mixtures melt in the range 5-15°C and are therefore usually encountered as liquids; toluene 2,4-diisocyanate is a solid, m.p. 22°C. As would be expected from their chemical reactivity and substantial volatility, TDI mixtures can represent a serious toxic hazard in use, having a marked effect on the respiratory system and the skin. Care is essentially needed in handling TDI.

Diphenylmethane diisocyanate (MDI)

On the other hand, MDI based on diaminodiphenylmethane is considerable safer to use, having a much lower volatility. However, the disadvantage of MDI is that it is less easily purified and consequently MDI is often used in the crude (undistilled) form. MDI is derived from phosgenation of the diamino diphenylmethanes forms by condensation of anilene with formaldehyde :

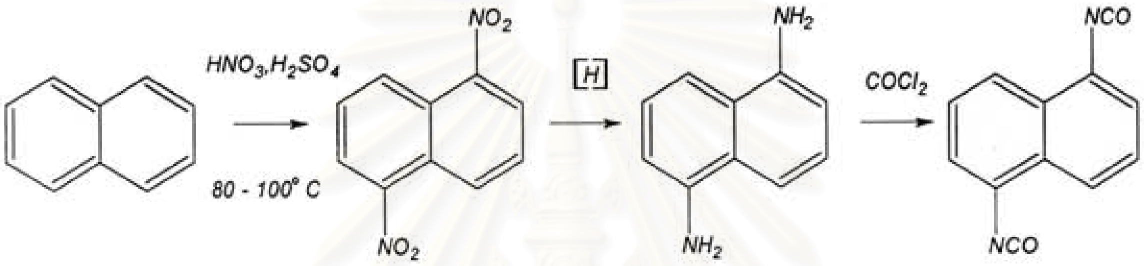


(6)

Pure 4,4′-diphenylmethane diisocyanate (4,4′-MDI) is a white to pale yellow solid of m.p. 38°C. It tends to form insoluble dimer when stored. The difficulty of handling solid pure MDI and its increased tendency to form dimer when stored as a liquid at over 40°C, have led to the development of modified pure MDIs which are liquid at ordinary temperatures and have a reduced tendency to dimerise.

Naphthylene 1,5-diisocyanate (NDI)

Naphthylene 1,5-diisocyanate is prepared from naphthalene. Its preparation is shown :



(7)

NDI is a solid, m.p. 128°C. It has a lower vapour pressure than TDI and is therefore less toxic in used; it does, however, have sensitizing properties. NDI provides polyurethanes of superior strength, and for that reason is used for special purpose products, primarily elastomeric ones.

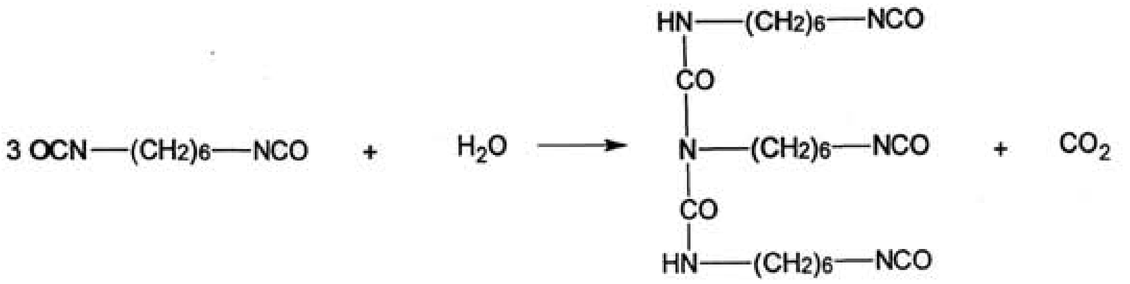
Hexamethyl diisocyanate (HDI)

Hexamethyl diisocyanate is prepared by the phosgenation of nylon 6,6 intermediate hexamethylene diamine.

$$H_2N{-}(CH_2)_6{-}NH_2 \xrightarrow{COCl_2} OCN{-}(CH_2)_6{-}NCO \qquad (8)$$

HDI is a liquid with a volatility of the same order as that of TDI. It is respiratory irritant and has powerful effect on the skin and eyes.

It is used in the manufacture of flexible polyurethane fibres. For the cross-linking of polyurethane coatings, it is generally used as the nonvolatile tri(hexamethylene isocyanate), biuret, obtained by the reaction of 3 moles of HDI with 1 mole of water.



$$3\,OCN{-}(CH_2)_6{-}NCO \;+\; H_2O \longrightarrow \begin{array}{l} HN{-}(CH_2)_6{-}NCO \\ \;|\\ CO \\ \;| \\ N{-}(CH_2)_6{-}NCO \\ \;| \\ CO \\ \;| \\ HN{-}(CH_2)_6{-}NCO \end{array} \;+\; CO_2$$

(9)

<u>*m*-Xylene diisocyanate (*m*-XDI)</u>

m-Xylene diisocyanate is an aromatic diisocyanate. The structure of XDI is shown in Fig. 2.4. It is a low viscous, colourless to pale yellow liquid and characteristic pungent with a weak but specific odour.

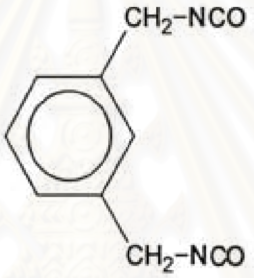


Fig. 2.4 The structure of *m*-xylene diisocyanate. (MITSUI CHEMICALS, INC.)

<u>Norbornane diisocyanate (NBDI)</u>

Norbornane diisocyanate, produced by Mitsui Chemicals Inc., is a new cycloaliphatic diisocyanate, and is a suitable raw material for the production of light-stable and weather-resistant polyurethanes. The reactivity of the two isocyanate groups is equal. The reactivity of NBDI is higher than that of IPDI, and similar to that of HDI. The structure of NBDI is shown in Fig. 2.5. It is a low viscous, colourless to slightly pale yellow liquid with a weak but specific odour.

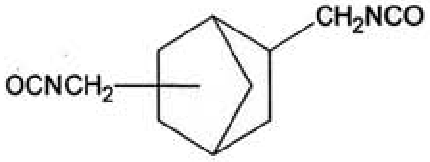
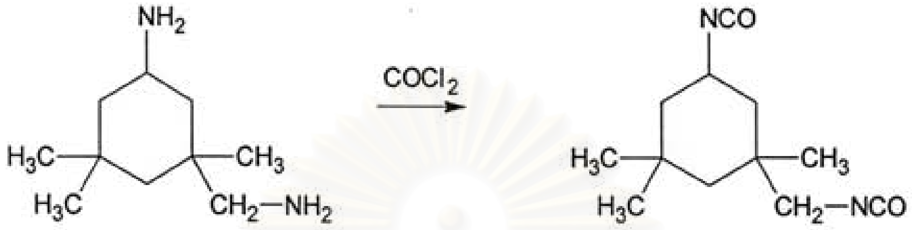


Fig. 2.5 The structure of norbornane diisocyanate. (MITSUI CHEMICALS, INC.)

Isophorone diisocyanate (IPDI)

Isophorone diisocyanate (3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate) is prepared by the phosgenation of isophorone diamine (1-amino-3-aminomethyl-3,3,3-trimethylcyclohexane) as shown belows.



(10)

IPDI is a cycloaliphatic diisocyanate and it is a preferred raw material for the synthesis of light-stable and weather-resistant polyurethanes. It is a low viscous liquid with a weak but specific odour. IPDI is used for the preparation of non-yellowing coating and elastomers. Unexpectedly, in IPDI, the reactivity of secondary-NCO group is about 1.3-2.5 times higher than of the primary -NCO, and IPDI itself is 4- to 5- fold more reactive toward the hydroxyl groups than HDI, which is also aliphatic. IPDI is a liquid with a vapour pressure which is significantly lower than that of TDI.

2.1.2 Polyols

A wide range of polyols is used in polyurethane manufacture. Most of the polyols used, however, fall into two classes : hydroxyl-terminated polyethers, or hydroxyl-terminated polyesters. 90% of the polyols used in manufacturing polyurethanes are polyethers with terminal hydroxyl groups. Hydroxyl-terminated polyesters are also used to obtain polyurethanes with special properties. Polyesters are usually more expensive than polyethers.

The structure of polyol plays a large part in determining the properties of the final urethane polymer. The molecular weight and functionality of the polyol are the main factors, but the structure of the polyol chains is also important. The characteristics of the polyols used for flexible and rigid polyurethane manufacture are shown in Table 2.2.

Table 2.2 Polyols used for polyurethane manufacture. [WOOD G., 1987]

Characteristic	Flexible foams and elastomers	Rigid foams, rigid plastics and stiff coatings
Molecular weight range	1000 - 6500	150 - 1600
Functionality range	2.0 - 3.0	3 - 8
Hydroxyl value range (mg KOH/g)	28 - 160	250 - 1000

The hydroxyl value (OHv) sometimes called the hydroxyl number of the polyol, is used as a measurement of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed in mg KOH/g of polyol. The hydroxyl value is defined as the number of milliweight (or milligrams) of potassium hydroxide equivalent to the active functions (hydroxyl content) of 1 g of the compound or polymer.

$$Hydroxyl\ value = \frac{56.1 \times functionality \times 1000}{Molecular\ weight} \tag{11}$$

a. Polyether polyols

The commercial polyether polyols used in the urethane field is relatively recent development. The first report of experiments with polyethers as intermediates for polyurethanes utilized polyethers derived from ethyloxide or propylene oxide. The first polyether designed specifically for use in preparing polyurethanes was a poly(oxytetra methylene) glycol derived from tetrahydrofuran. These are made by the addition of alkylene oxides, usually propylene oxide, onto alcohols or amines which are usually called starter or 'initiators'. The addition polymerization of propylene oxide occurs with either anionic(basic) and cationic(acidic) catalysis although commercial polyol product 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 base catalysis. Polyethers based of propylene oxide thus contain predominantly secondary hydroxyl end-group. Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups.

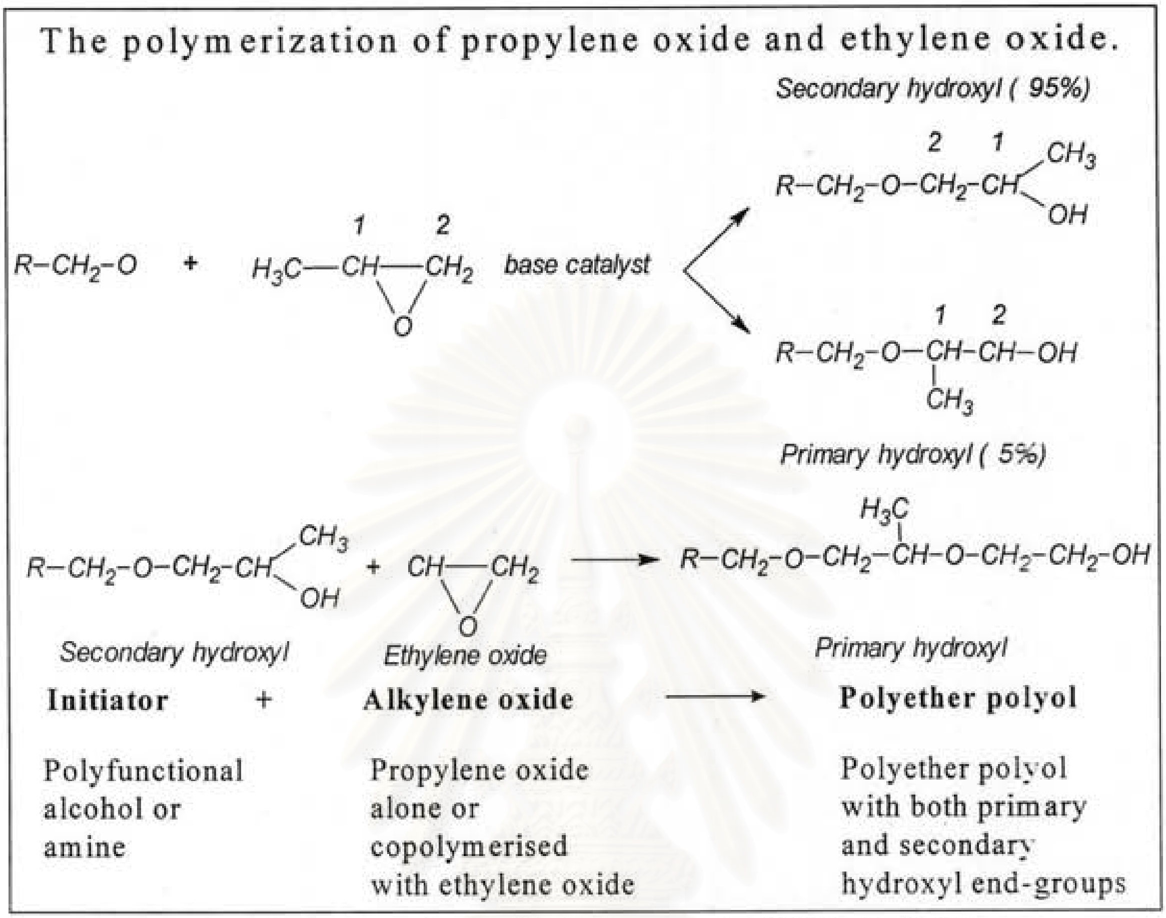


Fig. 2.6 The manufacture of polyether polyols. [WOOD G., 1987]

The manufacture of polyether polyols (shown in Fig. 2.6) is usually carried out in stainless steel or glass-lined reactors by essentially batch processes. The catalyst is usually sodium or potassium hydroxide in aqueous solution although sodium methoxide, potassium carbonate, and sodium acetate are also used. A polymerization initiator is employed to control the type of polyether polyols produced. Some typical polymerization initiators are listed in Table 2.3.

Table 2.3 Polymerization initiators: Polyether polyols for rigid polyurethanes. [WOOD G., 1987]

Alcohols	Amines	Functionality
Water		2
Ethylene glycol		2
Diethylene glycol		2
Glycerol	Trithanolamine	3
Trimethylolpropane		3
Pentaerythritol	Toluene diamine	4
	Ethylene diamine	4
	4,4′-diaminodiphenylmethane	4
	Diethylene triamine	5
Sorbitol		6
Sucrose		8

The polyethers used in polyurethane applications are nonvolatile and viscous liquids. Most of the polyethers are soluble in the common organic solvents such as alcohols, ketones, esters, hydrocarbons, and halogenated solvents.

b. Polyester polyols

Polyester polyols tend to be more expensive than polyether polyols and they are usually more viscous and therefore more difficult to handle. They also yield polyurethane polymers which are more easily hydrolyzed, consequently they are only used to make polyurethanes for demanding applications where the particular physical properties obtainable from polyesters are important. Polyester-based polyurethane elastomers combine high levels of tensile properties with resistance to flexing and abrasion. They also have good resistance to many types of oil.

The polyesters are prepared by reaction of dibasic acids (usually adipic acid but other components such as sebasic or phathalic acid may be presented) with diol such as ethylene glycol, 1,2-propylene glycol, and diethylene glycol (where linear polymer segments are required).

For preparation of the polyesters, conventional methods of polyesterification, i.e. reaction between acid and diol or polyol, are used, the water of condensation being removed by distillation and the reaction assisted, if necessary, by use of vacuum or an azeotrope. Branching can be introduced by the addition of a small amount of a triol to the reaction mixture.

One convenient preparation of polyesters involves reaction of the components without solvents. The glycol and triol, if desired, are added to the reactor and heated with stirring to 60-90°C. The acid component is added quickly and the mixture stirred and heated at such a rate the water distills out rapidly. The hydroxyl and acid components are used in such a ratio that nearly all acid groups react and the hydroxyl groups are in sufficient to control the molecular weight in the desired range :

$$(n+1)R\text{-}(OH)_2 + nR'\text{-}(COOH)_2 \longrightarrow HO\!\left[R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-O\right]_n\!H \qquad (12)$$

The reactivity of isocyanates with different type of active hydrogen compound can be placed in the following order :

aliphatic NH_2 > aromatic NH_2 > primary OH > water >
secondary OH > tertiary OH > phenolic OH > COOH

and

RNHCONHR > RCONHR > RNHCOOR

2.2 Additives

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

These additives include catalysts, chain-extenders, cross-linking agents, surface-active materials, flame-retardants, colouring materials and fillers. All practical polyurethanes systems include some of these auxiliary chemicals.

2.2.1 Catalyst

A number of catalysts can be used for the reaction of isocyanates with water and polyols and these include aliphatic and aromatic tertiary amines, and organo-metallic compounds, especially tin compounds, although compounds of mercury or lead are also used. Alkali metal salts of carboxylic acids and phenols, and symmetrical triazine derivatives are used to promote the polymerization of isocyanates.

a. Base catalysis

Bases are the most important group of urethane catalysts used in commercial practice, and their properties have been studied in depth.

Common used catalysts can be devided into two categories:

1. tertiary amines, which promote HOH/NCO reactions (water-blowing);
2. organic metal salts, which promote OH/NCO reactions (polymer-forming).

Amine catalysts:

The amine catalysts of isocyanate reactions are tertiary amines. Tertiary amines are the catalysts most widely used in producing 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 catalytic effect increases with increasing basicity but is reduced by steric hindrance of the aminic nitrogen.

One of the most active amine catalysts having a convenient spatial structure is triethylenediamine (diazabiscyclooctane, or DABCO) (Fig. 2.7):

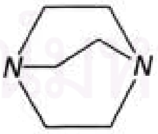


Fig. 2.7 The structure of DABCO. [HEPBURN C., 1992]

DABCO is supplied in form of a crystalline solid or in a more convenient 20-33% solution in ethylene-, dipropylene-, or butylene glycol or in dimethylethanolamine. Increased purity of the material reduces its odour. A DABCO-related catalyst with one nitrogen atom is also manufactured and used; it is known as quinuclidine (1,4-ethylenepiperidine).

b. Organometallic and other metal compounds

The organometallic catalysts are used to accelerate the urethane reaction. The most popular ones are stannous octane and dibuthyltin dilaurate. Stannous octoate is used in most flexible foam system, except pre-blended two-pack systems where its low hydrolytic stability is unacceptable.

2.2.2 Cross-linking agents and chain-extenders

Chain-extenders are difunctional substances, glycols, diamines or hydroxy amines; cross-linking agents have a functionality of three or more. Chain-extenders are used in flexible polyurethanes such as flexible foams, microcellular elastomers, cast elastomers and RIM systems. The difference between chain-extenders and cross-linking agents is not clear cut, since diamine extenders react so rapidly and vigorously with isocyanate groups.

The chain-extender reacts with diisocyanate to form a polyurethane or polyurea segment in the urethane polymer. It is usually added in sufficient amount to permit hard-segment segregation that results in an increase in the modulus and the hard-segment glass transition temperature (T_g) of the polymer. The T_g provides a measure of the polymer softening point and some indication of the upper limit of its working temperature. When diamines are used as additives, instead of glycols of similar molecular weight, they give faster reaction with isocyanates. The resulting polyurea hard-segment has a higher density of secondary bonding so that the T_g and the thermal stability of the polymer are both increased.

Cross-linkers are used to increase the level of covalent bonding in rigid polyurethanes such as some rigid foams and also as additives in many semi-rigid foam systems.

Chain-extenders and curing agents are used in both the one-shot and prepolymer processes for producing polyurethanes. Aromatic and aliphatic diamines are each used as curing agents but the former are more favoured because of their lower reactivity with isocyanates. A high level of polyurea hard-segment separation is required in order to obtain elastomers having a high modulus and this necessitates at least 3 to 4 molecular equivalents of chain-extender per oligomer chain.

2.2.4 Surfactants

Surface-active agents (SAAs) or surfactants are essential ingredients in the manufacture of most polyurethanes. Selected surfactants, or mixtures of surfactants, help in mixing incompatible components of the reaction mixture. They reduce the work required to increase the interfacial area, allow reduction of the bubble size and control of the structure, and enhancement of the foam stability. Surfactant plays a significant role at each stage of polyurethane formation:

(i) By facilitating the thorough mixing of polyurethane mixture components, if the latter are miscible over a limited range.

(ii) By stabilizing the bubble nuclei in a liquid reaction mixture, preventing the bubbles from coalescing to form larger-size bubbles.

(iii) By facilitating control over the fluidity of the polymerizing liquid mixture in the expansion process as a result of bubble growth.

(iv) By allowing tight control of the time and the degree of openness of the cell structure of the foams produced.

A wide variety of ionic compounds were originally used as SAA in polyurethane foam manufacture; for example sulphonated hydrocarbons, fatty acids or sodium salts of alkoxyglycols, as well as some non-ionic ones such as oxyethylenated alkylphenols, fatty acids, or alkylene oxide block copolymers of molecular weight 1500-3000. These SAAs are seldom used today then mainly for manufacture of polyester foam.

2.3 Reaction of isocyanates

Isocyanates, containing the highly unsaturated -N=C=O group, are very active with a host of compounds, and can also react with themselves. Isocyanate group is highly active, as it has two cumulative double bonds. The group can be written in several mesomeric forms :

$$-\overset{(-)}{\ddot{\underset{..}{N}}}-\overset{(+)}{C}=\ddot{\underset{..}{O}} \longleftrightarrow -\ddot{N}=C=\ddot{\underset{..}{O}} \longleftrightarrow -N=\overset{(+)}{C}-\overset{(-)}{\ddot{\underset{..}{O}}}: \qquad (13)$$

However, isocyanate group is generally represented in the from as $-\overset{\delta-}{N}=\overset{\delta+}{C}=\overset{\delta-}{O}$.

Accordingly, isocyanate reactions can be classified into following three groups.

(i) Polymerization of the isocyanate group.

(ii) Reactions of the isocyanate group with compounds containing active hydrogens.

(iii) Reactions of the isocyanate group with compounds not containing active hydrogens.

Reaction of isocyanates with compounds containing active hydrogen

The isocyanate group readily adds to compounds containing active hydrogen atom X-H, in a reaction in which the active hydrogen adds to the -NCO nitrogen, while the residue adds to the carbon atom :

$$\underset{H}{-N}=\underset{X}{C}=O \longrightarrow -NH-CO-X \qquad (14)$$

The X residue, linked to an active hydrogen atom, may be R-O-, R-S-, R-N=, and even a substituent-activated carbon atom, for example that adjacent to a carbonyl group.

The NCO group can generally react with compounds containing active hydrogen atoms as follows:

$$RNCO + R'OH \longrightarrow RNHCOOR' \qquad \text{Urethane} \quad (15)$$

$$RNCO + R'NH_2 \longrightarrow RNHCONHR' \qquad \text{Urea} \quad (16)$$

$$RNCO + R'COOH \longrightarrow RNHCOR' + CO_2 \qquad \text{Amide} \quad (17)$$

$$RNCO + H_2O \longrightarrow [RNHCOOH] \longrightarrow$$

$$RNH_2 + CO_2 \xrightarrow{RNCO} RNHCONHR \qquad \text{Urea} \quad (18)$$

2.4 Basic structure of thermoplastic polyurethane elastomers

A urethane elastomer can be regarded as a linear block copolymer of the type shown in Fig. 2.8. This segmented polymer structure can vary its properties over a very wide range of strength and stiffness by modification of its three basic building block: the polyols, diisocyanate and chain-extender.

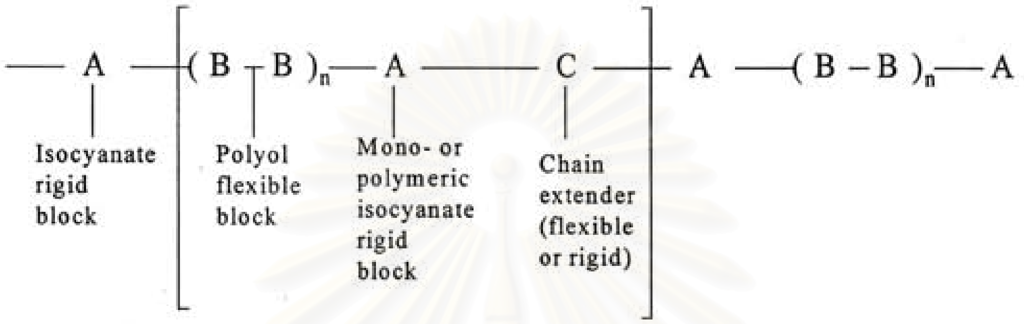


Fig. 2.8 The basic unit in a urethane block copolymer. [HEPBURN C., 1992]

Essentially, the hardness range covered is that of soft jelly-like structures to hard rigid plastics. Properties are related to segmented flexibility, chain entanglement, interchainforces and cross-linking. Evidence from X-ray diffraction, thermal analysis, birefringence and mechanical properties strongly supports the view that these polymers can be considered in terms of long (1000-2000 nm.) flexible segments and much shorter (150 nm.) rigid units which are chemically and hydrogen bonded together, the whole undergoing orientation on extension as indicated in Fig. 2.9. Modulus-temperature data usually shows at least two definite transitions, one below room temperature, which relates to segmental flexibility of the polyol and one above 100°C due to dissociation of the interchain forces in the rigid units.

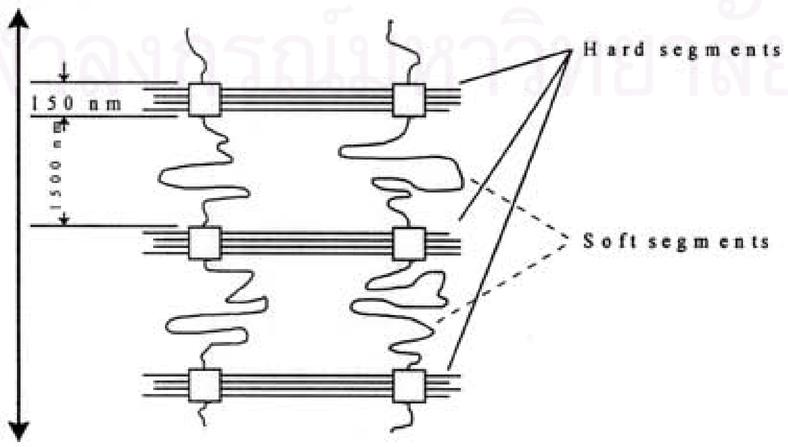


Fig. 2.9 Flexible and rigid segments in a polyurethane elastomer. [HEPBURN C., 1992]

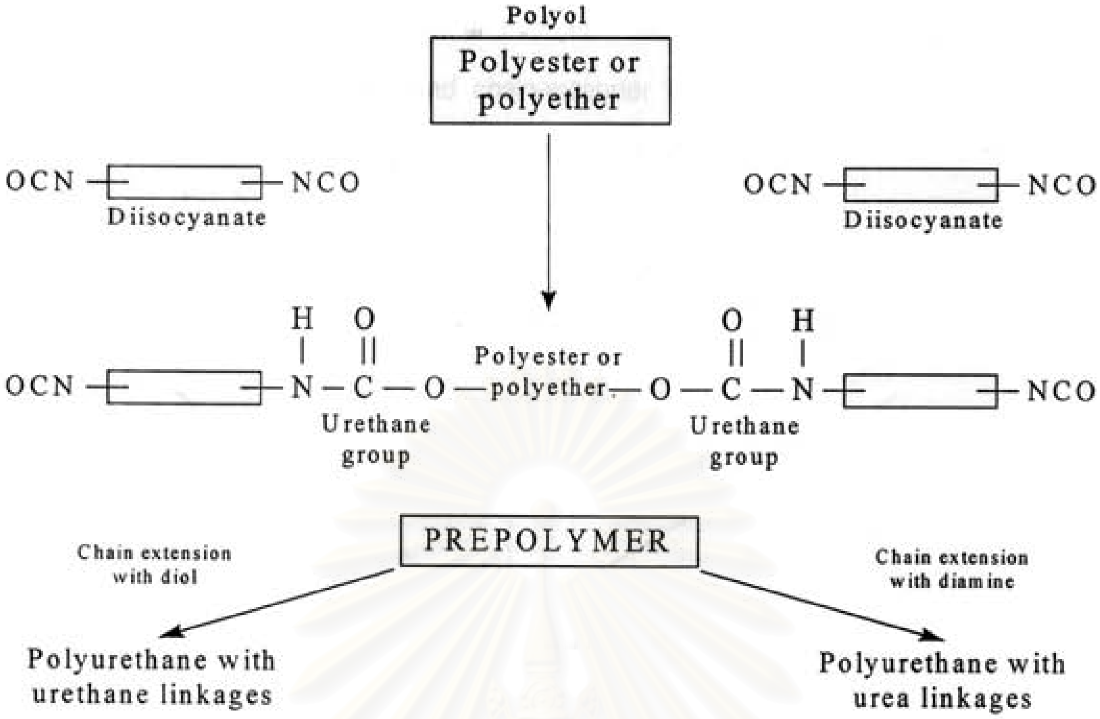


Fig. 2.10 Prepolymer route for the formation of a polyurethane elastomer.

[HEPBURN C., 1992]

The common route of chemical formation for all urethanes is illustrated in Fig. 2.10. It is referred to as the prepolymer method, since the 'final' polymer is formed in two separated steps. Initially the diisocyanate and polyol are reacted together to form an intermediate polymer of molecular weight 15000-20000 which is called a 'prepolymer' and is normally a thick viscous liquid or low-melting-point solid of low or no strength. This prepolymer, sometimes shelf-stabilized by means of 0.01-0.1% of an acid chloride (e.g. acylchloride) for storage purposes, is then converted into the final high molecular weight polymer by further reaction with a diol or diamine chain-extender.

This step is usually referred to as the chain extension stage, though sometimes the term 'cross-linking' is used if this better represents the elastomeric character of the final polymer. Also 'catalysis' is often used by some workers to describe this chain extension step.

Alternatively the entire polymer formation may be carried out by simultaneously mixing of polyols, diisocyanate and chain-extender (in the presence of catalysts). The reaction is referred to as the 'one-shot process' of polyurethane formation as schematically represented in Fig. 2.11.

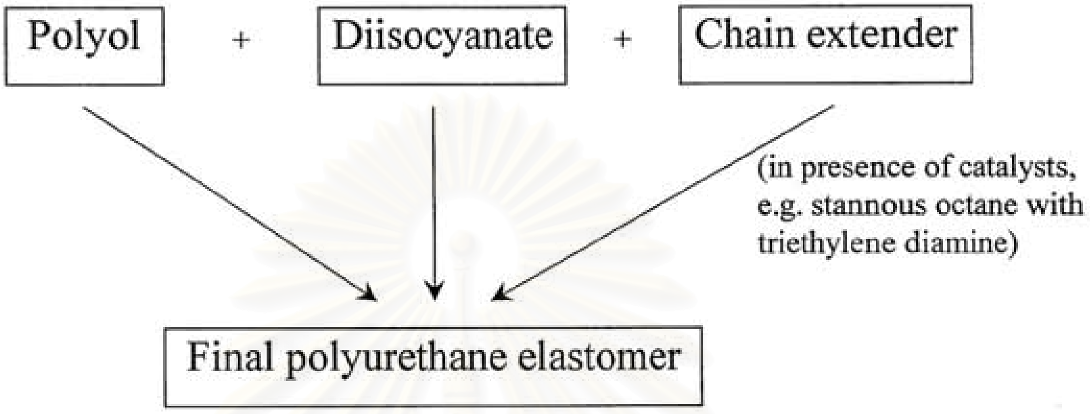


Fig. 2.11 One-shot process for polyurethane elastomer preparation. [HEPBURN C., 1992]

CHAPTER III

LITERATURE REVIEW

In this chapter, the literature reviews on polyurethane are summarized. MUKHERJEA R. N. and SAHA K. K. (1980) studied the effect of molecular weight of esters on film properties. The catalytic effect of 3-5% triethylamine, trithanolamine, and 2-diethylaminoethanol on curing of poly(ester urethane) films of sebacic acid-based hydroxy esters and polyester polyols, the effect of blending polyol, poly(butane diol carbonate) polyol with polyester polyols, and the effect of solvent and chemicals on poly(ester carbonate) urethane films were also investigated. In general, lower-molecular-weight esters give polyurethanes with higher melting points than those of the corresponding higher-molecular-weight polyester polyols of the same glycol. It has been observed that triethylamine is a good catalyst for curing these polymers, whereas triethanolamine gives a pasty mass. Addition of poly(butane diol carbonate) was found to improve the film properties considerably. Those film are flexible and elastic in nature, having higher elongation value than in case of polycarbonate polyol-based polyurethane films. However, the tensile strength decreases. Those films are only slightly affected by acetone, benzene, and methanol, but they have poor resistance toward dimethylformamide. Best polyurethane compositions were obtained when sebacic acid-based polyester polyols were blended with poly(butane diol carbonate) polyol in the ratio of 3:2. These polyurethanes show good tensile strength (120-215 kg/cm^3) and elongation (340-460%) properties, having high melting points (247-268°C) and good resistance to solvents and chemicals. Moreover, they are colourless and transparent.

SUNG C. S. P. *et. al.* (1980) studied properties such as, infrared absorption and mechanical properties of segmented poly(urethaneureas) based 2,4-TDI. The poly(urethaneureas) were prepared from 2,4-TDI, poly(tetramethylene oxide) (PTMO) of molecular weights 1000 and 2000, and anhydrous ethylenediamine as a chain extender. In both series, the absorption band at 3200-3500 cm^{-1} was assigned to the N-H hydrogen bonded and the peak at 3460 cm^{-1} was assigned to free N-H absorption peak. A peak at 1720 cm^{-1} and 1740 cm^{-1} was assigned to the hydrogen bonded urethane carbonyl and free urethane carbonyl, respectively. The hydrogen bonded urea carbonyl peak was observed at 1640 and 1660 cm^{-1}, while the free urea carbonyl peak was observed at 1695 cm^{-1}. The PTMO-2000 sample, which has a better phase segregation than the PTMO-1000 sample, exhibits better mechanical properties such as, higher elongation at break, greater toughness, lower hystersis, and a slower rate of stress relaxation, even though ultimate tensile strength is slightly lower.

BOGART J. W. C. V. *et. al.* (1983) studied structure-property relationships on polycaprolactone-polyurethanes. The materials studied were varied in hard-segment type (MDI/butanediol (BD) or H_{12}MDI/butanediol), soft-segment molecular weight (Mw of polycarpolactone = 830 or 2000), hard-segment content (23-77%) by weight. The MDI/BD (aromatic) hard-segments had semicrystalline hard-segment domains, while the H_{12}MDI/BD (aliphatic) hard-segments had mostly amorphous domains. The materials which contained a longer polycaprolactone soft-segment (Mw = 2000) exhibited better-defined microphase separation. All polyurethane materials exhibited a dramatic increase in Young's modulus and decrease in ultimate elongation as the hard-segment content was increased. Changing the hard-segment from aromatic to aliphatic gave materials with larger interfacial area and slightly higher tensile strength.

WANG C. B. and COOPER S. L. (1983) studied morphology and properties of segment polyether polyurethaneureas. Two series of polyether polyurethaneureas (PEUU) based on 4,4'-methylenebis(phenylene isocyanate), ethylenediamine, and either poly(tetramethylene oxide) at the molecular weight of 1000 or 2000 were synthesized. From the results of DSC, PEUU-1000 samples have a certain degree of hard- and soft-segment mixing. For PEUU-2000 samples, hard-segment solubilization in the soft-segment matrix is minimal. Comparison E' of PEUU-2000 series with PEUU-1000 series at the same hard-segment content reveals a higher plateau modulus in the former. The plateau modulus increases upon increasing the hard-segment content in the sample. The mechanical properties of these polyurethanes depend primarily on the sample's hard-segment content, although a higher concentration of urea groups in the PEUU-2000 series results in superior properties to those of the PEUU-1000 series at similar hard-segment weight fractions. The bonded urethane carbonyls of PEUU-2000 series increase upon increasing the hard-segment content, suggesting an increase in hard domain ordering. In the PEUU-1000 series, an increase of hard-segment content also results in a higher fraction of hydrogen-bonded urethane carbonyls, as more hard-segment ordering occurs and less hard-segment microdomains of very small size are dispersed in the polyether matrix phase.

MILLER J. A. *et. al.* (1985) studied the effects of hard-segment length distribution on the properties of polyether-polyurethane block copolymers. Polyurethanes based on poly(tetramethylene oxide), MDI and butanediol were synthesized by two methods, one-step and multi-step. The results showed that the one-step polymers have fewer hard-segments containing a single MDI unit than the corresponding multi-step samples. IR spectra showed that increase in hard-segment content of multi-step materials leads to a higher hard domain content as well as a higher fraction of hard-segments dissolved in the soft domains. The multi-step materials are more phase mixed than the single-step materials. The shift of the β peak to higher temperature with increasing hard-segments length can be attributed to a great fraction of hard-segment dissolved in the soft phase. The decrease in the magnitude of the β peak with increasing hard-segment length results from a decrease in the soft-segment content. The single-step materials exhibit higher Young's modulus and lower ultimate strength and elongation at break when compared to corresponding multi-step materials. The high Young's modulus of the single-step materials is consistent with the higher rubbery modulus observed in the dynamic mechanical test.

HARRIS R. F. *et. al.* (1990) studied the effect of hard-segment concentration (31.9-65.2%) on the properties of polyurethane elastomers based on poly(ethylene ether carbonate) and MDI/1,4-buthanediol. The results showed a systematic increase in solvent resistance in each solvent such as water, methanol, toluene and MEK, as the hard-segment contents of the polyurethane elastomers were increased. Ambient temperature flexural and tensile modulus showed a systematic increase in the stiffness of the polyurethane elastomers with increasing hard-segment content. For DMA results, the modulus of the rubbery plateau region increases and extends to higher temperatures as the hard-segment content is increased. Hardness and tensile strengths increase with increasing hard-segment content. The flexural storage modulus (E') curves showed that as the hard-segment content is increased, the soft-segment glass transition temperature (T_g) becomes broader, and the hard-segment melting point increases. The flexural loss modulus (E'') curves showed a relatively constant soft-segment glass transition temperature. The polyurethane elastomer with the hard-segment content has a somewhat higher soft-segment T_g.

BYRNE C. A. *et. al.* (1992) studied structure-property relationships of aliphatic polyurethane elastomers prepared from *tran*-1,4-diisocyanatocyclohexane (CHDI). Aliphatic polyurethane elastomers were prepared form *trans*-1,4-diisocyanatocyclohexane, poly (tetramethylene oxide), 1,4-butanediol and optionally trimethylolpropane. CHDI-based polyurethane elastomers are nearly transparent elastomers with low glass transition temperatures of approximately -80°C, and high final softening temperatures up to 270°C, with low hard phase contents of 20-30 percent. They are well phase separated and exhibit either paracrystallinity or crystallinity with small crystalline size after preparation. They have excellent mechanical properties compared to other polyurethane elastomers, and retain their modulus up to high temperature. Because of their excellent phase separation and low hard-segment content, with the resultant discrete domain, they exhibit very low hysteresis in compression and tension.

REK V. *et. al.* (1992) studied the effect of UV irradiation on the mechanical and thermomechanical properties of polyurethane elastomers based on various types of diisocyanates. Polyurethane elastomers were prepared by poly(caprolactone), either MDI or H_{12}MDI, and 1,4-butanediol as a chain extender and synthesized at NCO:OH ratios of 2:1 and 4:1. The results showed that the stability of the investigated polyurethane elastomers depended on the chemical structure of the diisocyanate and the hard-/soft-segment ratio. The processes of photoxidative degradation were more prevalent in polyurethane elastomers based on the cycloaliphatic isocyanate (H_{12}MDI) than those based on the aromatic isocyanate (MDI). In the case of polyurethane elastomers based on cycloaliphatic isocyanate it was found that the photodegradative processes were enhanced with increasing hard-segment concentration. Although polyurethane elastomers based on the aromatic isocyanate underwent colour changes, they exhibited better retention of mechanical properties compared to those based on the aliphatic isocyanate.

SENEKER S. D. *et. al.* (1992) studied the effect of hard-segment content varied from 20 to 60 weight percent. Polyurethane were prepared from polytetramethylene glycol (Mw = 1000) as a soft-segment polyol and combinations of 1,4-butane-diol, trimethylol propane (TMP) as a chain extender, and either 4,4′-dicyclohexylmethane diisocyanate (rMDI) or isophorone diisocyanate (IPDI). An interesting aspect is that the content of the solid *trans,trans* isomer of rMDI has a pronounced effect on the elastomer properties. Polyurethanes elastomers based on 20 to 100% of the *trans,trans*-rMDI isomer were prepared.

The results of this work were concluded that the thermoplastic elastomers based 20% *t,t*-rMDI have a greater dimensional stability at low hard-segment contents and a lower compression set than those based on IPDI. In cross-linked systems, polyurethane elastomers based 20% *t,t*-rMDI have a higher modulus, lower compression set and lower percent elongation than those based on IPDI. The *trans,trans* isomer of rMDI has a dramatic influence on the elastomer properties. Higher *t,t*-rMDI contents increase the mechanical properties such as the hardness, resilience, percent elongation, tensile strength and split-tear strength. The softening temperature increases without compromising the low soft-segment glass transition temperature. Also, the solvent resistance significantly improves with increasing *t,t*-rMDI content.

AHN T. O. *et. al.* (1994) studied the properties of polyurethanes with mixed chain extenders and mixed soft-segments. Polyurethaneurea elastomers (PUU) were prepared from 4,4'-diphenylmethane diisocyanate, poly(tetramethylene ether) glycol and poly(hexamethylene carbonate) glycol for mixed soft-segments, and 1,4-butanediol (BD) and isophorone diamine (IPDA) for mixed chain extenders. FT-IR spectra showed that most of the urea carbonyl groups associated in hydrogen bonding, while urethane carbonyls only partially did so. PUU based on IPDA has higher modulus than that based on BD. The structure of IPDA is substantially bulky compared with that of BD. It is likely that close packing of IPDA hard-segments is less feasible than that of RD segments, but, since the cohesive energy of urea groups is much larger than that of urethane groups, interactions between urea groups resulting from reaction of IPDA and isocyanate might contribute to an increasing in the modulus of PUUs.

MOORE R. and WU J. C. (1995) discussed why polytetramethylene glycol and adipate ester polyols are used in most high performance polyurethane systems in the world. Some key differences and similarities between two polyol types (polytetramethylene glycol (PTMEG) and adipate ester polyols) were made and compared with the lower performing polypropylene glycol (PPG) type polyols.

The results of this work were concluded that the two kinds of soft-segment generally are complimentary to each other for some basic properties. For applications where longer term hydrolytic stability, low temperature flexibility, microbe (bacteria, fungus) resistance, and high resilience are important, then PTMEG is the soft-segment of choice. For oil & solvent resistance, heat resistance, very low modulus, and high tear strength, then the ester formulations are generally better suited. Many other properties, such as tensile strength, compression set, flex fatigue, etc., may be widely varied with relatively simple formulation adjustments. Polypropylene glycol is the most widely used in the world, but its application is almost all confined to flexible foams. For high performance solid elastomers or high performance microcellular foams, the PPG type polyols have considerable poorer properties than the other types. In addition, the PPG types have inferior dynamic properties. One redeeming feature is easier handling because of low viscosity and being liquid at room temperature. So for high performance applications, the PPG type soft-segment cannot match the performance of either the PTMEG or adipate esters.

STEPHENS B. D. and MULLINS S. M. (1996) determined the effect of *trans,trans*-Desmodur W content on the elastomer properties and the range of properties obtainable from elastomers based on *t*-CHDI, high *t,t*-Desmodur W and Desmodur W and various molecular weights of polytetramethylene glycol (Mw = 650, 1000 and 2000) as the soft-segment polyol and 1,4-butadiol as the chain extender. The hard-segment content varied from 20 to 55 weight percent. The Desmodur W is the best diisocyanate for extrusion, injection moulding, tubing and melt temperature range applications. This work focused on a specific range of diisocyanate and diol did not give any significant differences. It is apparent that the physical properties are not affected by the ratio of the diisocyanate isomer. There was noticeable improvement with the high *t,t*-Desmodur W, it preferred just as well as the Desmodur W.

KANEKO Y. *et. al.* (US. Pat. No. 3,963,681) improved the mechanical properties of polyether urethane elastomer by using selected polyether glycol. Polyurethane elastomers were prepared by using polyfunctional isocyanate, curing agent and polyether having active hydrogen terminal groups, wherein the weight average of 1000 to less than 4500 and the molecular weight distribution curve of said polyether has at least two peaks, at least one of which is located in the higher molecular weight region and at least another one of which is located in the lower molecular weight region than the rheological critical molecular weight of said polyether and wherein the equivalent ratio (d) of active hydrogen of a curing agent to the isocyanate group of said polyfunctional isocyanate is in the range of $0.9<d<1.2$.

KIBLER R. W. *et. al.* (US. Pat. No. 4,463,155) improved dynamic properties, such as Texus Flex and cut growth resistance with a minimum loss of other comparable polyurethane systems. Polyurethane elastomers are derived from the reaction of polyether diol such as polytetrahydrofuran diol, having a number average molecular weight at 1000-4000, preferably about 2000, with a polyether diisocyanate properties prepolymer, the amount of diol representing about 5-20 percent of the combined weight of diol and prepolymer, with simultaneous chain extension and a diamine curing agent such as Caytur-21. Caytur-21 comprises a 49.5% dioctyl phthalate (DOP) dispersion of sodium chloride complex of three moles of methylene dianiline per mole of NaCl.

QUAY J. R. and CASEY J. P. (US. Pat. No. 4,892,920) studied a process for producing polyurethane/polyurea elastomers by utilizing a cyclohexane diisocyanate (CHDI) and essentially free of oligomeric CHDI by-products. The prepolymer is prepared by reacting a CHDI with along chain diol at least 90% by weight where the mole ratio of CHDI to polyol is in the range of at least 6 to 20:1 and preferably in the range of from 10 to 16:1 with reaction temperatures ranging from 40 to about 100°C, typically, 65-80°C. After formation of the prepolymer, the unreacted CHDI is removed from the prepolymer, e.g., less than 0.15% by weight. The elastomer is made by reacting the resultant prepolymer with a diol or diamine chain extender. Polyurethane elastomers have excellent modulus, tensile and shear storage modulus.

SCHLUETER JR. E. L. *et. al.* (US. Pat. No. 5,656,720) improved mechanical properties of polyurethane elastomer. Polyurethane elastomers were obtained by the reaction of a polytetramethylene ether glycol having the formula $HO[(CH_2)_4O]_nH$ where n is from 39 to 41, and from about 22 to about 26 parts by weight per 100 parts by weight of said glycol of a diisocyanate selected from the group consisting of diphenylmethane diisocyanates, toluene diisocyanates, naphthalene diisocyanates and blends thereof and a sufficient amount of chain extenders and cross-linking agents to provide a cross-linked elastomer. The chain extenders and cross-linking agents comprise a mixture of from about 75% to 60% by weight of diol chain extender having the formula $HO(R_1)OH$ (R_1 is a straight or branched chain alkyl group having from 2 to 12 carbon atoms) and from about 25% to 40% of a triol cross-linker having the formula $R'—C—[(OH)_a(CH_2OH)_b]$ (R′ is H, CH_3 or C_2H_5, a is 0 or 1, b is 2 or 3 and a+b = 3). The polyurethane elastomers have high wear resistance and low compression set. Mechanical properties remain relatively stable over a broad range of temperatures and relative humidities.

BARKSBY N. *et. al.* (US. Pat. No. 5,696,221) improved the physical properties, particularly hardness and rebound of polyurethane elastomers. Elastomers were prepared by the diamine chain extension or moisture cure of low isocyanate group content and toluene diisocyanate-based prepolymers, which were prepared from a polyol component comprising a high molecular weight, low unsaturation polyoxypropylene diol and a low molecular weight diol. The elastomers are useful for applications such as rollers and other applications where hardness and rebound are important.

CHAPTER IV

EXPERIMENT

The experiment can be divided into two sections. The first section is the experiment of moisture cured polyurethane elastomers. In this section, moisture cured polyurethane elastomers were prepared and taken to study the effects of diisocyanates and the effects of NCO% on the properties of the moisture cured polyurethane elastomers. The second section is the experiment of two-component polyurethane elastomers. In this section, two-component polyurethane elastomers were prepared and taken to study the effects of diisocyanates and the effects of curing agents on the properties of the two-component polyurethane elastomers.

4.1 Moisture cured polyurethane elastomers

The experimental works on moisture cured polyurethane elastomers were taken to study the effects of diisocyanates, norbornane diisocyanate (NBDI) and isophorone diisocyanate (IPDI), and the effects of NCO%, 6% and 8%, on the characteristic, mechanical properties, the infrared absorption, and the dynamic mechanical properties of polyurethane elastomers. Moisture cured polyurethane elastomers were prepared from Diol-2000 as the polyol, diisocyanate, either norbornane diisocyanate or isophorone diisocyanate, and AE-300 as a cross-linking agent.

The experimental works on moisture cured polyurethane elastomers consists of two parts. The first part is the moisture cured polyurethane elastomer preparation. In this part, four different prepolymers were synthesized and then the NCO% and the viscosity of prepolymers were determined. After that, elastomer films were prepared by crosslinking the prepolymer chains with AE-300 at NCO-Index[*] of 2 and cured by moisture. Four different moisture cured polyurethane elastomers were obtained as detailed in Table 4.1, and after that the gel time of the film was determined. The second part is the measurement of

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[*] NCO-Index : equivalent mole ratio of isocyanate:polyol

elastomer film properties. In this part, mechanical properties such as tensile strength, %elongation at break and tear strength of polyurethane elastomer before and after weathering test were measured. The infrared absorption and dynamic mechanical properties such as tan δ, storage and loss modulus of polyurethane elastomers were also determined. The schematic diagram of experimental works on moisture cured polyurethane elastomers was shown in Fig. 4.1.

Table 4.1 Four moisture cured polyurethane elastomers.

Synthesis no.	Diisocyanate	NCO%	Notation
1	NBDI	6%	6N
2	IPDI	6%	6I
3	NBDI	8%	8N
4	IPDI	8%	8I

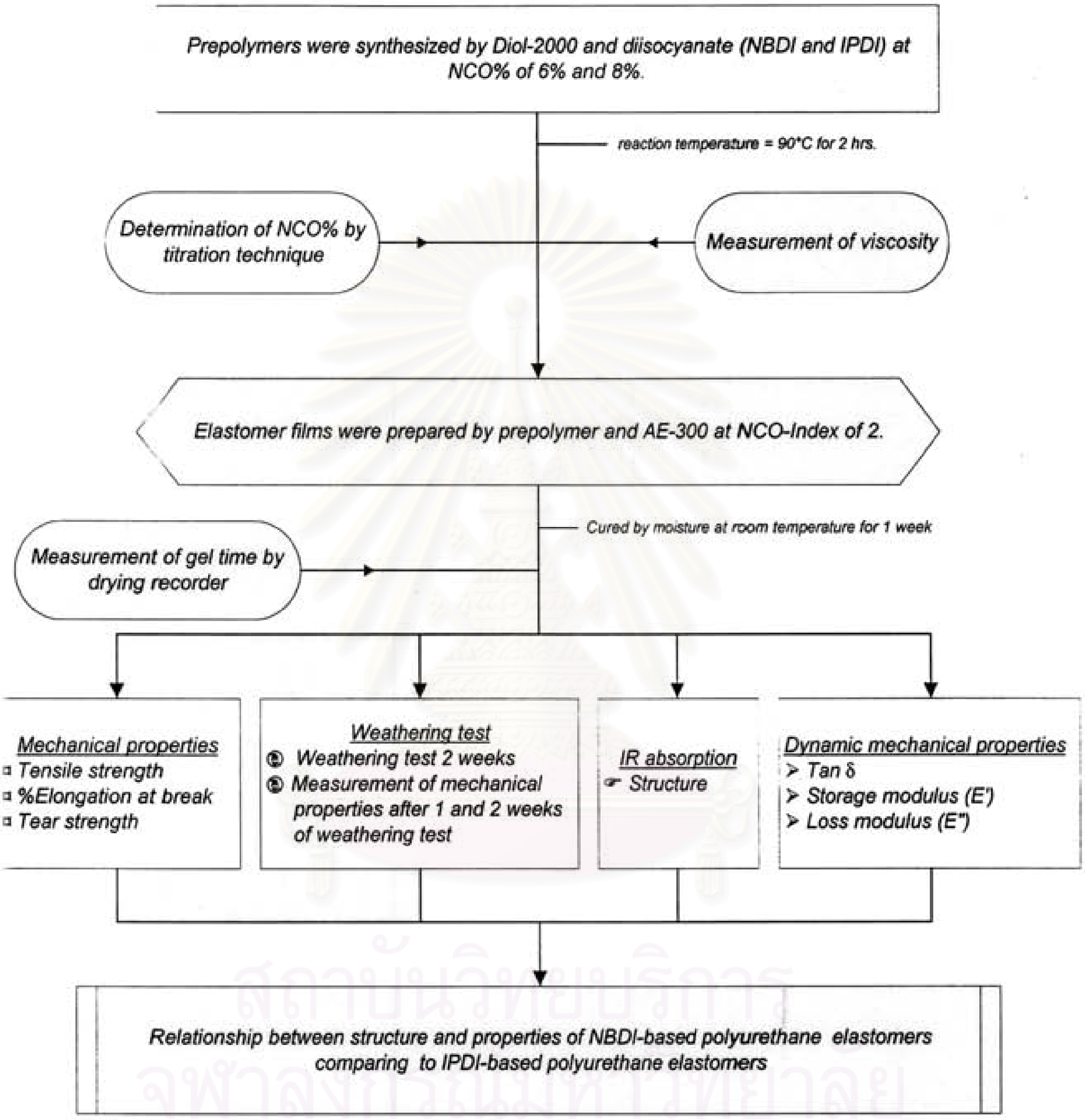

Figure 4.1 The schematic diagram of experimental works on moisture cured polyurethane elastomers.

4.1.1 Preparation and characteristic of elastomer film

4.1.1.1 Prepolymer synthesis

a. Chemical and raw material preparation

- Polyol : Polyether polyol used in this study is Diol-2000. Diol-2000 was supplied by MCI. Diol-2000 is a tradename of polypropylene glycol (Mw = 2000). Diol-2000 is pale yellow liquid. The specifications of Diol-2000 are shown in Table 4.2.

Table 4.2 Specifications of Diol-2000. [MITSUI CHEMICAL, INC.]

Properties	Value	Unit
Hydroxyl number	56 ± 3	mg. KOH/g
Water content	0.025	%
Viscosity at 25°C	315 ± 55	cP.
Colour (APHA)	100 MAX	
pH-value	5 – 8	

- Diisocyanates : Two different types of diisocyanate, which are norbornane diisocyanate (NBDI) and isophorone diisocyanate (IPDI), are used to produce moisture cured polyurethane elastomers. Both are supplied by MCI.

<u>Norbornane diisocyanate (NBDI)</u>

NBDI is a new cycloaliphatic diisocyanate, and is a suitable raw material for the production of light-stable and weather-resistant polyurethanes. The properties of NBDI are shown in Table 4.3.

Table 4.3 The properties of norbornane diisocyanate. [MITSUI CHEMICAL, INC.]

Properties	Value	Unit
NCO content	40.8	% by weight
Purity	>98	% by weight
Density at 20 °C	1.14	g/cm^3
Viscosity at 25 °C	9	cP.
Colour (APHA)	10	-
Vapour pressure	135/2	°C /mmHg
	159/6	°C /mmHg
Flash point (closed cup)	177	°C
Ignition temperature	440	°C

<u>Isophorone diisocyanate (IPDI)</u>

IPDI is a cycloaliphatic diisocyanate and it is a preferred raw material for the synthesis of light-stable and weather-resistant polyurethanes. It is a low viscous liquid with a weak but specific odour. IPDI is used for the preparation of non-yellowing coating and elastomers. The properties of IPDI are shown in Table 4.4.

Table 4.4 The properties of isophorone diisocyanate. [MITSUI CHEMICAL, INC.]

Properties	Value	Unit
NCO content	37.5-37.8	% by weight
Purity	>99.5	% by weight
Density at 20 °C	1.058-10.64	g/cm^3
Viscosity at 23 °C	13-15	MPa.s
Colour (APHA)	<30	-
Flash point (closed cup)	155	°C
Ignition temperature	430	°C

- Catalyst : Dibuthyltin dilaurate is an organometallic catalyst, which is used to accelerate the reaction between isocyanate group and hydroxyl group or urethane reaction.

b. Synthesis apparatus

1. Distillation flask (separation type) : 1000 ml.
2. Temperature controller and thermocouple type K : 89°C (set point)
3. Clamp
4. Riko-Slidetrans : Type RSA-10 : 50 V.
5. Stirrer : 200 rpm.
6. Agitator
7. N_2 gas supplier
8. Mantle heater
9. Mechanical Jack
10. Electronic balance : Two decimals.

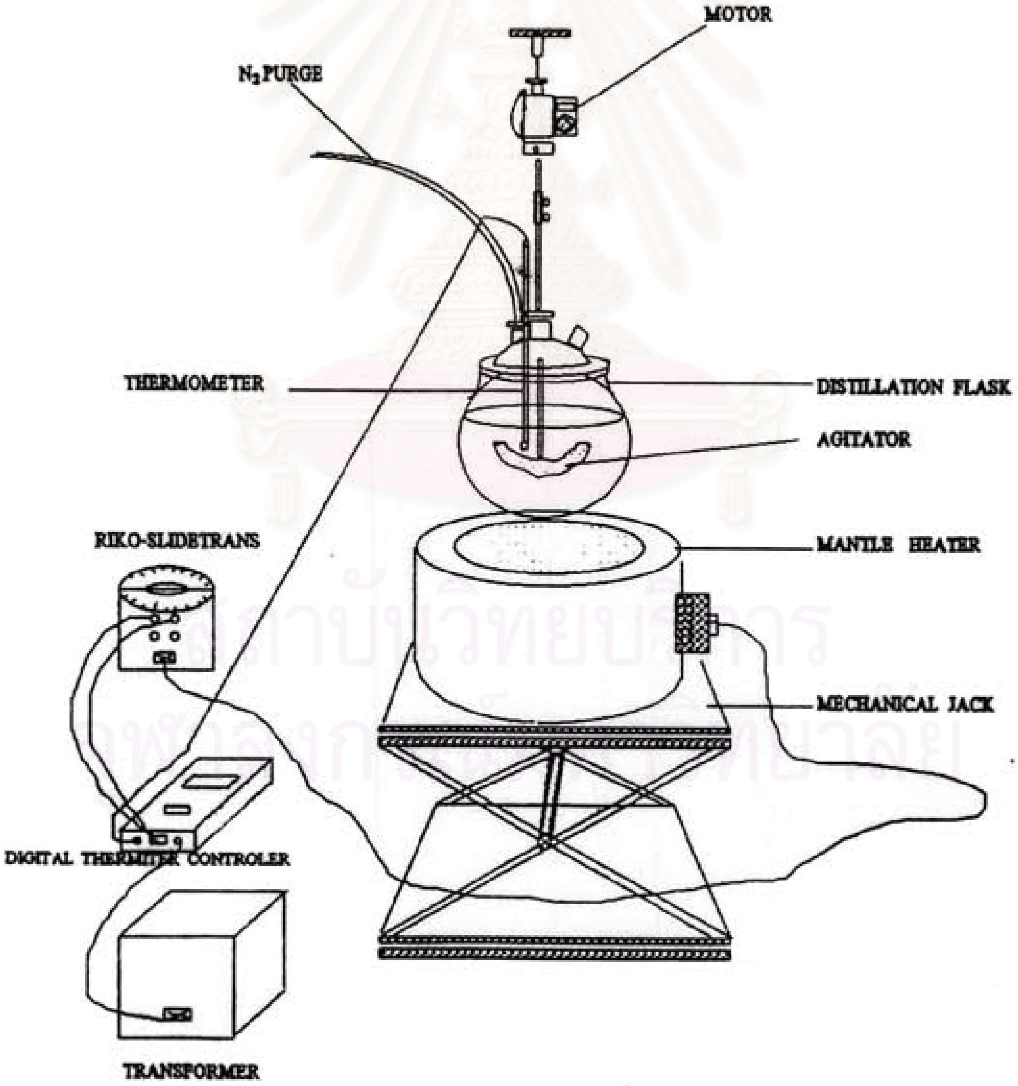

Figure 4.2 Laboratory apparatus for the prepolymer synthesis.

c. Synthesis procedure

The prepolymer was prepared using NCO% of prepolymer at 6% and 8%. Diol-2000 and diisocyanate (NBDI or IPDI) were mixed in a distillation flask and the mixture was stirred under nitrogen stream at 90±2°C for two hours (0.4 grams of dibutyltin dilaurate was used as a catalyst to accelerate the reaction). After that, the mixture (prepolymer) was cooled to 60°C and the viscosity and the actual NCO% of isocyanate prepolymer were measured by a viscometer and titration technique, respectively.

4.1.1.2 Determination of prepolymer NCO%

a. Reagent and chemical preparation

- Dry toluene : Dry toluene was prepared by using molecular sieve to absorb moisture in toluene and kept for 1 week. A chemical grade of toluene supplied by J.T. Baker was used.
- Di-n-butylamine : A chemical grade of di-n-butylamine produced by Kanto Chemical, Inc. was donated by MCI.
- Bromocresol green indicator (BCG indicator) : BCG indicator is a saturated bromocresol green powder in toluene. A chemical grade of bromocresol green powder produced by Kanto Chemical, Inc. was donated by MCI.
- Dry isopropanol : Dry isopropanol was prepared by using molecular sieve to absorb moisture in isopropanol and kept for 1 week. A chemical grade of isopropanol was supplied by APS Ajax Finechem.
- Hydrochloric acid : A chemical grade of HCl was supplied by BDH Laboratory Supplies.
- Molecular sieve type 4A : Molecular sieve was supplied by Ajax Laboratory Chemical.

b. Titration apparatus

1. Magnetic stirrer
2. Erlenmeyer flask and cap : 200 ml.
3. Burette : 50 ml. for HCl
4. Stand and base (for Burette)
5. Pipette : 10 ml. for amine
6. Cylinder : 50 ml. for toluene
7. Cylinder : 100 ml. for IPA
8. Electronic balance : four decimals.

c. Titration procedure

The titration procedure (follows JIS K 7301 standard) involved dissolving prepolymer* in 25.0 grams of dry toluene and reacting with 10.0 ml. of 1N di-n-butylamine for 20 minutes. Bromocresol green indicator solution and 120-150 ml. of isopropanol were added and the solution was titrated with 0.5N HCl (see appendix A, Table A-1 - A-3). The actual NCO% of prepolymer can be calculated from the equation belows.

* Weight of prepolymer sample was calculated by:

$$Weight\ \ of\ \ prepolymer\ \ sample\ [S] = \frac{20}{NCO\%\ \ (known,\ \ 6\%\ \ or\ \ 8\%)}$$

and

$$actual\ \ NCO\% = \frac{42.02 \times 0.5 \times (C - B) \times f}{S \times 1000} \times 100$$

where

S = Sample weight (g)

C = Quantity of 0.5 N HCl standard solution required for blank test (ml.)

B = Quantity of 0.5 N HCl standard solution required for titration of sample (ml.)

f = factor of 0.5 N HCl standard solution (ml.)

4.1.1.3 The measurement of prepolymer viscosity

The viscosity of prepolymers was determined at the temperature of 25°C by using Visco Mate VM-150 model from Toki Sangyo Co., Ltd. at Thai Mitsui Specialty Chemical Co, Ltd. (TMSC).

4.1.1.4 Elastomer film preparation

a. Reagent and chemical preparation

- Prepolymer : NBDI- and IPDI-based prepolymer at NCO% of 6% and 8% are used to produce moisture cured polyurethane elastomer.
- Cross-linking agent : AE-300 (OHv=750) is a cross-linking agent used to produce moisture cured polyurethane elastomer. AE-300 was donated by MCI. AE-300 is the tradename of MCI.
- Methylene chloride : A chemical grade of methylene chloride was supplied by J. T. Baker.

b. Elastomer film apparatus

1. Stirrer and propeller : 450 rpm.
2. Polyethylene cup : 300 ml.
3. Vacuum pump and dessicator
4. Glass plate : 300 x 600 mm^2
5. Applicator : 0.2 mm.
6. Electronic balance : two decimals

c. Elastomer film preparation procedure

To prepare elastomer films, the prepolymer chain was cross-linked with AE-300 solution at NCO-Index = 2. AE-300 solution was prepared from AE-300 and methylene chloride at the ratio of 70:30 (grams:grams). AE-300 solution was mixed with prepolymer in a cup and air bubble was removed by using a desiccator and a vacuum pump. A mixture of prepolymer and AE-300 solution was poured on a glass plate to make a film by using an applicator (the thickness of applicator is 0.2 mm.). The sample plate was kept in a dust free room for 1 week.

4.1.1.5 The measurement of gel time

The gel time of moisture-cured polyurethane elastomer film was determined using drying recorder at room temperature. Polyurethane elastomer was poured on the glass plate ($2.5 \times 30 \times 0.4$ mm^3) with four sides of beaker tapes. The drying recorder is shown in Fig. 4.3.

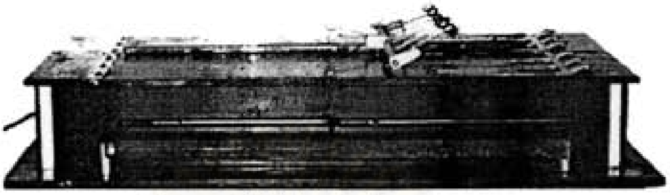

Figure 4.3 The drying recorder.

4.1.2 The measurement of elastomer film properties

4.1.2.1 The measurement of mechanical properties

The testing method for polyurethane elastomers follows JIS K 7311 standard. The tensile strength, elongation and tear strength of the films were determined using Tensilon machine RTA series at Thai Mitsui Specialty Co., Ltd.. Since the temperature has an effect on film mechanical properties and the humidity has an effect on curing properties, the temperature and humidity in the test room was controlled at 23°C/50% Rh.

a. Measurement condition

-Tensile and tear strength test

- Load cell : 5 Kgf.
- Load cell head speed : 300 mm./min.
- Recorder chart speed : 200 mm./min.

1. $TS = \dfrac{F_B}{S}$

TS = Tensile strength (kgf./cm^2)
F_B = Maximum load (kgf.)
S = Cross section area (cm^2)

2. $EL = \dfrac{L_1 - L_0}{L_0} \times 100$

EL = Elongation (%)
L_0 = Beginning distance (20 mm.)
L_1 = Elongation distance before sample break (mm.)

3. $TR = \dfrac{F_B}{B}$

TR = Tear strength (kgf./cm)
F_B = Maximum load (kgf.)
B = Thickness (cm.)

b. Dimension of specimen

The shape of specimen used for tensile strength, elongation and tear strength tests is shown in Fig. 4.4.

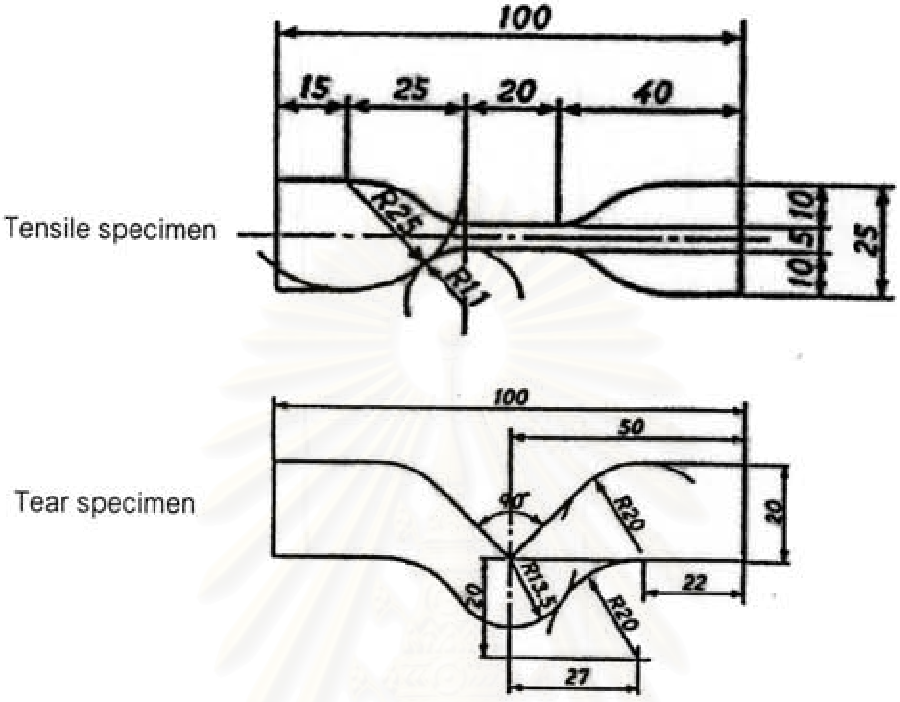

Figure 4.4 The shape of tensile and tear specimen for testing. [JIS K 7311 standard]

4.1.2.2 The weathering test

The changes of mechanical properties of outdoor polyurethane elastomers can be caused by atmospheric conditions such as sunshine, wind, rains, etc. Polyurethane elastomers were left outside buildings in an atmospheric environment for about 2 weeks. The mechanical properties of polyurethane elastomer after 1 and 2 weeks of weathering test were determined using the same measurement described in the previous section.

4.1.2.3 The measurement of infrared absorption

The chemical structure of polyurethane elastomers were studied by Fourier Transform Infrared Spectroscopy (FTIR) technique. Spectrums of the polyurethane elastomer thin films were recorded on a Perkin-Elmer Model 1760X using 32 scans at a resolution of 8 cm^{-1} between 4000 and 400 cm^{-1}.

4.1.2.4 The measurement of the dynamic mechanical properties

The dynamic mechanical properties such as the loss modulus, the storage modulus and the tan δ were determined using Dynamic Mechanical Thermal Analyzer (DMTA), Mk III model from Rheometric Science. The test conditions were set as follows.

Mode of testing	Tension
Running temperature	-120 to 250°C
Ramp	3°C/min.
Frequency	1 Hz.
Strain	Standard
Collecting data	Every 2 sec.
Sample dimension	11 x 10 x 0.13-0.15 mm^3

4.2 Two-component polyurethane elastomers

The experimental works on two-component polyurethane elastomers were taken to study the effects of diisocyanates (norbornane diisocyanate (NBDI), isophorone diisocyanate (IPDI), m-xylene diisocyanate (XDI) and toluene diisocyanate (TDI)) and the effects of curing agents (ethacure100 and ethacure300) on the characteristic, mechanical properties, the weathering properties, the infrared absorption, the differential scanning calorimetry and the dynamic mechanical properties of the two-component polyurethane elastomers. Two-component polyurethane elastomers were prepared from Diol-2000, diisocyanate (norbornane diisocyanate, isophorone diisocyanate, m-xylene diisocyanate or toluene diisocyanate) and either ethacure100 or ethacure300 as the curing agent.

The experimental works consist of two parts. The first part is the elastomer sheet preparation. In this part, six different prepolymers were synthesized and determined the NCO% and the viscosity of prepolymers. After that, elastomer sheets were prepared. The prepolymer chains were extended with curing agents at mole ratio NCO/NH of 1.1. Six different two-component polyurethane elastomers were obtained as detailed in Table 4.5 and after that the gel time of the sheet was determined. The second part is the measurement of elastomer sheet properties. In this part, the mechanical properties such as tensile strength, %elongation at break, modulus at 100% and 300% elongation and tear strength of polyurethane elastomers after preparation were measured. These properties of polyurethane elastomers were remeasured after heat aging, water immersion, and weathering test. Then infrared absorption, glass transition temperature, and dynamic mechanical properties such as tan δ, storage modulus and loss modulus of polyurethane elastomers were determined. The schematic diagram of experimental works on two-component polyurethane elastomers was shown in Fig. 4.5.

Table 4.5 Six two-component polyurethane elastomers.

Synthesis no.	Diisocyanate	Ethacure	Notation
1	NBDI	100	N100
2	IPDI	100	I100
3	NBDI	300	N300
4	IPDI	300	I300
5	XDI	300	X300
6	TDI	300	T300

*X100 and T100 cannot be prepared because the reaction of XDI or TDI with ethacure100 is very fast.

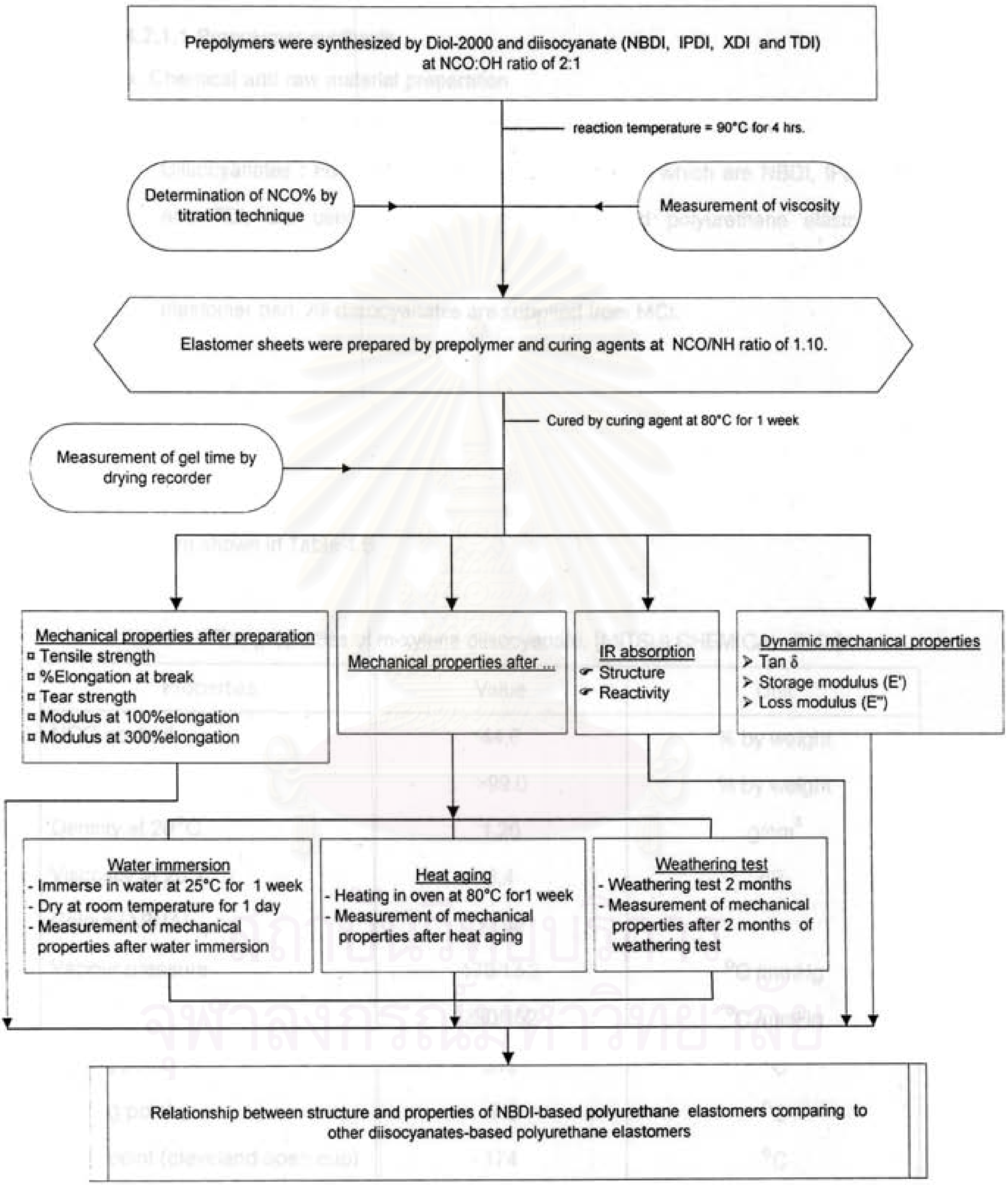

Figure 4.5 The schematic diagram of experimental works on two-component polyurethane elastomers.

4.2.1 Preparation and characteristic of elastomer sheet

4.2.1.1 Prepolymer synthesis

a. Chemical and raw material preparation

- Polyol : Diol-2000 is used to produce two-component polyurethane elastomer.
- Diisocyanates : Four different types of diisocyanate, which are NBDI, IPDI, XDI and TDI, are used to produce moisture cured polyurethane elastomers. The details of NBDI and IPDI are shown in moisture cured polyurethane elastomer part. All diisocyanates are supplied from MCI.

m-Xylene diisocyanate (XDI)

XDI is an aromatic diisocyanate. It is a low viscous, colourless to pale yellow liquid and characteristic pungent with a weak but specific odour. The properties of XDI are shown in Table 4.6.

Table 4.6 The properties of m-xylene diisocyanate. [MITSUI CHEMICAL, INC.]

Properties	Value	Unit
NCO content	44.6	% by weight
Purity	>99.0	% by weight
Density at 20°C	1.20	g/cm^3
Viscosity at 25°C	3.4	cP.
Colour (APHA)	<100	-
Vapour pressure	170/13.2	°C /mmHg
	230/102	°C /mmHg
Boiling point	315	°C
Melting point	-7.2	°C
Flash point (cleveland open cup)	174	°C

Toluene diisocyanate (TDI)

TDI is an aromatic diisocyanate. It is a low viscous, colourless to pale yellow liquid. The properties of toluene diisocyanate are shown in Table 4.7.

Table 4.7 The properties of toluene diisocyanate. [MITSUI CHEMICAL, INC.]

Properties	Value	Unit
NCO content	48.3	% by weight
Purity	99.5	% by weight
Specific gravity at 25°C	1.22	g/cm^3
Viscosity at 25°C	3	cP.
Vapour pressure	3.3	Pa/25°C
Boiling point	251	°C
Flash point	135	°C

- Catalyst : Catalyst is dibuthyltin dilaurate.

b. Synthesis apparatus

Synthesis apparatus is the same as the one used in moisture cured polyurethane elastomer part.

c. Synthesis procedure

Synthesis procedure is similar to that for moisture cured polyurethane elastomer. The prepolymer was synthesized at the mole ratio of NCO:OH = 2:1.

4.2.1.2 Determination of prepolymer NCO%

Actual NCO% of prepolymer was determined by the titration technique (follows JIS K 7301 standard) that is the same as for moisture cured polyurethane elastomer part (see appendix A, Table A-4 - A-6).

4.2.1.3 The measurement of prepolymer viscosity

The viscosity of prepolymer was determined at temperature of 25°C by using viscometer model from HAAKE at the faculty of chemical engineering, Burapha University.

4.2.1.4 Elastomer sheet preparation

a. Reagent and chemical preparation

- Prepolymer : NBDI-, IPDI-, XDI- and TDI-based prepolymers at mole ratio of NCO:OH = 2:1 are used to produce two-component polyurethane elastomers.
- Curing agents : Two different types of curing agents, ethacure100 (Fig. 4.6) and ethacure300 (Fig. 4.7), are used to produce two-component polyurethane elastomers. They are supplied by MCI. Ethacure100 or diethyltoluenediamine (DETDA) and ethacure300 or di-(methylthio)toluenediamine (DMTDA) are registered as the trademark of Albemarle Corporation.

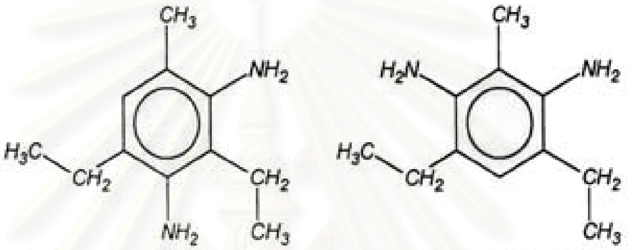

Fig. 4.6 The structure of ethacure100. [ALBEMAREL COR.]

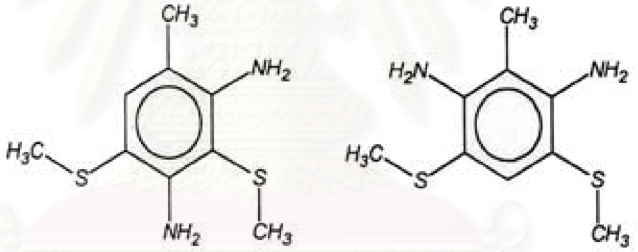

Fig. 4.7 The structure of ethacure300. [ALBEMAREL COR.]

- Surfactant : Silicone L-45 is used as a surfactant to reduce surface tension of two-component polyurethane elastomers. Silicone L-45 was supplied by MCI.

b. Elastomer sheet preparation apparatus

1. Stirrer and propeller	: 600 rpm.
2. Polyethylene cup	: 300 ml.
3. Vacuum pump and dessicator	
4. Teflon coated tray	: 300 x 300 x 2 mm^3
5. Electronic balance	: two decimals
6. Oven	: 80 °C

c. Elastomer sheet preparation procedure

To prepare elastomer sheets, the prepolymer chain was extended with curing agent (ethacure300 or ethacure100) at NCO/NH = 1.10. The curing agent was mixed with prepolymer and one drop of silicone L-45 was added (Silicone L-45 is used to reduce surface tension so it helps to remove bubbles.). Air bubble was then removed using a desiccator and a vacuum pump. A mixture was poured on a tray to make a sheet (the thickness of the sheet is approximately 2 mm.). The sample sheet was kept in an oven at 80°C for 1 week.

4.2.1.5 The measurement of gel time

The measurement of gel time of two-component polyurethane elastomer sheet is similar to that used for moisture cured polyurethane elastomer part.

4.2.2 The measurement of elastomer sheet properties

4.2.2.1 The measurement of mechanical properties

The testing method for polyurethane elastomers follows JIS K 7311 standard. The tensile strength, elongation, tear strength, modulus at 100% and 300% (M100 and M300) of the elastomer sheets was determined using Lloyd instrument model R2000. Since the temperature and humidity has an effect on sheet mechanical properties, the temperature and humidity in the test room was controlled at 23°C/50% Rh.

a. Measurement condition

-Tensile and tear strength test

- Load cell : 1000 N.
- Load cell head speed : 300 mm./min.

b. Dimension of specimen

The shape of specimen used for tensile strength, elongation and tear strength tests is the same as those of moisture cured polyurethane elastomers.

4.2.2.2 The water immersion

The changes of mechanical properties of two-component polyurethane elastomers caused by water were determined. Two-component polyurethane elastomers were immersed in water at 25°C for about 1 week, after that, two-component polyurethane elastomers were dried for 1 day at room temperature. The mechanical properties of two-component polyurethane elastomer after water immersion were determined using the same method described in the previous section.

4.2.2.3 The heat aging

The changes of mechanical properties of two-component polyurethane elastomer caused by heat were determined. Two-component polyurethane elastomers were left in an oven at 80°C for about 1 week. The mechanical properties of two-component polyurethane elastomers after 1 week of heat aging were determined using the same method described in the previous section.

4.2.2.4 The weathering test

The changes of mechanical properties of outdoors two-component polyurethane elastomers can be caused by atmospheric conditions such as sunshine, wind, rains, etc. Two-component polyurethane elastomers were left outside buildings in an atmospheric environment for about 2 months. The mechanical properties of two-component polyurethane elastomers after 2 months of weathering test were determined using the same method described in the previous section.

4.2.2.5 The measurement of infrared absorption

The basic structure and reaction of two-component polyurethane elastomers were studied by Fourier Transform Infrared Spectroscopy (FT-IR) technique. FT-IR technique is used to observe the changes of NCO group in the structure. The NCO group disappears after the curing reaction is complete. Two-component polyurethane elastomers were pasted on the NaCl plate and kept in an oven at 80°C for 1, 3, 4 and 5 days until the curing reaction is complete. This is a simple method, which can be used to study the curing reaction. Spectrums of the two-component polyurethane elastomers were recorded on a FT-IR Perkin-Elmer Model 1760X using 32 scans at a resolution of 8 cm^{-1} between 4000 and 625 cm^{-1}.

4.2.2.6 The measurement of the differential scanning calorimetry

The glass transition temperatures of two-component polyurethane elastomer were determined using Differential scanning calorimeter (DSC) at R&D Center of MCI. The test conditions were set as follows.

Running temperature	-120 to 160°C
Heating rate	15°C/min.
N_2 gas flow rate	200 ml/min.
Collecting data	Every 0.5 sec.

4.2.2.7 The measurement of the dynamic mechanical properties

The dynamic mechanical properties such as the loss modulus, the storage modulus and the tan δ were determined using Dynamic Mechanical Spectrometer (DMS) at R&D Center of MCI. The test conditions were set as follows.

Mode of testing	Tension
Running temperature	-120 to 160 °C
Ramp	2 °C/min.
Frequency	1 Hz.
Collecting data	Every 1 sec.

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Moisture cured polyurethane elastomers

5.1.1 Characteristics of prepolymers and moisture cured polyurethane elastomers

The results on NCO% and viscosity of prepolymers are shown in Table 5.1. For the NCO% of prepolymers, the actual NCO% of prepolymers is close to the theoretical NCO% of prepolymers (6% and 8%). For the viscosity of prepolymers shown in Fig. 5.1, it is clear that NBDI-based prepolymers have higher viscosity than IPDI-based prepolymers. Considering each type of prepolymer (NBDI and IPDI) with increasing the NCO% from 6% to 8%, it is clearly seen that increasing NCO%, i.e. increasing amount of diisocyanate, will decrease the viscosity of prepolymers because diisocyanate has very low viscosity. Normally, increasing in polymer viscosity results from increasing in molecular weight of polymer. Thus NBDI-based prepolymer should has higher molecular weight than IPDI-based prepolymer. In the same way, main polymer chain of NBDI-based prepolymer should be longer than that of IPDI-based prepolymer.

Table 5.1 Characteristics of prepolymers.

Sample	Actual NCO%	Viscosity at 25°C (cp.)
6N	5.9761	4325
6I	6.0644	3675
8N	7.8707	3125
8I	7.9081	2400

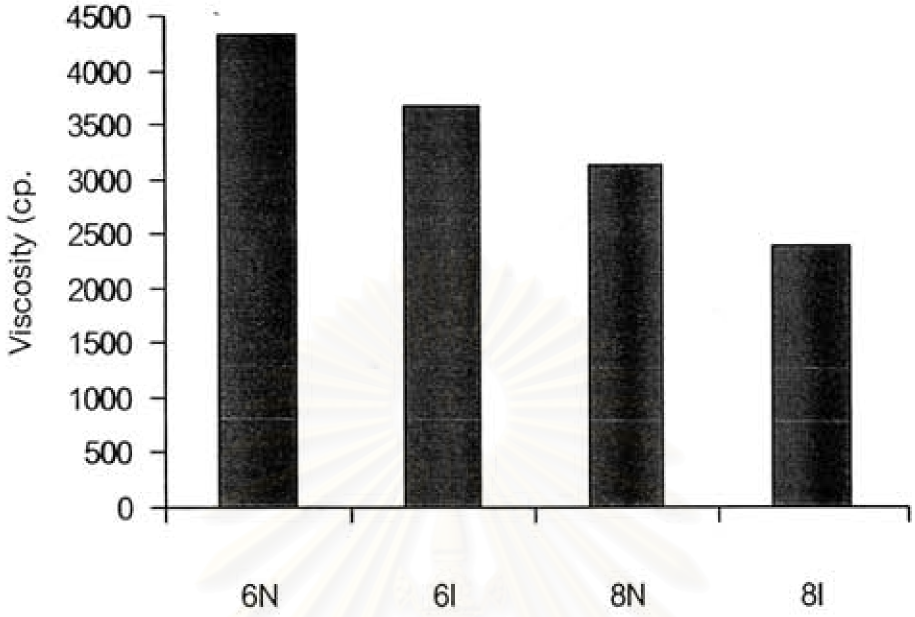

Figure 5.1 Viscosity of prepolymers.

The results on gel time of moisture cured polyurethane elastomers are shown in Table 5.2. NBDI-based polyurethane elastomers have lower gel time than IPDI-based polyurethane elastomers. This indicates that NBDI has more reactivity than IPDI.

Table 5.2 Gel time of moisture cured polyurethane elastomers.

Sample	Gel time (hrs.)
6N	1.5-11
6I	11-30
8N	2-9
8I	8-25

5.1.2 Mechanical properties of moisture cured polyurethane elastomers before weathering test

The results on the tensile strength, the elongation and the tear strength of moisture cured polyurethane elastomers before weathering test are shown in Table 5.3.

Table 5.3 Mechanical properties of moisture cured polyurethane elastomers before weathering test.

Sample	Diisocyanate (wt%)	AE-300 (wt%)	Total hard-segments (wt%)	%Elongation (%)	Tensile strength (kgf/cm^2)	Tear strength (kgf/cm)
6N	21.7	5.1	26.9	246.5	24.4	4.8
6I	23.2	5.1	28.3	314.0	42.3	4.7
8N	25.5	6.6	32.1	230.0	53.1	6.4
8I	27.3	6.6	33.9	296.3	93.2	10.1

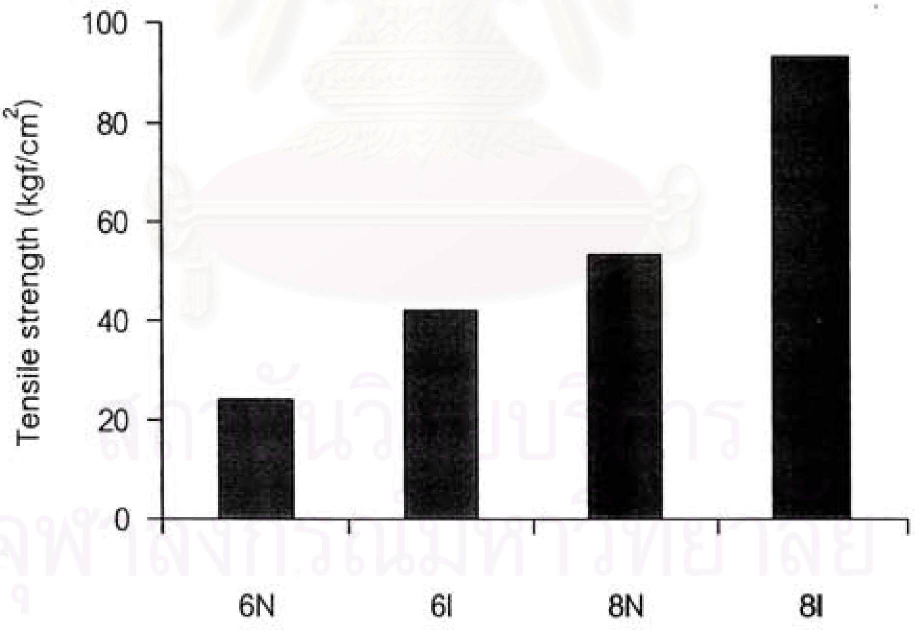

Figure 5.2 Tensile strength of moisture cured polyurethane elastomers before weathering test.

The tensile strength of IPDI- and NBDI-based polyurethane elastomers before weathering test at different NCO% is compared in Fig. 5.2. It is clear that the IPDI-based polyurethane elastomers have higher tensile strength than the NBDI-based polyurethane elastomers at equivalent NCO%. Meaningly, the NCO% represents the hard-segment content of the polyurethane elastomers. The hard-segment content in the structure of polyurethane elastomers is generally responded for the strength of the polymers. At each NCO%, the IPDI-based polyurethane elastomers have higher total hard-segment content than NBDI-based polyurethane elastomers (see Table 5.3). The IPDI-based polyurethane elastomers would therefore show higher tensile strength compared to the NBDI-based polyurethane elastomers.

At the NCO% of 6% and 8%, the tensile strength of IPDI-based polyurethane elastomers is higher than that of NBDI-based polyurethane elastomers by about 73.6% and 75.3%, respectively. The %difference of the tensile strength at high NCO% is slightly higher than that at low NCO%.

Considering each type of polyurethane elastomer (NBDI and IPDI) with increasing the NCO% from 6% to 8%, it is clear that increasing NCO%, i.e. increasing hard-segment content, will increase the tensile strength of the polyurethane elastomers. The NBDI-based polyurethane elastomers at NCO% of 8% have higher tensile strength than that at NCO% of 6% about 118.1% while the IPDI-based polyurethane elastomers at NCO% of 8% have higher tensile strength than that at NCO% of 6% about 120.3%.

The substantial increase in the tensile strength with increasing the NCO%, i.e. the hard-segment content, is attributed to an increasing in the degree of interconnectivity of the hard-segment domains as the sample composition changes from a predominantly soft-segment material to a predominantly hard-segment material [MILLER, J. A., *et. al.*, 1985].

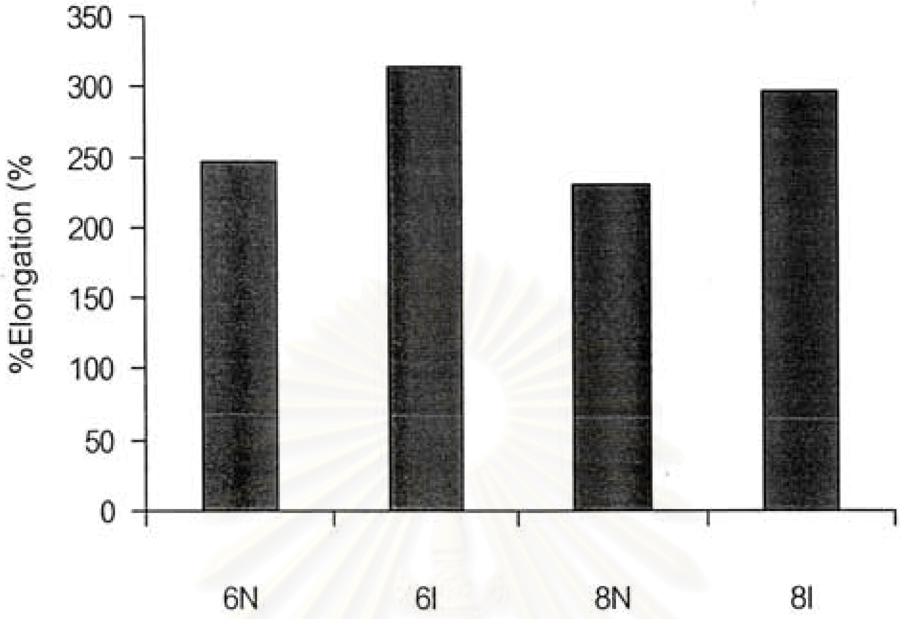

Figure 5.3 %Elongation of moisture cured polyurethane elastomers before weathering test.

The %elongation of the IPDI- and NBDI-based polyurethane elastomers before weathering test at different NCO% is compared in Fig. 5.3. It can be seen that the IPDI-based polyurethane elastomers have higher %elongation than the NBDI-based polyurethane elastomers at equivalent NCO%.

At NCO% of 6% and 8%, IPDI-based polyurethane elastomers have higher %elongation than NBDI-based polyurethane elastomers by about 27.4% and 28.8%, respectively. The difference in the %elongation of IPDI- and NBDI-based polyurethane elastomers at each NCO% is very similar.

When considering each type of polyurethane elastomer (NBDI and IPDI), it is clearly noticed that increasing NCO% decreases the %elongation of the polyurethane elastomers. Increasing NCO% from 6% to 8%, the %elongation of NBDI-based polyurethane elastomer and IPDI-based polyurethane elastomer is lower by 6.7% and 5.7%, respectively. By increasing the NCO%, the sample composition changes from a predominantly soft-segment material to a predominantly hard-segment material.

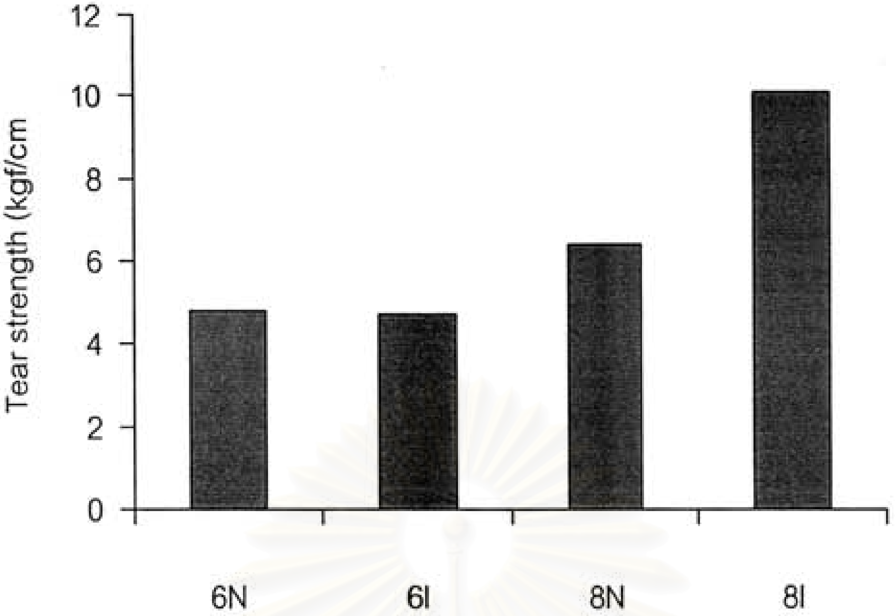

Figure 5.4 Tear strength of moisture cured polyurethane elastomers before weathering test.

The tear strength of the IPDI- and NBDI-based polyurethane elastomers before weathering test at different NCO% is compared in Fig. 5.4. It is shown that the IPDI-based polyurethane elastomers have higher tear strength than the NBDI-based polyurethane elastomers at high NCO%, while at low NCO% the tear strength of NBDI- and IPDI-based polyurethane elastomers is similar.

At NCO% of 6%, the tear strength of IPDI- and NBDI-based polyurethane elastomer is very similar, while at NCO% of 8%, IPDI-based polyurethane elastomers have higher the tear strength than NBDI-based polyurethane elastomers by about 58.2%. The effect of diisocyanate on the tear strength can be observed at high NCO%.

Considering each type of polyurethane elastomer (NBDI and IPDI) with increasing NCO% from 6% to 8%, it is clearly seen that increasing NCO% will increase the tear strength of the polyurethane elastomers. Increasing NCO% from 6% to 8%, the tear strength of NBDI-based polyurethane elastomer and IPDI-based polyurethane elastomer is higher by 32.7% and 113.6%, respectively. This phenomenon could be contributed from the same reasons as in the case of the tensile strength.

However, the tear strength results can be sensitively influenced by the thickness of polyurethane elastomer film sample rather than other properties. The thickness of the samples should be controlled to be the same so the tear strength results can be clearly seen.

5.1.3 Mechanical properties of moisture cured polyurethane elastomers after weathering test

The results on the tensile strength, the elongation and the tear strength of polyurethane elastomers after weathering test are shown in Table 5.4, comparing to the results before weathering test.

Table 5.4 Mechanical properties of moisture cured polyurethane elastomers before and after weathering test.

Sample	%Elongation (%)			Tensile strength (kgf/cm^2)			Tear strength (kgf/cm)		
	0 week*	1 week	2 weeks	0 week*	1 week	2 weeks	0 week*	1 week	2 weeks
6N	246.5	463.3	582.5	24.4	22.5	18.4	4.8	3.6	3.1
6I	314.0	491.7	628.8	42.3	28.4	20.2	4.7	4.7	4.4
8N	230.0	355.0	431.0	53.1	46.9	33.9	6.4	5.6	5.7
8I	296.3	421.7	449.0	93.2	81.5	55.4	10.1	8.6	7.7

*0 week = before weathering test

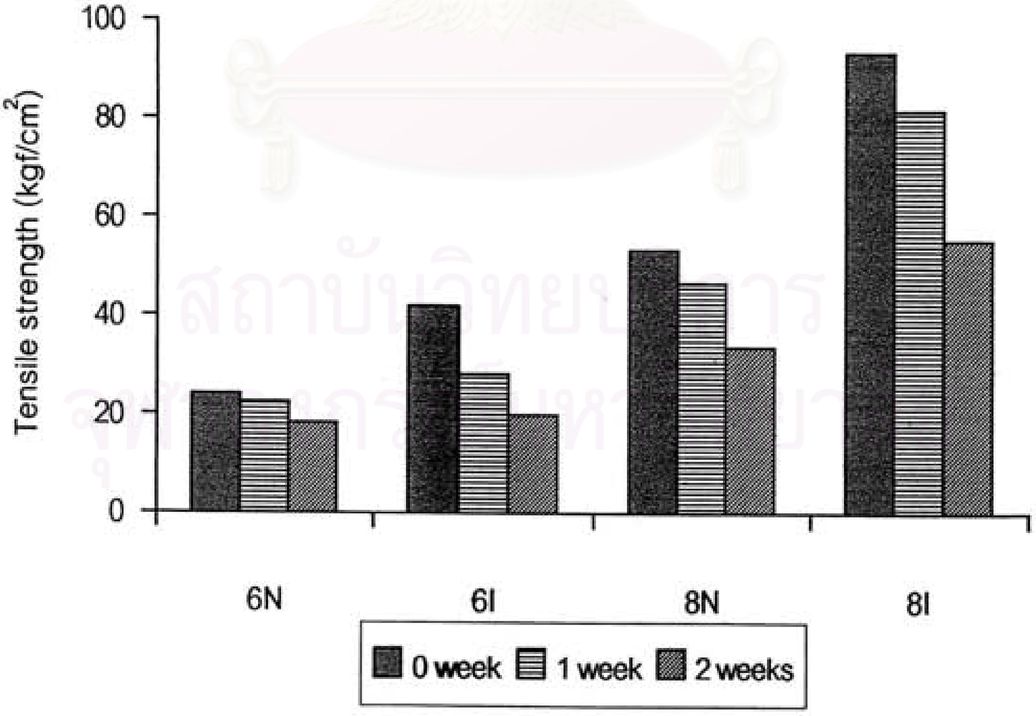

Figure 5.5 Tensile strength of moisture cured polyurethane elastomers before and after weathering test.

The tensile strength of IPDI- and NBDI-based polyurethane elastomer before and after weathering test at different NCO% is compared in Fig. 5.5. It is clear that the tensile strength of all samples after weathering test is lower than that before weathering test. Increasing time of weathering test decreases tensile strength of all samples.

After 1 week of weathering test, at the NCO% of 6%, the tensile strength of NBDI- and IPDI-based polyurethane elastomer is lower than that before weathering test (at 0 week) by about 7.7% and 32.7%, respectively. At the NCO% of 8%, the tensile strength of NBDI- and IPDI-based polyurethane elastomer is lower than that before weathering test by about 11.8% and 12.6%, respectively.

After 2 weeks of weathering test, at NCO% of 6%, the NBDI- and IPDI-based polyurethane elastomers have lower tensile strength than that before weathering test by 24.3% and 52.3%, respectively. At the NCO% of 8%, the NBDI- and IPDI-based polyurethane elastomers have lower tensile strength than that before weathering test by 36.2% and 40.6%, respectively.

It is clear that, after weathering test, the decreasing in the tensile strength of NBDI-based polyurethane elastomers is smaller than that of IPDI-based polyurethane elastomer for both levels of NCO%. This shows that NBDI-based polyurethane elastomer has higher weathering resistance than IPDI-based polyurethane elastomer. However, PERRY D. D. *et. al.* (1975) found that IPDI segments are characterized by inherent stability against UV degradation.

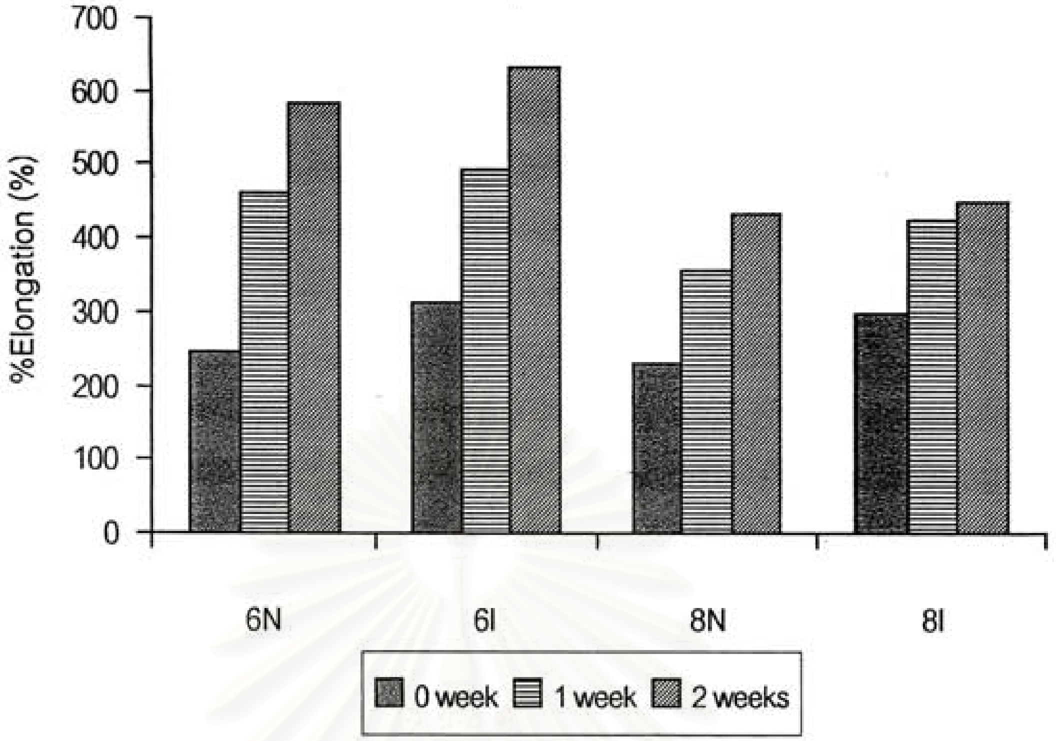

Figure 5.6 %Elongation of moisture cured polyurethane elastomer before and after weathering test.

The %elongation of the NBDI- and IPDI-based polyurethane elastomers before and after weathering test at different NCO% is compared in Fig. 5.6. It can be seen that the polyurethane elastomer after weathering test have higher %elongation than that before weathering test.

Combining the results of tensile strength and the %elongation after weathering test, it can be noticed that increasing time of weathering test increases %elongation but decreases tensile strength of polyurethane elastomer. This corresponds to one type of the typical effects of degradation process on physical properties of polymer [RABEK, J. F., 1995]. It is reported that the scission of cross-link by UV radiation during the photodegradation process causes an increase in elongation and a decrease in tensile strength. It can be suggested that the weathering test has as effect on the flexibility of the soft-segment and the rigidity of the hard-segment. This might correspond to the work of UV irradiation on polyurethane elastomer studied by IR technique [REK, V., *et. al.*, 1992]. It was reported that after UV irradiation, the structure of polyurethane elastomer has changed associated with the degradative process. This influenced the flexibility of the amorphous soft-segments and their interaction with hard-segments.

After 1 week of weathering test, at the NCO% of 6%, the NBDI- and IPDI-based polyurethane elastomers have higher %elongation than that before weathering test by about 88% and 56.6%, respectively. At the NCO% of 8%, the %elongation of NBDI- and IPDI-based polyurethane elastomer is higher than that before weathering test by about 54.3% and 42.3%, respectively.

After 2 weeks of weathering test, at NCO% of 6%, the NBDI- and IPDI-based polyurethane elastomers have higher %elongation than that before weathering test by 136.3% and 100.2%, respectively. At the NCO% of 8%, the NBDI- and IPDI-based polyurethane elastomers have higher %elongation than that before weathering test by 87.4% and 51.6%, respectively.

It is clearly seen that, after weathering test, NBDI-based polyurethane elastomers have higher %increment of the %elongation than IPDI-based polyurethane elastomers.

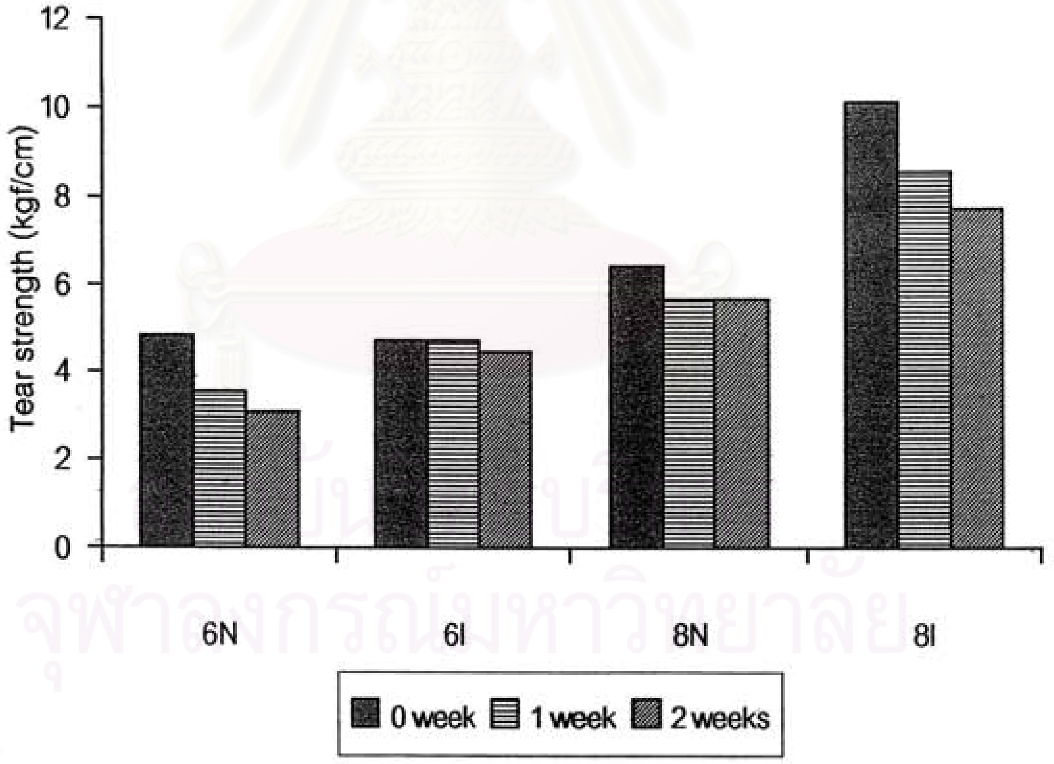

Figure 5.7 Tear strength of moisture cured polyurethane elastomer before and after weathering test.

The tear strength of IPDI- and NBDI-based polyurethane elastomer before and after weathering test at different NCO% is compared in Fig. 5.7. It is clear that the tear strength of all samples after weathering test is lower than that before weathering test. Increasing time of weathering test decreases tear strength of all samples.

After 1 week of weathering test, at the NCO% of 6%, the tear strength of NBDI- and IPDI-based polyurethane elastomer is lower than that before weathering test by about 26% and 0%, respectively. At the NCO% of 8%, the tear strength of NBDI- and IPDI-based polyurethane elastomer is lower than that before weathering test by about 11.7% and 15.2%, respectively.

After 2 weeks of weathering test, at NCO% of 6%, the NBDI- and IPDI-based polyurethane elastomers have lower tear strength than that before weathering test by about 35.5% and 5.8%, respectively. At the NCO% of 8%, the NBDI- and IPDI-based polyurethane elastomers have lower tear strength than that before weathering test by about 11.1% and 23.4%, respectively.

Effects of weathering test on the tear strength of both NBDI- and IPDI-based polyurethane elastomer is to decrease their tear strength. Unlike the tensile strength, stronger effect of weathering test on decreasing of tear strength of IPDI-based polyurethane elastomer than on NBDI-based polyurethane elastomer could not be observed.

5.1.4 Infrared absorption of moisture cured polyurethane elastomers

In this work, polyurethane elastomers were synthesized by the reaction of polyether polyol (Diol-2000), diisocyanate (NBDI or IPDI) and cross-linking agent (AE-300). The basic structures of the polyurethane elastomers were studied by FT-IR spectroscopic technique. The important functional groups of polyurethane elastomer are N-H, C=O, and C-O. In pure urethane hard domain, hydrogen bonding results from the hydrogen atoms of N-H groups serving as proton donors and the C=O groups acting as proton acceptors. When the urethane hard-segment and the polytetramethylene oxide (polyether polyol) soft-segment are mixed at the molecular level, the oxygens in the polytetramethylene oxide backbone also act as proton acceptors in forming H bonds with the N-H groups of the hard-segment urethane groups [MILLER, J. A., *et. al.*, 1985]. IR spectra for each polyurethane elastomer sample (6I, 6N, 8I and 8N) are shown in Fig. 5.8, Fig. 5.9, Fig. 5.10, and Fig. 5.11, respectively.

Considering the IR spectrum of the IPDI-based polyurethane elastomer at the NCO% of 6%, shown in Fig. 5.8, several important bands are labelled and the details of each absorption peak can be analyzed as follows.

The N-H absorption is usually located between 3500 and 3200 cm^{-1}. This consists of amine and amide group such as primary, secondary and tertiary N-H stretching. The strong peak observed at 3335 cm^{-1} is assigned to hydrogen-bonded N-H group while the free N-H stretching appears as a small shoulder at 3425 cm^{-1}.

The carbonyl absorption (C=O) is usually located between 1730 and 1700 cm^{-1}. These consist of free urethane, hydrogen-bonded urethane, free urea and hydrogen-bonded urea carbonyl groups. The peak observed at 1715 cm^{-1} is assigned to the free urethane carbonyl group and the overlap of free urethane carbonyl peak observed at 1700 cm^{-1} is assigned to the hydrogen-bonded urethane carbonyl group. The overlap of urethane carbonyl peak at 1660 cm^{-1} could be attributed to hydrogen-bonded urea carbonyl group while the free urea carbonyl peak at 1695 cm^{-1} is not observed.

The N-H bending absorption (amide II, mainly δN-H, mixed with νC-N) is usually located between 1560 and 1500 cm^{-1}. The peak observed at 1536 cm^{-1} could be assigned to amide II. In addition, another peak observed at 1243 cm^{-1} could be assigned to amide III.

The C-O absorption is located between 1150 and 1070 cm^{-1}. The broad peak observed at 1103 cm^{-1} could be assigned to an asymmetry C-O group.

Several C-H stretching bands are located between 3000 and 2800 cm^{-1}. The four peaks observed at 2972, 2931, 2898 and 2872 cm^{-1} could be assigned to the asymmetric C-H stretching of CH_3, asymmetric C-H stretching of CH_2, symmetric C-H stretching for CH_3 and symmetric C-H stretching CH_2, respectively.

The asymmetric C-H bending of CH_3 and CH_2 could be observed at 1459 cm^{-1}. And the symmetric C-H bending for CH_3 could be indicated at 1375 cm^{-1}.

C-N stretching absorption is usually located between 1230 to 1030 cm^{-1}. The peak observed at 1020 cm^{-1} could be assigned to C-N stretching.

However, there is a peak observed at 1303 cm^{-1}, near amide III peak that cannot be identified.

Considering the IR spectra of the NBDI-based polyurethane elastomers at NCO% of 6% and 8% (Fig. 5.9 and Fig. 5.11, respectively), the spectra are very similar to IPDI-based polyurethane elastomers at NCO% of 6% and 8% (Fig. 5.8 and Fig. 5.10, respectively). A few differences can be observed at the symmetric C-H stretching of CH_3, the hydrogen-bonded urea carbonyl peak, and the peak at 1303 cm^{-1} (located near amide III). IPDI-based polyurethane elastomer has slightly lower %Transmittance of the symmetric C-H stretching of CH_3 than NBDI-based polyurethane elastomer. This might be because IPDI-based polyurethane elastomer has more CH_3 groups than NBDI-based polyurethane elastomer.

Considering hydrogen-bonded urea carbonyl peak, it is clear that IPDI-based polyurethane elastomer has slightly lower %Transmittance of hydrogen-bonded urea carbonyl peak than NBDI-based polyurethane elastomer. This might be due to that IPDI-based polyurethane elastomer has more hydrogen-bonded urea carbonyl groups than NBDI-based polyurethane elastomer. This might imply that the strength of IPDI-based polyurethane elastomer is higher than that of NBDI-based polyurethane elastomer which is in agreement with the results on the tensile strength in the previous section.

For the undefined peak (located near amide III, marked * in each IR spectrum of each polyurethane elastomer sample), this peak overlaps with amide III peak for the case of

NBDI-based polyurethane elastomer but the undefined peak splits from amide III peak for the case of IPDI-based polyurethane elastomer.

Considering the IR spectra of the IPDI- and NBDI-based polyurethane elastomers at NCO% of 8% (Fig. 5.10 and Fig. 5.11), the spectra are very similar to those of polyurethane elastomers at NCO% of 6% (Fig. 5.8 and Fig. 5.9). A few differences can be observed at hydrogen-bonded N-H peak, hydrogen-bonded urethane, and hydrogen-bonded urea carbonyl peak. %Transmittance of hydrogen-bonded N-H peak, hydrogen-bonded urethane, and hydrogen-bonded urea carbonyl peak of polyurethane elastomer at the NCO% of 8% is slightly lower than that of polyurethane elastomer at NCO% of 6%. This can be because the amount of hydrogen-bonded N-H groups, hydrogen-bonded urethane, and hydrogen-bonded urea carbonyl groups of polyurethane elastomer at NCO% of 8% is more than that at NCO% of 6%. This result might imply that the strength of polyurethane elastomer at NCO% of 8% is higher than that at NCO% of 6%.

However, the effects of increasing the NCO% on the hydrogen-bonded N-H peak, hydrogen-bonded urethane and hydrogen-bonded urea carbonyl peak observed in this work are rather small. Another factor mainly affects the %Transmittance is the sample thickness which might not be exactly the same for every sample.

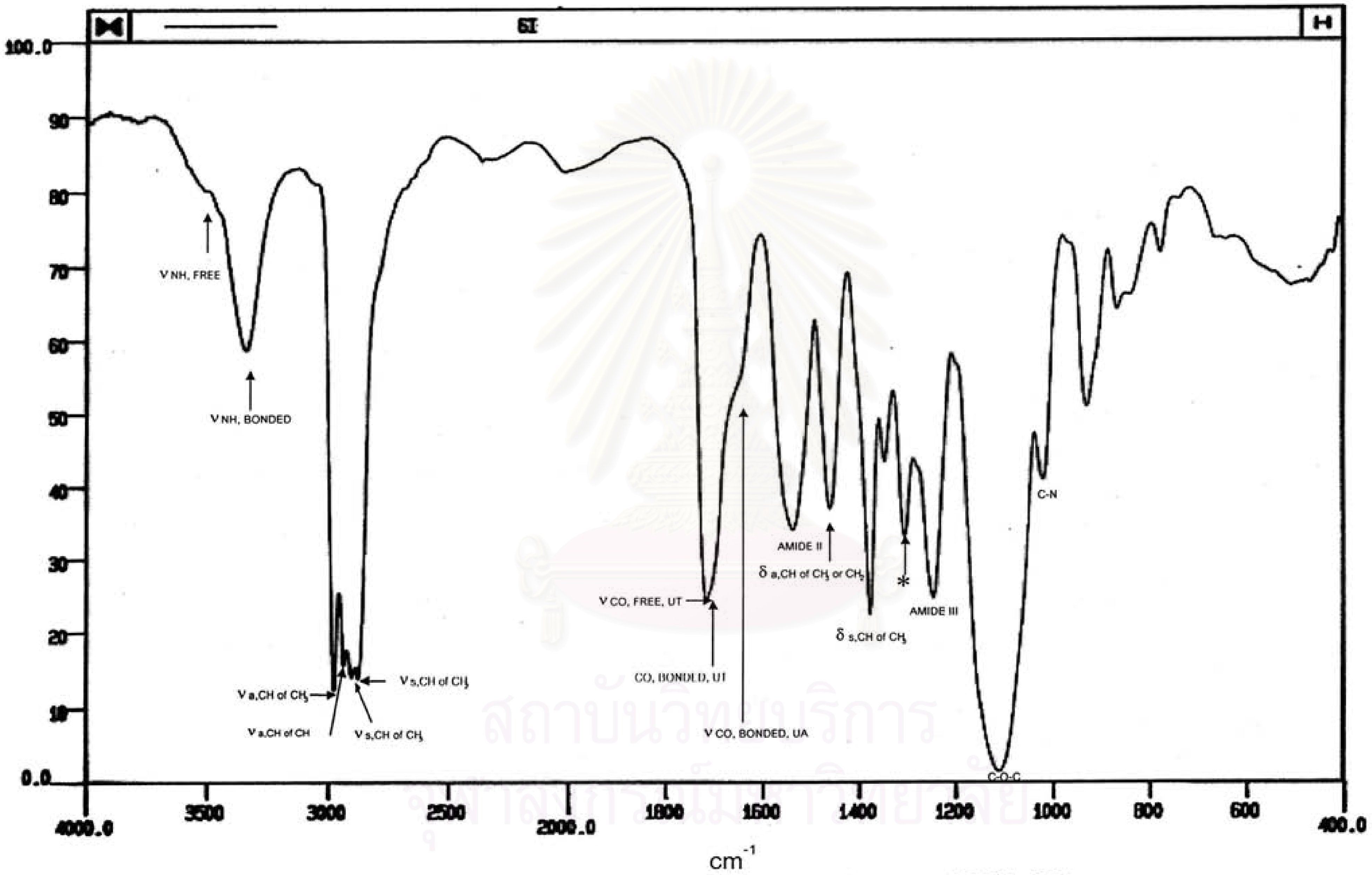

Figure 5.8 Infrared absorption of IPDI-based polyurethane elastomer at NCO% of 6%.

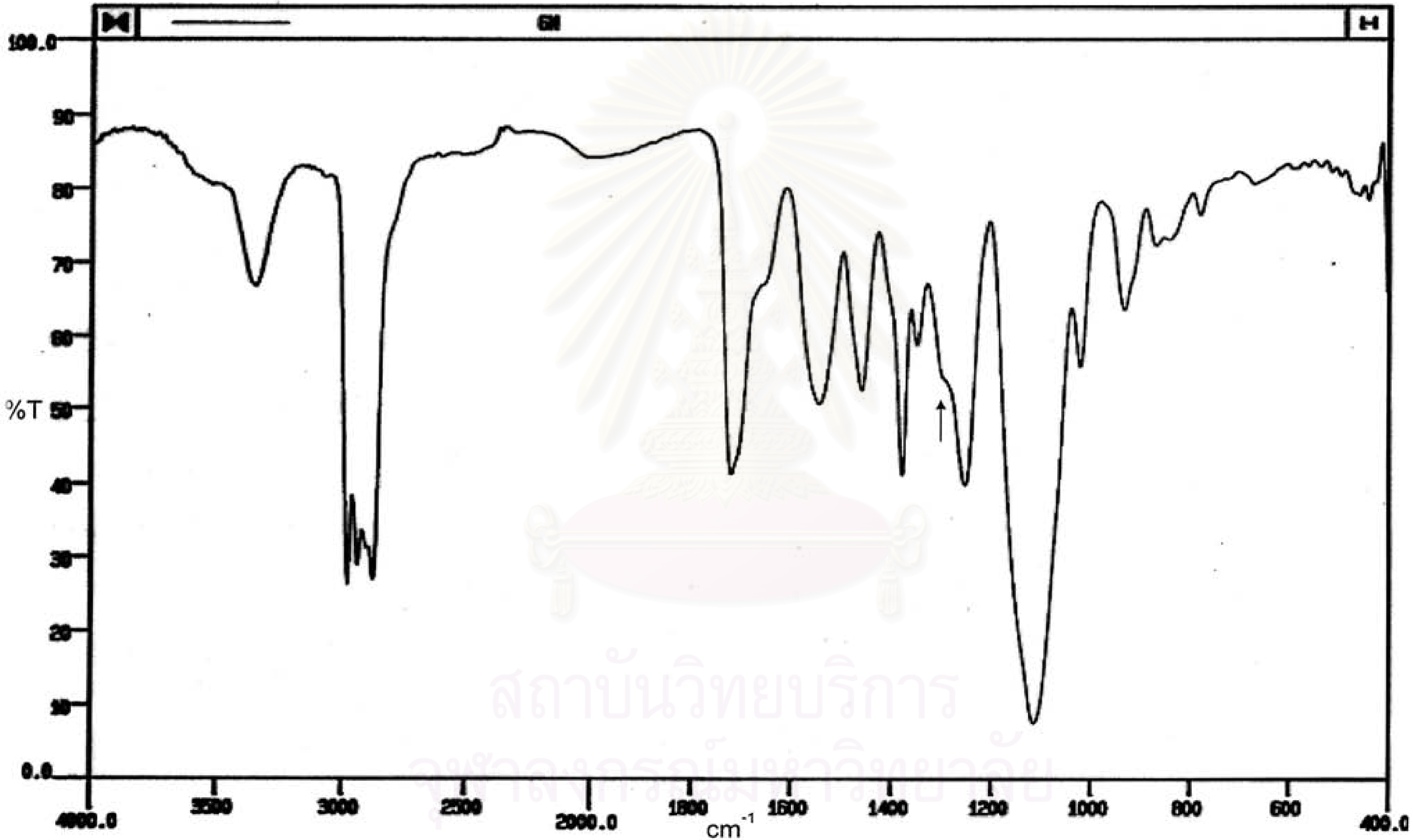

Figure 5.9 Infrared absorption of NBDI-based polyurethane elastomer at NCO% of 6%.

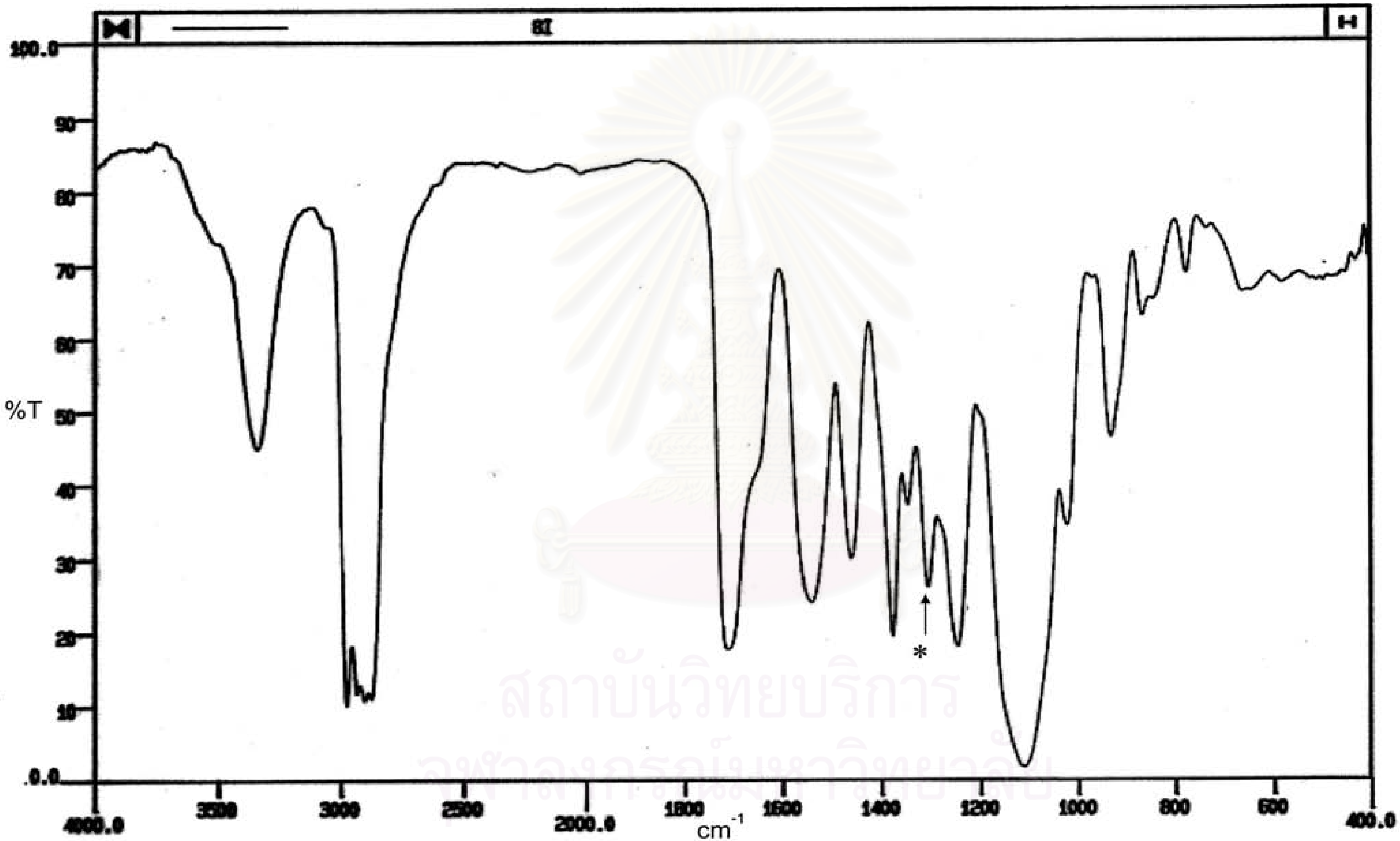

Figure 5.10 Infrared absorption of IPDI-based polyurethane elastomer at NCO% of 8%.

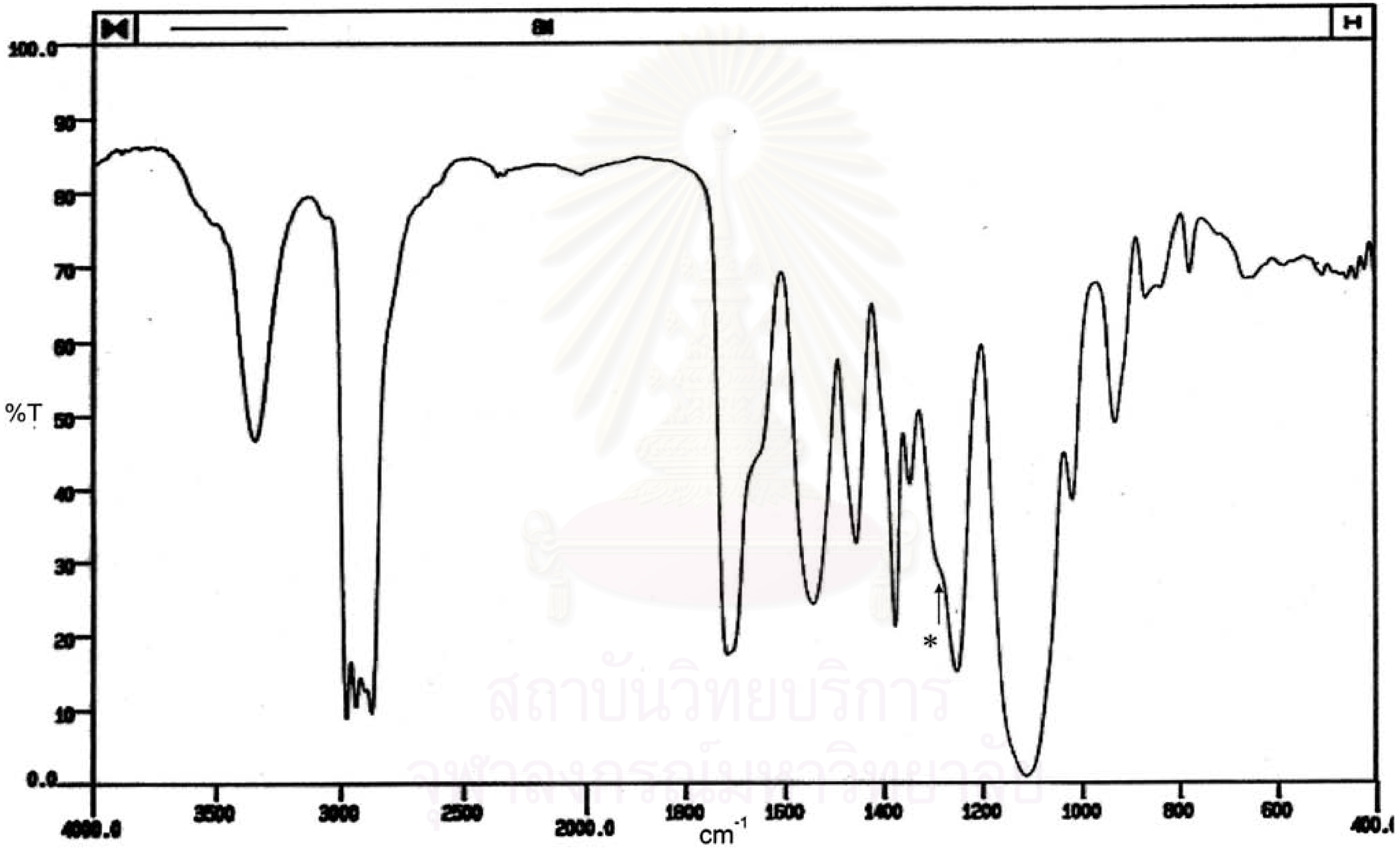

Figure 5.11 Infrared absorption of NBDI-based polyurethane elastomer at NCO% of 8%.

5.1.5 Dynamic mechanical properties of moisture cured polyurethane elastomers

The tan δ of IPDI- and NBDI-based polyurethane elastomers is shown in Fig. 5.12. The storage modulus of IPDI- and NBDI-based polyurethane elastomers is shown in Fig. 5.13.

Considering IPDI-based polyurethane elastomers, the polymers show two relaxation peaks. The first relaxation process, β_S relaxation, occurring between -60 to –10°C corresponds to the soft-segment glass transition temperature. This exhibits the motion of soft-segment. The second relaxation process, β_H relaxation, occurring between 0 to 70°C shows the hard-segment glass transition temperature. The tan δ curves for the IPDI-based polyurethane elastomers could indicate that the IPDI-based polyurethane elastomers are an incompatible system consisting of two phases, one is dominant by the hard-segment domain and the other one is dominant by the soft-segment domain. This shows that IPDI-based polyurethane elastomer has a good phase separation. The properties of one phase are generally independent of the morphology and volume fraction of the other phase [BOGART, V., *et. al.*, 1983].

When increasing the NCO% from 6% to 8%, the magnitude of the β_S relaxation peak of IPDI-based polyurethane elastomer decreased which resulted from the decreasing of the soft-segment content, i.e. increasing of the hard-segment content. The position of the β_H relaxation peak also moved to higher temperature as increasing the NCO%. This might be due to the higher hard-segment molecular weight or a greater fraction of hard-segments dissolved in soft phase at the NCO% of 8% [MILLER, J. A., *et. al.*, 1985].

Considering NBDI-based polyurethane elastomers, it was noticed from Fig. 5.12 NBDI-based polyurethane elastomers have only one relaxation process, β relaxation, that located between -60 to 30°C. This is different from the IPDI-based polyurethane elastomers. This could indicate that the NBDI-based polyurethane elastomers exhibit a nearly compatible system. This shows that NBDI-based polyurethane elastomer has a poor phase separation. The low temperature of the single β relaxation remains relatively constant at roughly -60°C, which corresponds closely to the low temperature of the β_S relaxation in the incompatible IPDI-based polyurethane elastomer. Furthermore, the high temperature end of the β peak falls in a relatively larger range as the NCO% increases from 6% to 8%.

However, one might argue that the tan δ curve of NBDI-based polyurethane elastomer at the NCO% = 8% seems to exhibit two relaxation peaks, β_S and β_H relaxation, which means that the system is incompatible. In this case, it would indicate that at NCO% = 6% (low hard-segment content), the system is compatible but at NCO% = 8% (high hard-segment content), the NBDI-based polyurethane elastomer is an incompatible material. This behaviour was also reported for the system of H_{12}MDI-based polycapolactone (Mw = 830) polyurethanes by BOGART V. *et. al*. (1983).

Another point similar to IPDI-based polyurethane elastomers, when increasing NCO% from 6% to 8%, is that the magnitude of the β relaxation peak decreased. This again results from the increasing of the hard-segment content. This corresponds to the sign of the second relaxation peak of the hard-segment glass transition process suggested earlier.

Comparing the tan δ curve of IPDI-based polyurethane elastomer to NBDI-based polyurethane elastomer at equivalent NCO%, it is clear that the magnitude of β relaxation of NBDI-based polyurethane elastomers is higher than that of β_S relaxation of IPDI-based polyurethane elastomers. It indicates that IPDI-based polyurethane elastomer has higher hard-segment content than NBDI-based polyurethane elastomer. Decreasing the magnitude of the β_S relaxation peak with increasing hard-segment content results from a decrease in the soft-segment content [BOGART, V., *et. al*., 1983]. Comparing phase separation of both polyurethane elastomers, IPDI-based polyurethane elastomer has better phase separation than NBDI-based polyurethane elastomer.

Considering the storage modulus in Fig. 5.13, it can be seen that the storage modulus of both IPDI- and NBDI-based polyurethane elastomer gradually drops and shows a long rubbery plateau but the values of the storage modulus of IPDI-based polyurethane elastomer is higher than that of NBDI-based polyurethane elastomer.

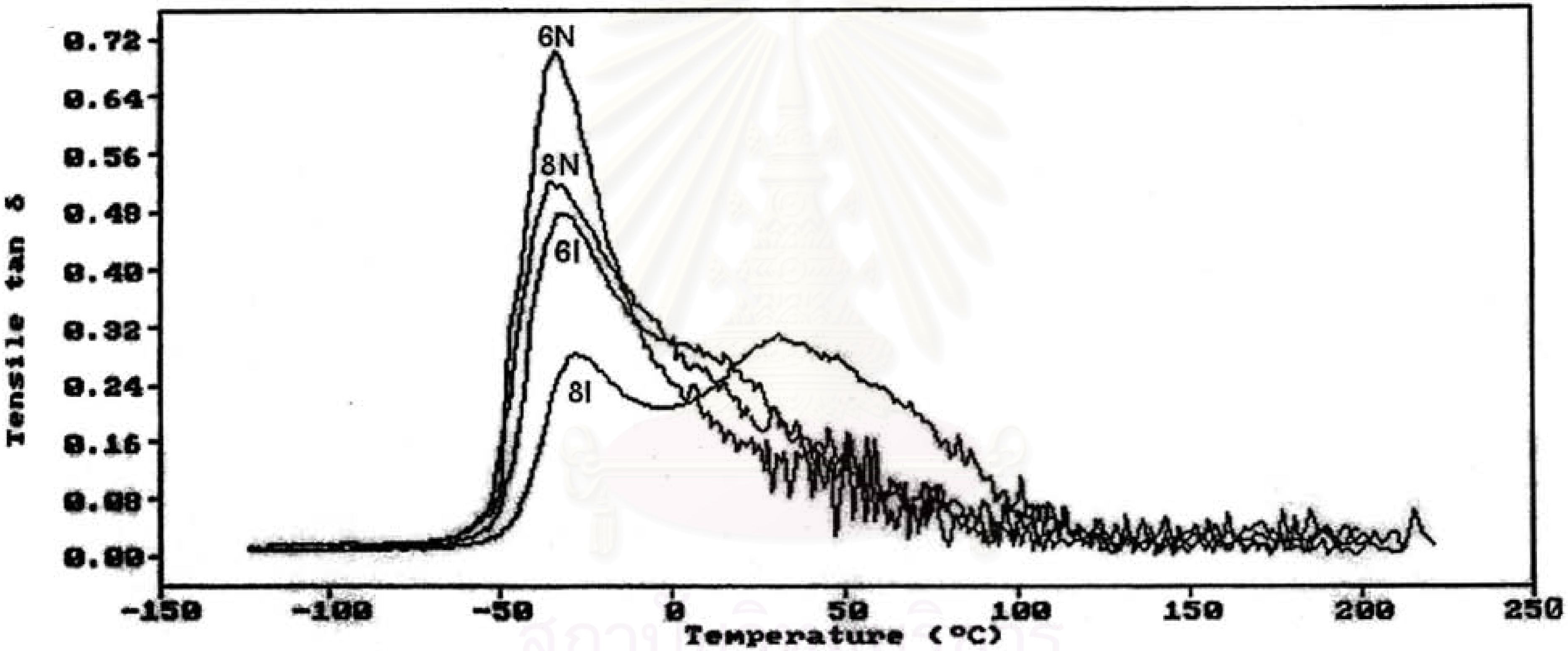

Figure 5.12 The tan δ of IPDI- and NBDI-based polyurethane elastomers at NCO% of 6% and 8%.

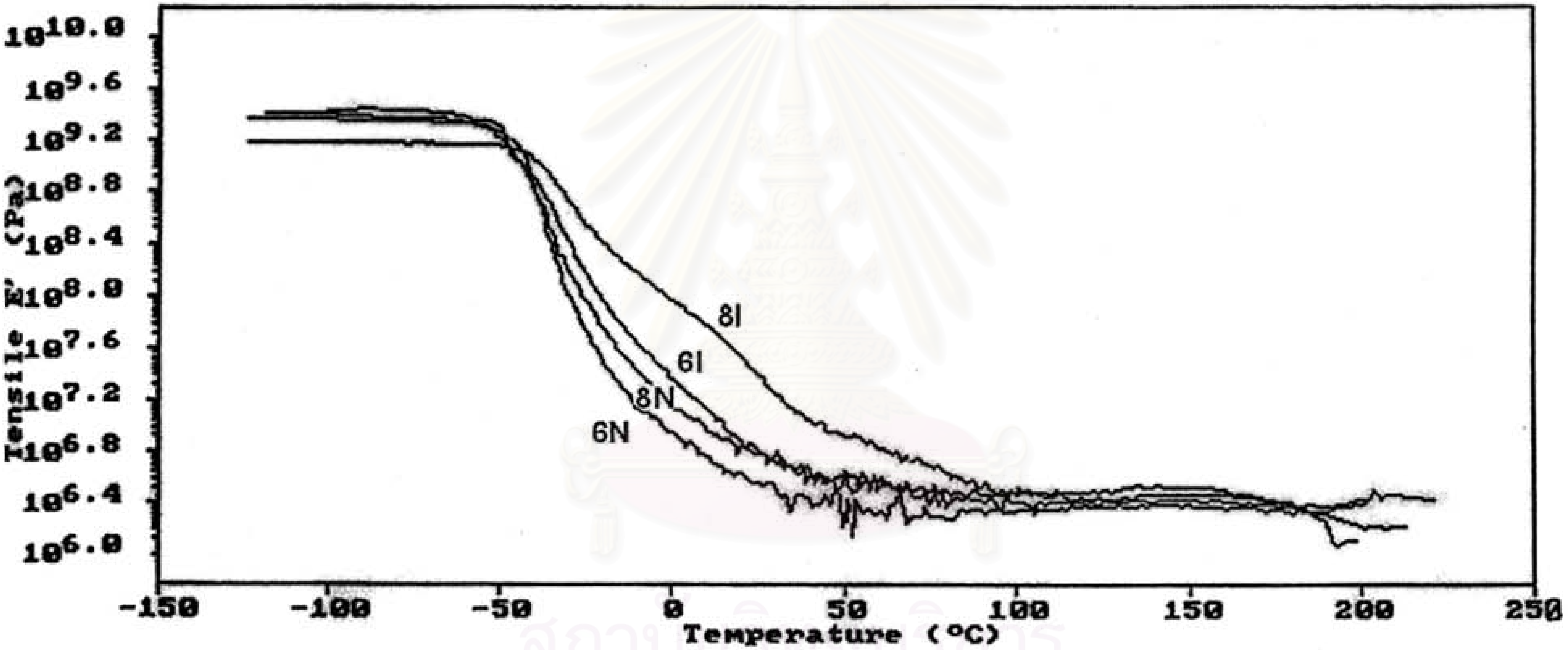

Figure 5.13 The storage modulus of IPDI- and NBDI-based polyurethane elastomers at NCO% of 6% and 8%.

5.2 Two-component polyurethane elastomers

5.2.1 Characteristics of prepolymers and two-component polyurethane elastomers

The results on NCO% and viscosity of prepolymers are shown in Table 5.5. For the NCO% of prepolymers, prepolymers were prepared by the reaction of Diol-2000 and diisocyanates (NBDI, IPDI, m-XDI and TDI) at the mole ratio of NCO:OH = 2:1. The actual NCO% of prepolymers is close to the theoretical NCO% of prepolymers and it is approximately 3.13-3.26%. For the viscosity of prepolymers shown in Fig. 5.14, it is clear that NBDI-based prepolymer has the highest viscosity.

Table 5.5 Characteristics of prepolymers.

Sample	Actual NCO%	Viscosity at 25°C (cp.)
NBDI-based prepolymer	3.26	8340
IPDI-based prepolymer	3.20	6100
m-XDI-based prepolymer	3.13	7660
TDI-based prepolymer	3.19	8110

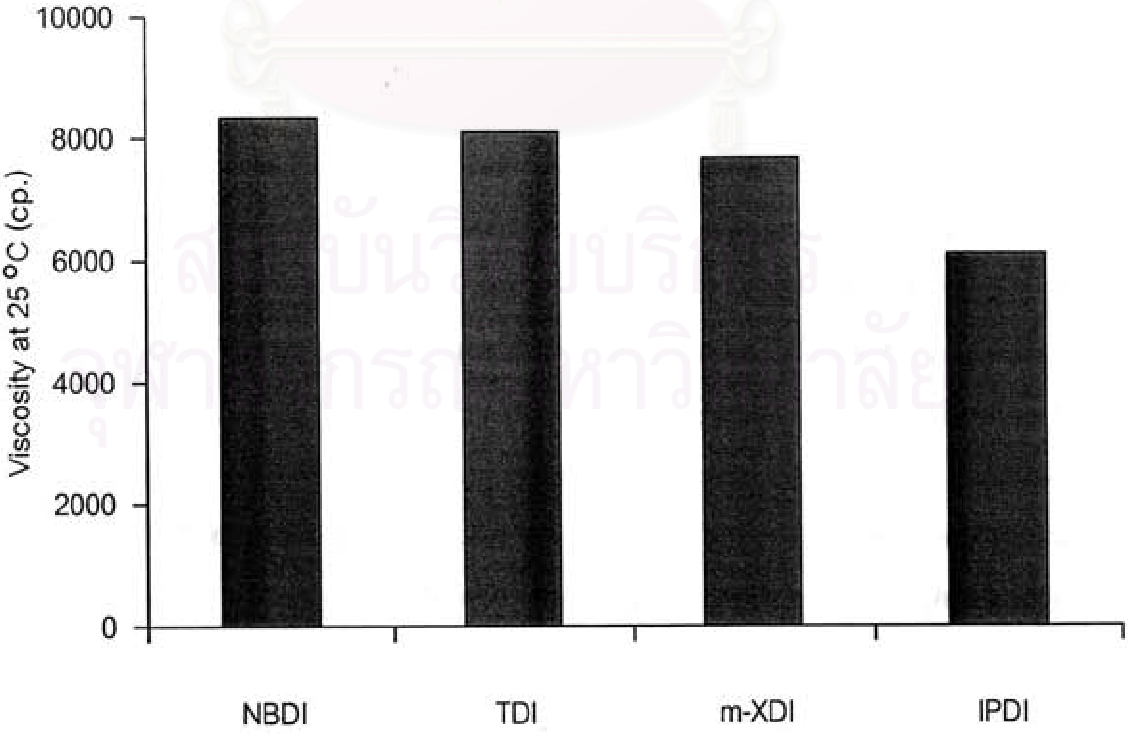

Figure 5.14 Viscosity of prepolymer.

The results on gel time of two-component polyurethane elastomers are shown in Table 5.6. The gel time of polyurethane elastomers shows the reactivity of diisocyanates.

Table 5.6 Gel time of two-component polyurethane elastomers.

Sample	Gel Time (hrs.)
N100	0.12 – 1.25
I100	0.75 – 7.5
X300	0.42 – 1
T300	0.83 – 4
N300	5 – 25
I300	42→1 week

Considering two different types of curing agent (ethacure100 and ethacure300), it is clear that the gel time of NBDI- and IPDI-ethacure100-based polyurethane elastomers is shorter than that of NBDI- and IPDI-ethacure300-based polyurethane elastomers. In the other words, the reaction of ethacure100 and prepolymers is quicker than that of ethacure300 and prepolymers. This shows ethacure100 has higher reactivity than ethacure300. This might be indicated by the steric hindrance effect of the sulfur atom of ethacure300. (See structures of ethacure100 and ethacure300 in Fig. 4.6 and Fig. 4.7, respectively)

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomer) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clearly noticed that the gel time of NBDI-based polyurethane elastomer is shorter than that of IPDI-based polyurethane elastomer. This shows NBDI has higher reactivity than IPDI. For ethacure300, it is clear that the gel time of XDI-based polyurethane elastomer is shorter than that prepared from the others. The gel time of XDI- and TDI-based polyurethane elastomers is shorter than that of NBDI- and IPDI-based polyurethane elastomers and the gel time of NBDI-based polyurethane elastomer is shorter than that of IPDI-based polyurethane elastomer. This might show that the degree of reactivity of these prepolymer samples is in the order of : XDI-based > TDI-based > NBDI-based >> IPDI-based prepolymers. This can be indicated that the reactivity of aromatic diisocyanate is higher than that of aliphatic diisocyanate.

5.2.2 The appearance of two-component polyurethane elastomers before and after weathering test

The appearance of two-component polyurethane elastomers (N100, I100, N300, I300, X300, and T300) observed before weathering test (after preparation) are shown in Fig. 5.15, Fig. 5.16, Fig. 5.17, Fig. 5.18, Fig. 5.19 and Fig. 5.20, respectively. Considering two different types of curing agent (ethacure100 and ethaucre300), the colour of ethacure100-based polyurethane elastomer is transparent and the surface appearance of ethacure100-based polyurethane elastomer looks smooth and stiff. The colour of ethacure300-based polyurethane elastomer is pale yellow. The surface appearance of NBDI- and IPDI-ethacure300-based polyurethane elastomer looks smooth and sticky, while that of XDI- and TDI-ethacure300-based polyurethane elastomer looks smooth and stiff.

The absorption of radiation is an essential first step to photodegradation, strongly absorbed radiation will be attenuated as it passes through the polymer and reaction will be concentrated in the surface layers. It is for this reason that a "skin effect" is frequently observed in photo-initialed reactions [GRASSIE N. and SCOTT G., 1985]. The appearance of polyurethane elastomer is then observed after weathering test for different periods of time. Considering two different types of curing agent (ethacure100 and ethacure300), after 5 hours of weathering test, the colour of ethacure100-based polyurethane elastomer does not change, while that of ethacure300-based polyurethane elastomer changes to be yellow. The surface appearance of both polyurethane elastomers does not change.

The discolouration of ethacure300-based polyurethane elastomer might be explained by two reasons. The first reason is the formation of quinoid structure in the structure of polyurethane elastomer after UV absorption. This case can be divided by two different types of diisocyanate (aromatic and aliphatic diisocyanates), aromatic diisocyanate-based polyurethane elastomers undergo a colour change upon UV irradiation due to the transformation to quinoid structure [REK, V., *et. al.*, 1992]. Yellow colouration can also be a result of the formation of monoquinone imide and/or diquinone imide [RABEK, J. F., 1995]. On the other hand, the colour of aliphatic diisocyanate-based polyurethane elastomers does not change after UV-irradiation. The second reason might be from the sulfur atom colouring in the structure of ethacure300.

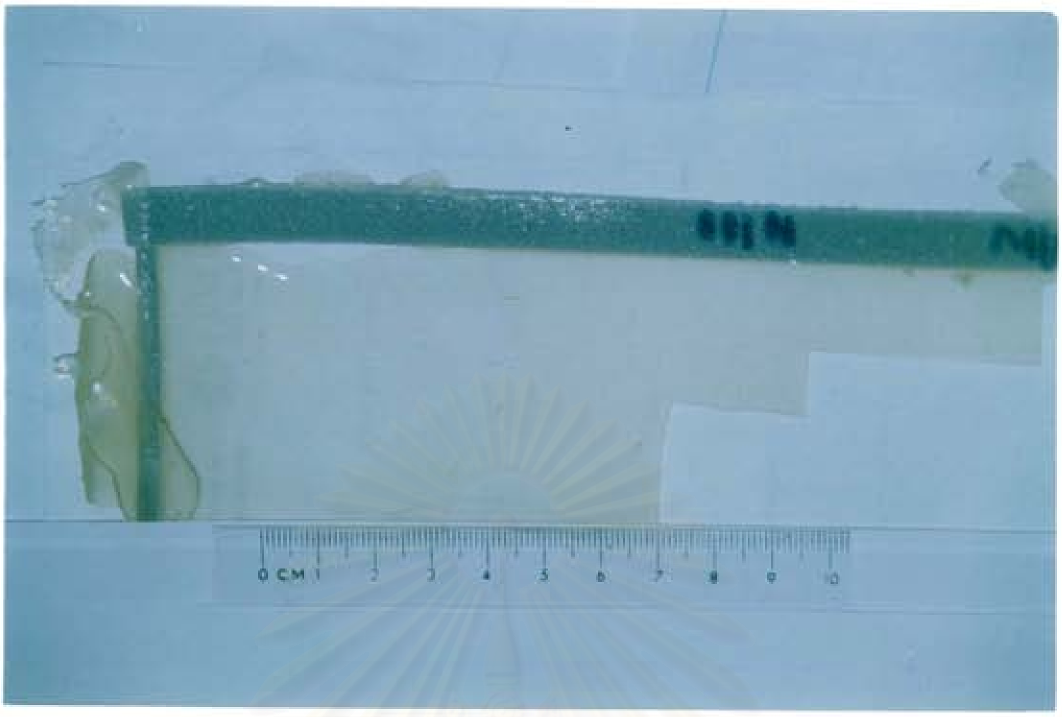

Figure 5.15 The appearance of N100 observed before weathering test.

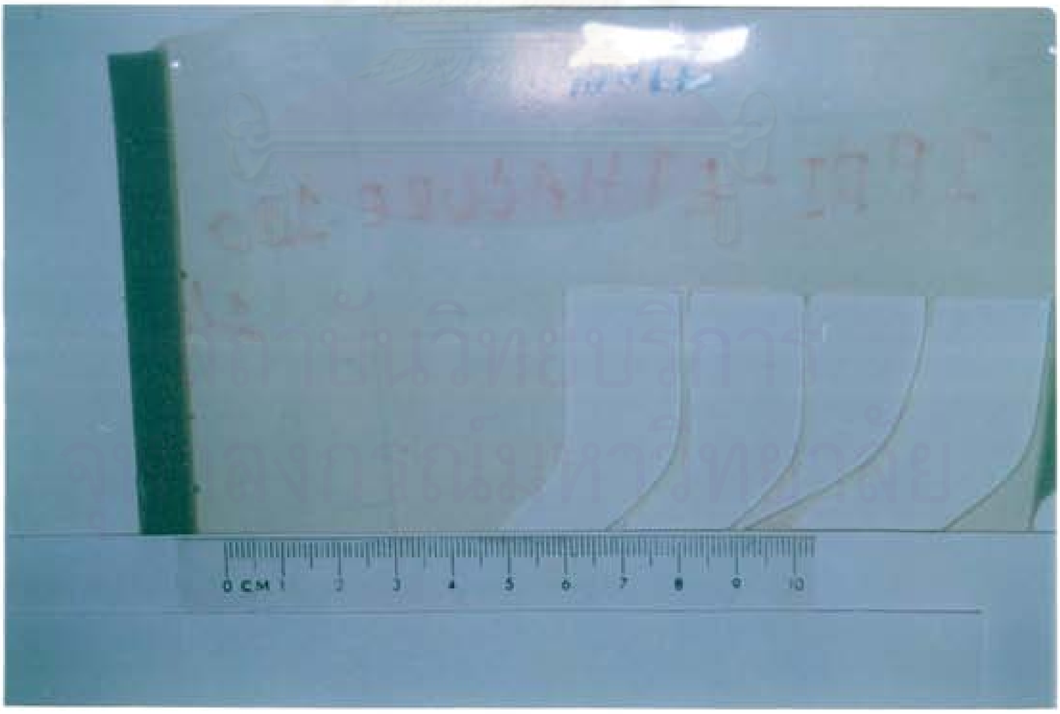

Figure 5.16 The appearance of I100 observed before weathering test.

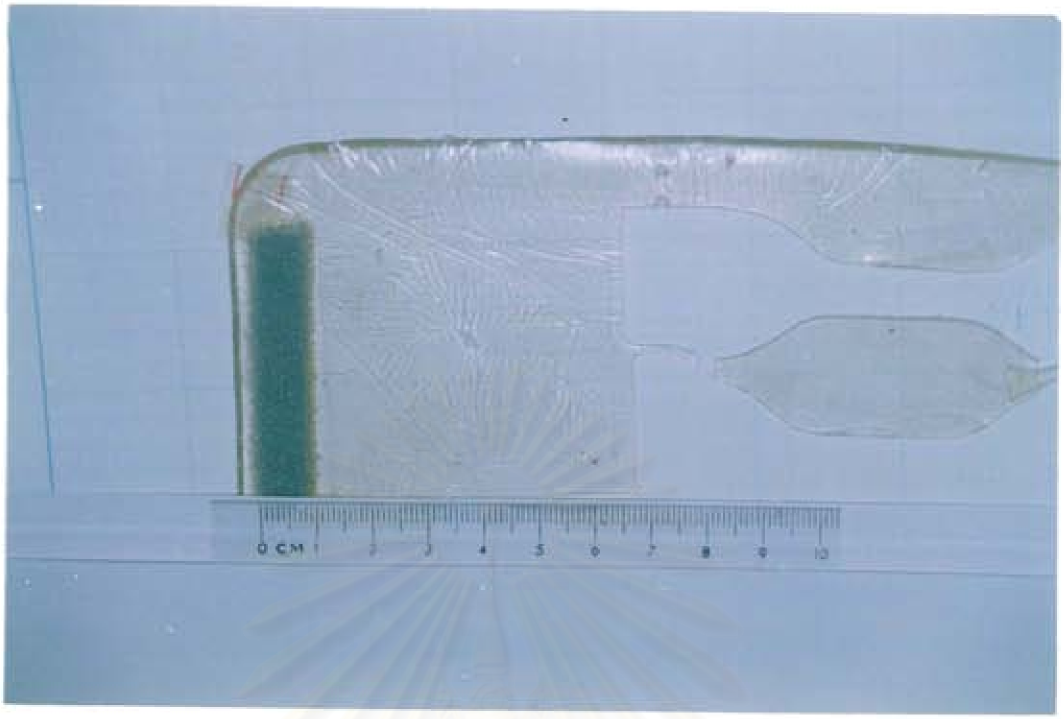

Figure 5.17 The appearance of N300 observed before weathering test.

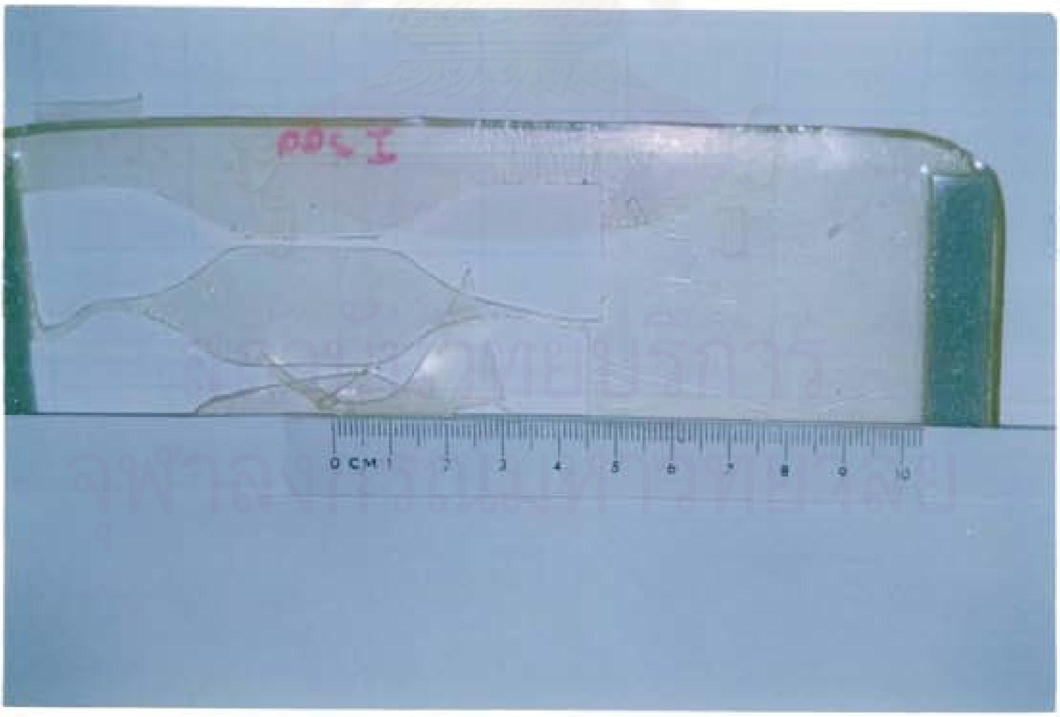

Figure 5.18 The appearance of I300 observed before weathering test.

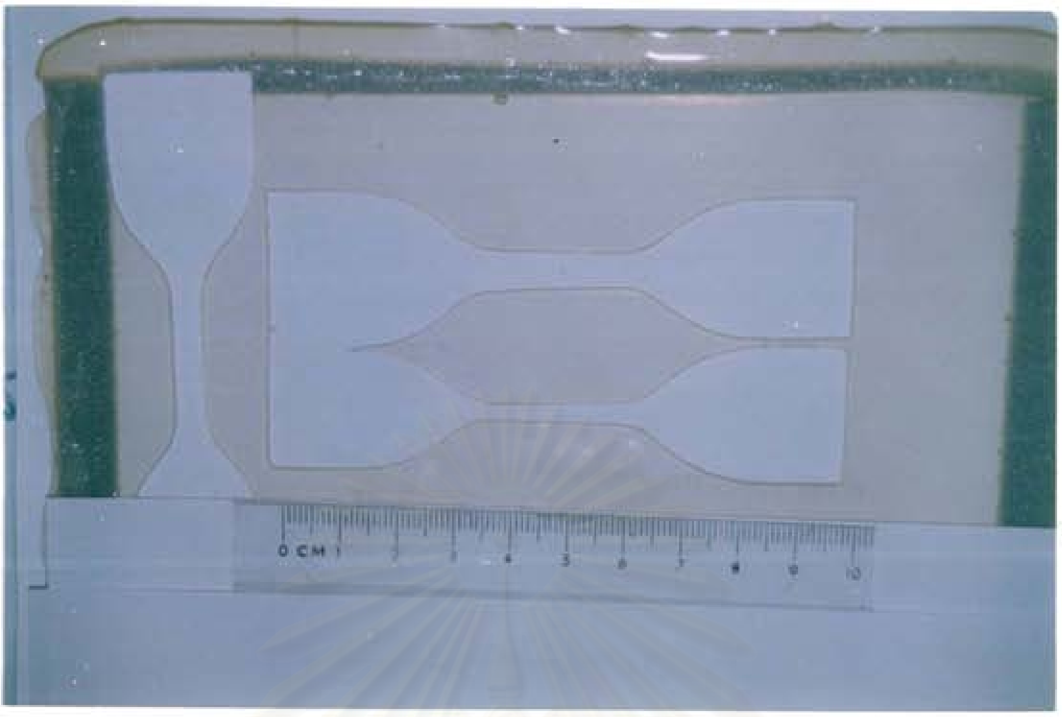

Figure 5.19 The appearance of X300 observed before weathering test.

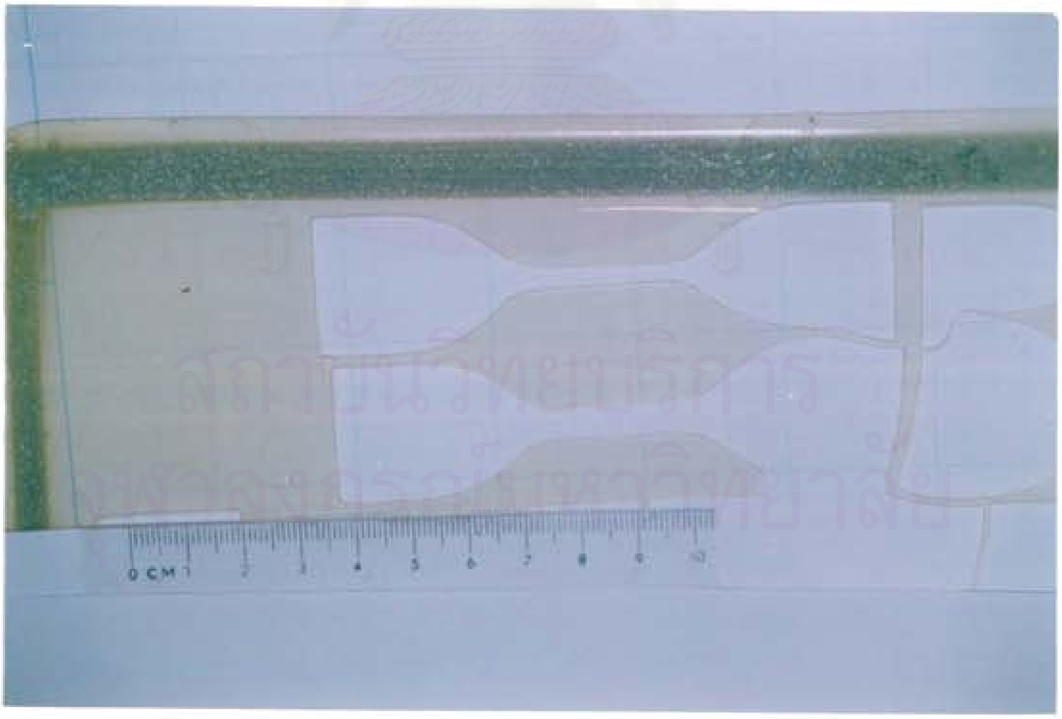

Figure 5.20 The appearance of T300 observed before weathering test.

After 2 weeks of weathering test, the appearance of two-component polyurethane elastomers can be summarized as shown in Table 5.7.

Table 5.7 The appearance of two-component polyurethane elastomers after 2 weeks of weathering test.

Sample	Colour		Surface		
	Transparent	Yellow	Cracking	Sticky	No change
N100	○	X			◎
I100	◎			X	
N300	X	◎			◎
I300	X	◎	X		
X300	X	◎	Δ		
T300	X	◎			◎

◎ : 4 (most)   ○ : 3   Δ : 2   X : 1 (least)

Considering NBDI- and IPDI-based polyurethane elastomer prepared from two different types of curing agent (ethacure300 and ethacure100) after 2 weeks of weathering test, the colour of ethacure300-based polyurethane elastomer changes to be dark yellow while that of ethacure100-based polyurethane elastomer slightly change. Comparing both IPDI-based polyurethane elastomers, it is clearly seen that the surface appearance of ethacure100 sample change to be sticky but that of ethacure300 does not change. This might show ethacure300-based polyurethane elastomer has higher weathering resistance than ethacure100-based polyurethane elastomer but the ethacure100 has higher discolouration resistance than ethacure300.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomer) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, the colour of NBDI-based polyurethane elastomer slightly changes to be pale yellow while that of IPDI-based polyurethane elastomer does not change. In general, polyurethane elastomers based on cyclo-aliphatic isocyanate do not change colour with UV irradiation [REK, V., *et. al.*, 1992]. However, the colour of NBDI-based polyurethane elastomer change to be pale yellow, although NBDI is a cyclo-aliphatic diisocyanate. This should be because of the impurity in NBDI. The surface appearance of NBDI-based polyurethane elastomer does not change while that of IPDI-based polyurethane elastomer is sticky. This might show that NBDI has higher weathering resistance than IPDI but IPDI has higher discolouration resistance than NBDI.

For ethacure300, the colour of all two-component polyurethane elastomers changes to be dark yellow. The surface of XDI- and IPDI-based polyurethane elastomer starts to crack and looks very stiff but that of NBDI- and TDI-based polyurethane elastomer does not change. The surface cracking on XDI-based polyurethane elastomer is more than that on IPDI-based polyurethane elastomer. This might show that the degree of weathering resistance of these polyurethane elastomer samples is in the order of : NBDI-based and TDI-based > IPDI-based > XDI-based polyurethane elastomers.

After 4 weeks of weathering test, the appearance of each polyurethane elastomer can be summarized as shown in Table 5.8.

Table 5.8 The appearance of two-component polyurethane elastomers after 4 weeks of weathering test.

Sample	Colour		Surface		
	Transparent	Yellow	Cracking	Sticky	No change
N100	○	Δ	X		
I100	◎			Δ	
N300	X	◎			◎
I300	X	◎	Δ	X	
X300	X	◎	○		
T300	X	◎	X		

◎ : 4 (most) ○ : 3 Δ : 2 X : 1 (least)

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomer) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, the colour of NBDI- and IPDI-based polyurethane elastomer is pale yellow and transparent, respectively. The surface of NBDI-based polyurethane elastomer starts to crack but that of IPDI-based polyurethane elastomer is sticky and stiff. The upper surface of IPDI-based polyurethane elastomer is stiff but the lower surface of IPDI-based polyurethane elastomer is very sticky. Moreover, some tensile specimens of IPDI-based polyurethane elastomer are deformed.

For ethacure300, the colour of all two-component polyurethane elastomers is dark yellow. The surface of TDI-based polyurethane elastomer starts to crack. The surface cracking on XDI- and IPDI-based polyurethane elastomer is more than that after 2 weeks. This shows that increasing time of weathering test increases the surface cracking. The surface appearance of IPDI-based polyurethane elastomer is sticky (both upper and lower surfaces) while that of NBDI-based polyurethane elastomer does not change.

After 6 weeks of weathering test, the appearance of each polyurethane elastomer can be summarized as shown in Table 5.9.

Table 5.9 The appearance of two-component polyurethane elastomers after 6 weeks of weathering test.

Sample	Colour		Surface		
	Transparent	Yellow	Cracking	Sticky	No change
N100	○	Δ	Δ		
I100	◎			○	
N300	X	◎	X		
I300	X	◎	○	Δ	
X300	X	◎	○	X	
T300	X	◎	X		

◎ : 4 (most) ○ : 3 Δ : 2 X : 1 (least)

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomer) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, the colour of NBDI- and IPDI-based polyurethane elastomer is similar to that after 4 weeks of weathering test. The surface cracking on NBDI-based polyurethane elastomer is more than that after 4 weeks. The surface appearance of IPDI-based polyurethane elastomer is sticky and stiff. Most of the samples (both tensile and tear specimens) of IPDI-based polyurethane elastomer are deformed.

For ethacure300, the colour of each two-component polyurethane elastomer is similar to that after 4 weeks. The surface cracking on XDI-, IPDI- and TDI-based polyurethane elastomer is increased. The surface appearance of IPDI-based polyurethane elastomer is sticky (both upper and lower surfaces). Both sides of XDI-based polyurethane elastomer surfaces are sticky; moreover, some tensile specimens of XDI-based polyurethane elastomer are deformed. The surface of NBDI-based polyurethane elastomer starts to crack.

After 8 weeks of weathering test, the appearance of each polyurethane elastomer sample (N100, I100, N300, I300, X300, and T300) are shown in Fig. 5.21, Fig. 5.22, Fig. 5.23, Fig. 5.24, Fig. 5.25 and Fig. 5.26, respectively, which can be summarized as shown in Table 5.10.

Table 5.10 The appearance of two-component polyurethane elastomers after 8 weeks of weathering test.

Sample	Colour		Surface		
	Transparent	Yellow	Cracking	Sticky	No change
N100	○	Δ	Δ		
I100	◎			○	
N300	X	◎	X		
I300	X	◎	○	Δ	
X300	X	◎	○	X	
T300	X	◎	X		

◎ : 4 (most) ○ : 3 Δ : 2 X : 1 (least)

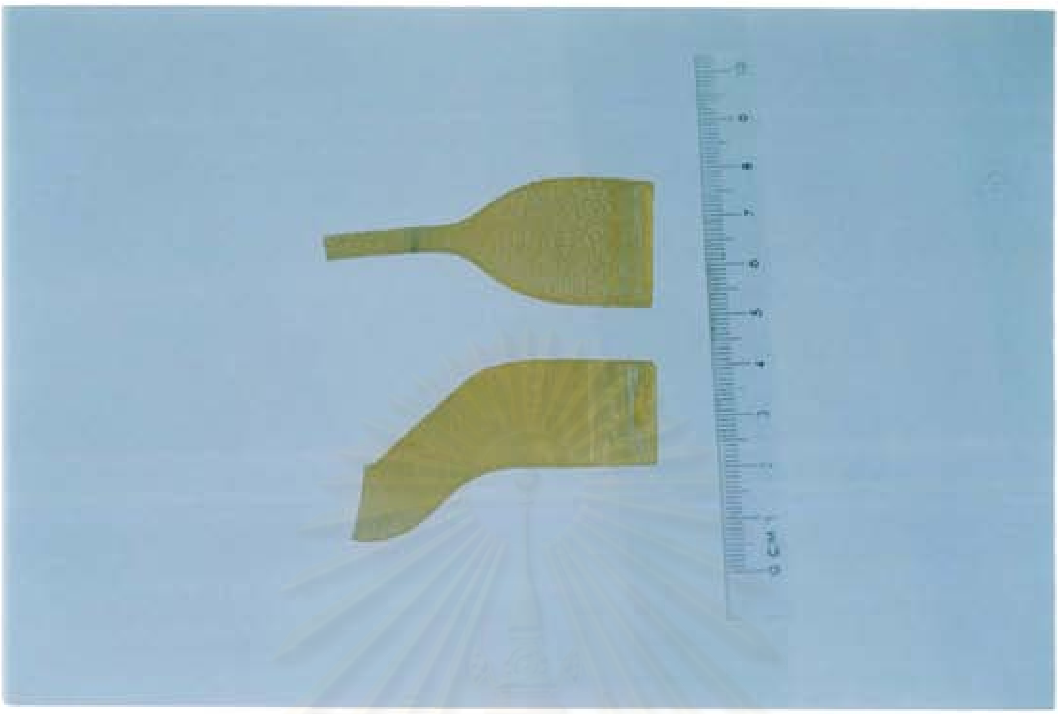

Figure 5.21 The appearance of N100 observed after 8 weeks of weathering test.

Figure 5.22 The appearance of I100 observed after 8 weeks of weathering test.

Figure 5.23 The appearance of N300 observed after 8 weeks of weathering test.

Figure 5.24 The appearance of I300 observed after 8 weeks of weathering test.

Figure 5.25 The appearance of X300 observed after 8 weeks of weathering test.

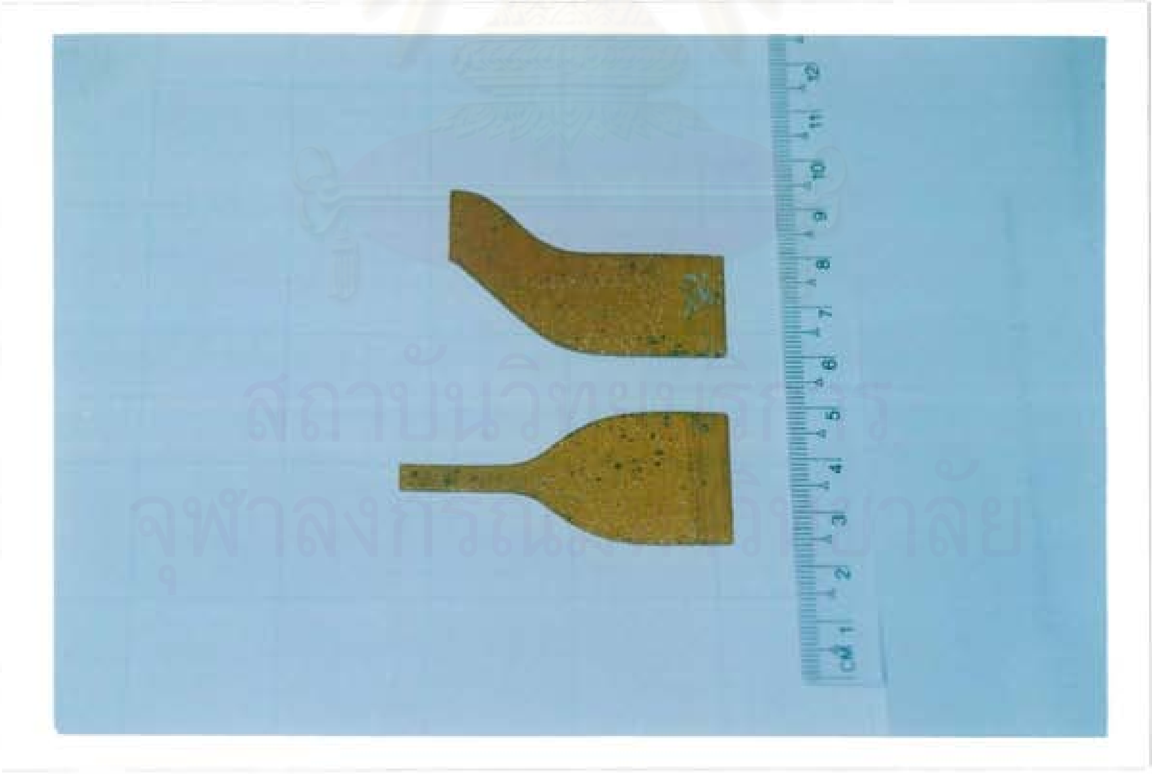

Figure 5.26 The appearance of T300 observed after 8 weeks of weathering test.

5.2.3 The stress-strain behaviour of two-component polyurethane elastomers after preparation

The stress-strain behaviour of two-component polyurethane elastomers depends on the physical and mechanical properties. The stress-strain curves of two-component polyurethane elastomers are shown in Fig. 5.27. It is clearly seen that IPDI-ethacure100-based polyurethane elastomer is tougher than other polyurethane elastomers.

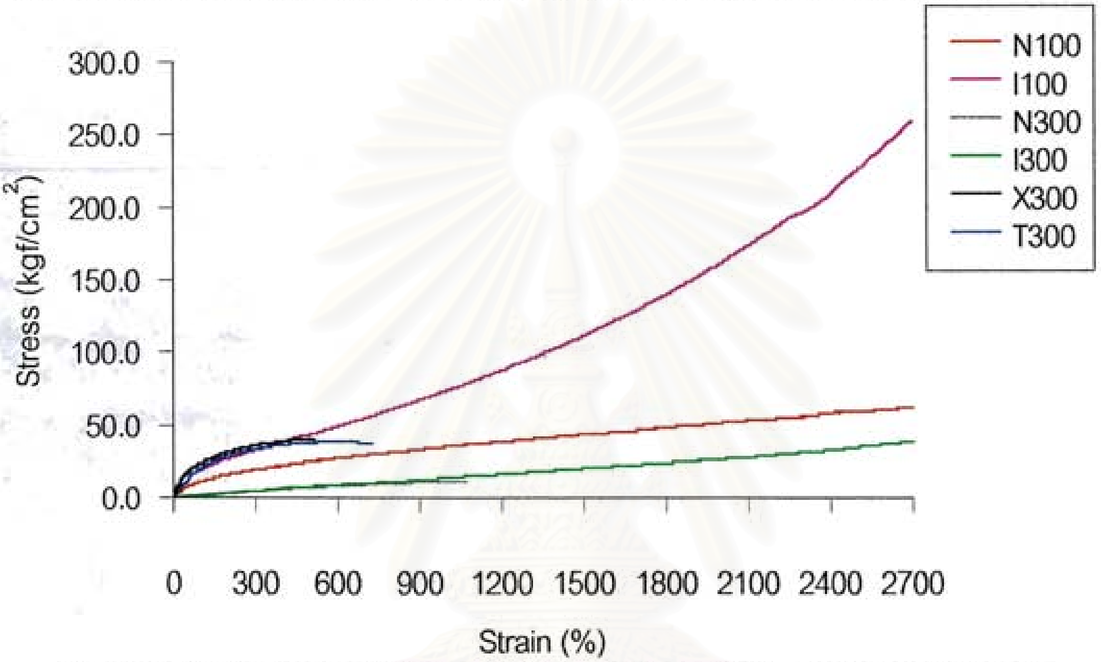

Figure 5.27 The stress-strain curve of two-component polyurethane elastomers.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that IPDI-based polyurethane elastomer is tougher than NBDI-based polyurethane elastomer. For ethacure300, it is clearly noticed that aromatic diisocyanate (XDI and TDI)-based polyurethane elastomers are stronger than aliphatic diisocyanate (NBDI and IPDI)-based polyurethane elastomers, while aliphatic diisocyanate-based polyurethane elastomers are tougher than aromatic diisocyanate-based polyurethane elastomers.

Comparing NBDI- and IPDI-based polyurethane elastomers prepared from two different types of curing agent (ethacure300 and ethacure100), it is clear that ethacure100-based polyurethane elastomers are tougher and stiffer than ethacure300-based polyurethane elastomers.

5.2.4 Mechanical properties of two-component polyurethane elastomers after preparation

The results on the tensile strength, the %elongation, the tear strength, the modulus at 100% and 300% elongation of two-component polyurethane elastomers after preparation are shown in Table 5.11. Normally, the values of tensile strength and %elongation of polymers are measured at the maximum value when the polymer breaks. In this work, NBDI-ethacure100-, IPDI-ethacure100- and IPDI-ethacure300-based polyurethane elastomers are very tough and they do not break at the maximum extension of the instrument. Consequently, the tensile strength and elongation values of those polyurethane elastomers are taken at the maximum elongation.

Table 5.11 The results on the tensile strength, the %elongation, the tear strength, the modulus at 100% and 300% elongation of two-component polyurethane elastomers after preparation.

Sample	Total hard segments (wt%)	Mechanical properties after preparation				
		%Elongation (%)	Tensile strength (kgf/cm^2)	M100 (kgf/cm^2)	M300 (kgf/cm^2)	Tear strength (kgf/cm)
N100	0.22	>1450	>60.3	10.3	6.1	36.0
I100	0.23	>984	>241.7	18.5	11.1	53.1
N300	0.23	842	9.1	1.6	1.3	3.0
I300	0.24	>521	>57.2	2.2	2.1	16.7
X300	0.22	492	38.3	22.8	11.6	27.3
T300	0.21	311	33.9	21.1	10.6	27.6

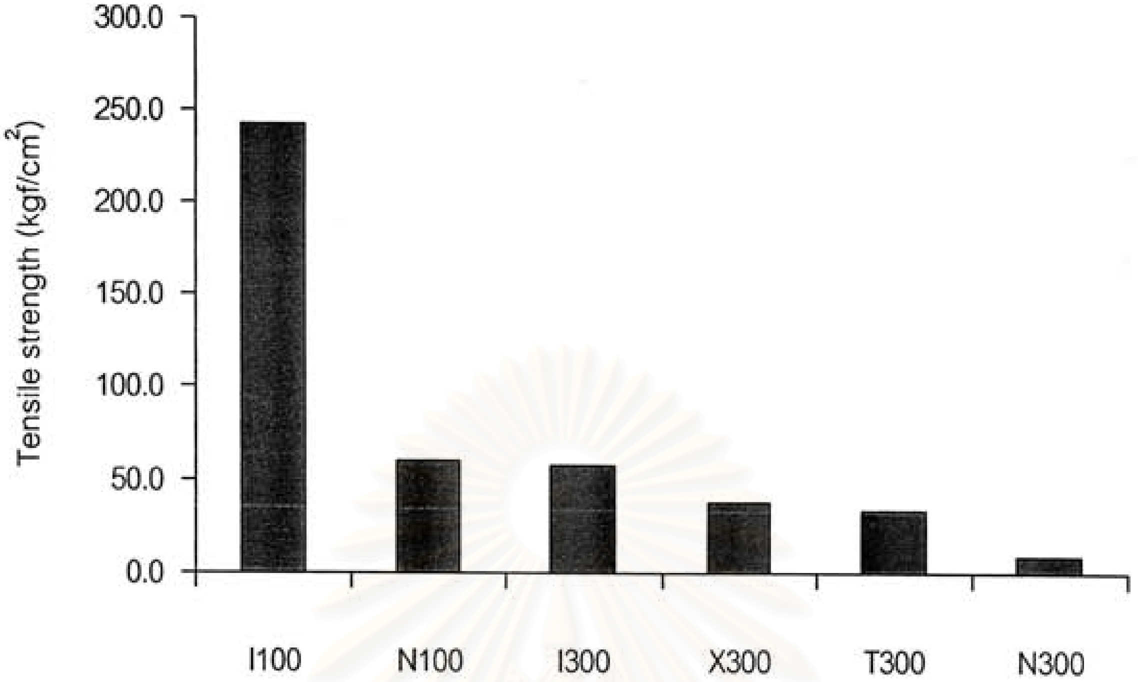

Figure 5.28 The tensile strength of two-component polyurethane elastomers after preparation.

The tensile strength of two-component polyurethane elastomers after preparation is compared in Fig. 5.28. It is clear that IPDI-ethacure100-based polyurethane elastomer has the highest tensile strength. Ethacure100-based polyurethane elastomers have higher tensile strength than ethacure300-based polyurethane elastomers.

Considering the hard-segment content of two-component polyurethane elastomers, the hard-segment content in the structure of polyurethane elastomers is generally responded for the strength of the polyurethane elastomers. The hard-segment content of all two-component polyurethane elastomers is approximately the same. This indicates that, in this case, the hard-segment content is not responded for the difference in the strength of two-component polyurethane elastomers; therefore, the difference in the strength of the two-component polyurethane elastomers might be caused by different types of diisocyanate and curing agent.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that the tensile strength of IPDI-based polyurethane elastomer is much higher than that of NBDI-based polyurethane elastomer.

The difference in the strength between NBDI- and IPDI-based polyurethane elastomer should be because of the difference in chemical structures of raw materials particularly diisocyanates. The difference in chemical structures between NBDI and IPDI is the NCO group configuration (See Fig. 2.5 and Fig 2.3a, respectively). The NCO group configuration of NBDI is more flexible than that of IPDI. This might imply that urethane and urea bonding of NBDI-based polyurethane elastomer is more flexible than that of IPDI-based polyurethane elastomer. In other words, urethane and urea bonding of IPDI-based polyurethane elastomer is more rigid and stiffer than that of NBDI-based polyurethane elastomer. Therefore, IPDI-based polyurethane elastomer has higher strength than NBDI-based polyurethane elastomer.

The other possible reason which might have an effect on the strength of NBDI-based polyurethane elastomer is the isomers of NBDI. This, however, needs to be further studied.

Considering ethacure300, it is clear that IPDI-based polyurethane elastomer has higher tensile strength than those prepared from other diisocyanates. NBDI-based polyurethane elastomer has very low tensile strength. This might be because the surface appearance of NBDI-based polyurethane elastomer looked soft and sticky.

Comparing NBDI- and IPDI-based polyurethane elastomer prepared from two different types of curing agent (ethacure300 and ethacure100), it is clear that NBDI- and IPDI-ethacure100-based polyurethane elastomers have higher tensile strength than those of ethacure300-based polyurethane elastomers by about 561% and 323%, respectively. This might be caused by the steric hindrance effect of the sulfur atom of ethacure300.

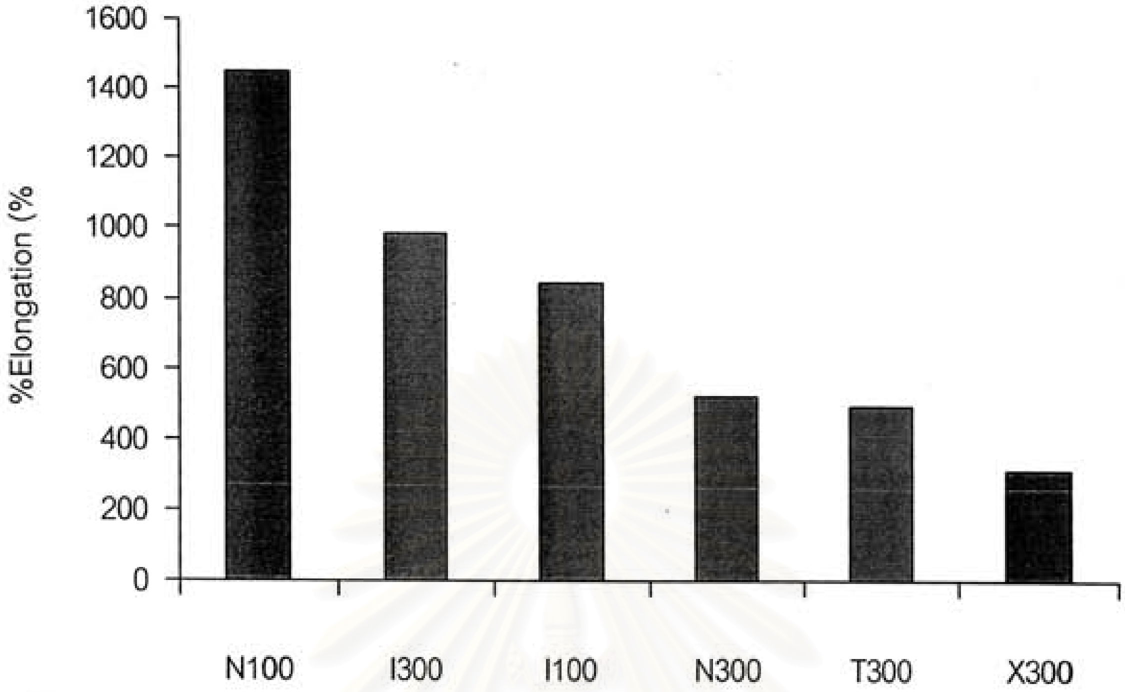

Figure 5.29 The %elongation of two-component polyurethane elastomers after preparation.

The %elongation of two-component polyurethane elastomers after preparation is compared in Fig. 5.29. It can be seen that NBDI-ethacure100-based polyurethane elastomer has the highest %elongation.

Considering different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clearly noticed that NBDI-based polyurethane elastomer has higher %elongation than IPDI-based polyurethane elastomer. For ethacure300, the %elongation of IPDI-based polyurethane elastomer is higher than those prepared from the other three diisocyanates. The difference on %elongation of both NBDI- and IPDI-based polyurethane elastomers does not show a clear trend.

Dai J. *et. al.* (1991) studied the similar works on the difference in tensile strength of IPDI, TDI and XDI-based urethane (meth)acrylate. It was reported that IPDI-based materials exhibited a higher Young's modulus and stress at break than TDI- and XDI-based materials. These results were not in accordance with the general rule that aromatic compounds often have better mechanical properties than non-aromatic compounds. They may be related to the high IPDI-HEMA segment content due to IPDI having the highest Mw among the three components. TDI and XDI are similar in structure, but their ultimate mechanical properties were different because of slight differences in their structures. No significant difference in elongation at break was observed.

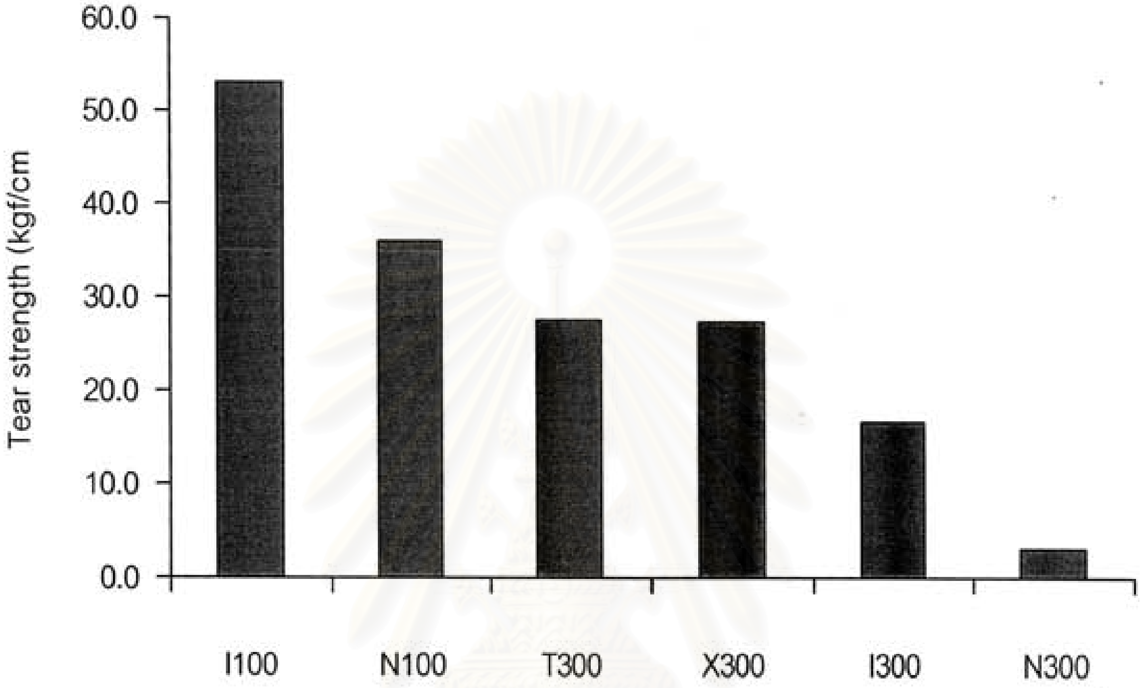

Figure 5.30 The tear strength of two-component polyurethane elastomers after preparation.

The tear strength of two-component polyurethane elastomers after preparation is compared in Fig. 5.30. It is clearly noticed that IPDI-ethacure100-based polyurethane elastomer has the highest tear strength. Furthermore, the tear strength of both NBDI- and IPDI-ethacure100-based polyurethane elastomer is higher than that of the others prepared from the ethacure300. Considering the hard-segment content, the hard-segment content is not responded for the difference in strength of two-component polyurethane elastomers as discussed previously.

Considering different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that IPDI-based polyurethane elastomer has higher tear strength than NBDI-based polyurethane elastomer. For ethacure300, it can be seen that the tear strength of TDI- and XDI-based polyurethane elastomer is higher than that prepared from the other diisocyanates.

Comparing NBDI- and IPDI-based polyurethane elastomer prepared from two different types of curing agent (ethacure300 and ethacure100), it is clear that NBDI- and IPDI-based polyurethane elastomer based on ethacure100 has higher tear strength than those based on ethacure300 by about 1084% and 218%, respectively. This might be attributed by the steric hindrance effect of sulfur atom.

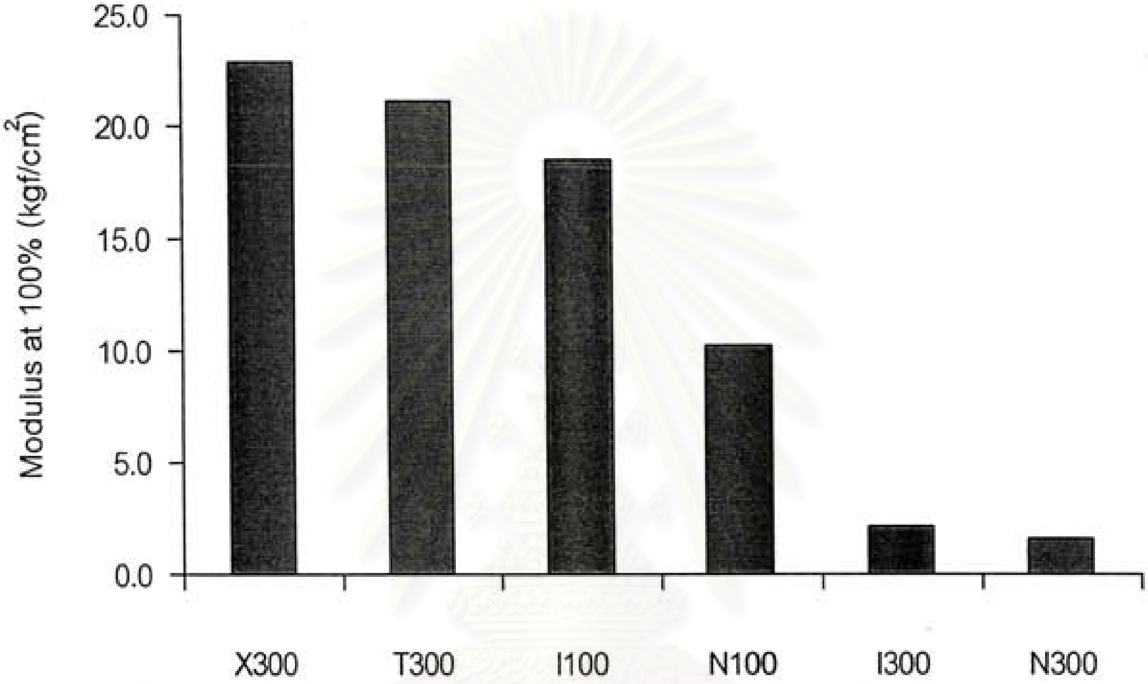

Figure 5.31 The modulus at 100% elongation of two-component polyurethane elastomers after preparation.

The modulus at 100% elongation (M100) of two-component polyurethane elastomers after preparation is compared in Fig. 5.31. It is clear that XDI-ethacure300-based polyurethane elastomer has the highest M100.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the M100 of IPDI-based polyurethane elastomer is much higher than that of NBDI-based polyurethane elastomer. Considering ethacure300, it is clear that XDI-based polyurethane elastomer has the highest M100. The M100 of IPDI-based polyurethane elastomer is slightly higher than that of NBDI-based polyurethane elastomer. For each curing agent, NBDI-based polyurethane elastomer has the lowest M100.

Comparing NBDI- and IPDI-based polyurethane elastomer prepared from two different types of curing agent (ethacure300 and ethacure100), it is clearly noticed that NBDI- and IPDI-ethacure100-based polyurethane elastomers have higher M100 than those of ethacure300-based polyurethane elastomers by about 545% and 761%, respectively.

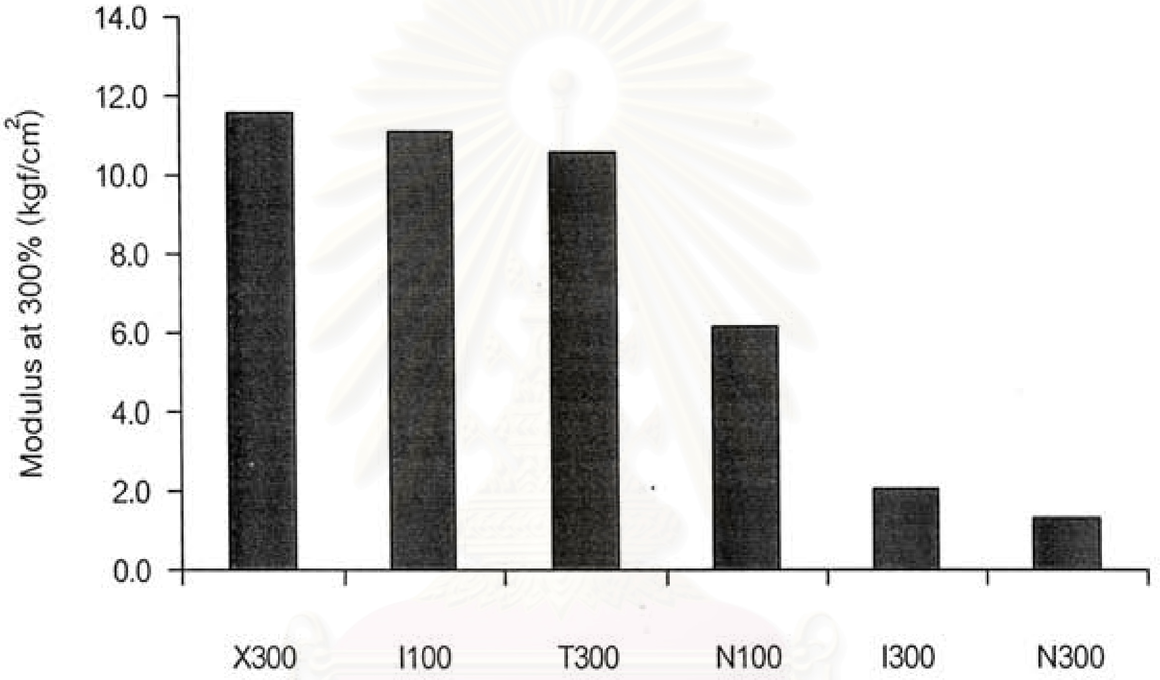

Figure 5.32 The modulus at 300% elongation of two-component polyurethane elastomers after preparation.

The modulus at 300% elongation (M300) of two-component polyurethane elastomers after preparation is compared in Fig. 5.32. It is clear that XDI-ethacure300-based polyurethane elastomer has the highest M300.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), the results are in the same trend as the results of M100.

Comparing NBDI- and IPDI-based polyurethane elastomer prepared from two different types of curing agent (ethacure300 and ethacure100), the results are similar to the results of M100. NBDI- and IPDI-ethacure100-based polyurethane elastomers have higher

M300 than those of ethacure300-based polyurethane elastomers by about 375% and 437%, respectively.

From the results on the mechanical properties of the pair of NBDI- and IPDI-based polyurethane elastomers (particularly tensile strength and modulus), it could be concluded that IPDI-based polyurethane elastomer has much better mechanical properties than NBDI-based polyurethane elastomer. This could be caused by the following factors different between IPDI and NBDI :

1) The intramolecular H-bonding in the hard segment of the IPDI- and NBDI-based polyurethane elastomers.
2) The domain of the phase separation in the IPDI- and NBDI-based polyurethane elastomers.
3) The chemical structure of the IPDI- and NBDI-based polyurethane elastomers which could results in the flexibility/stiffness of the polyurethane elastomers.

However, these possible factors need to be further proved.

In comparison of the mechanical properties of the ethacure100- and ethacure300-based polyurethane elastomers, it could be concluded that ethacure100-based polyurethane elastomer gives superior mechanical properties to ethacure300-based polyurethane elastomer. This might be caused by the steric hindrance effect of the sulfur atom of ethacure300, comparing to the carbon atom of ethacure100 (See Fig. 4.6 and Fig. 4.7).

5.2.5 Mechanical properties of two-component polyurethane elastomers after water immersion, heat aging and weathering test

For the results on weathering test, the values of the tensile strength, %elongation and tear strength of all samples are taken at break except IPDI-ethacure300-based polyurethane elastomer. All values are taken at maximum elongation.

The results on the tensile strength after water immersion, heat aging and weathering test are shown in Table 5.12, comparing to the results after preparation.

Table 5.12 Tensile strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

Sample	Tensile strength (kgf/cm^2)			
	After preparation	After 1 week of water immersion	After 1 week of heat aging	After 2 months of weathering test
N100	>60.3	>61.2	>60.3	25.1
I100	>241.7	>235.4	>244.0	2.1
N300	9.1	10.4	10.5	7.6
I300	>57.2	>52.3	>61.5	>20.7
X300	38.3	36.9	49.9	7.6
T300	33.9	35.1	36.1	27.7

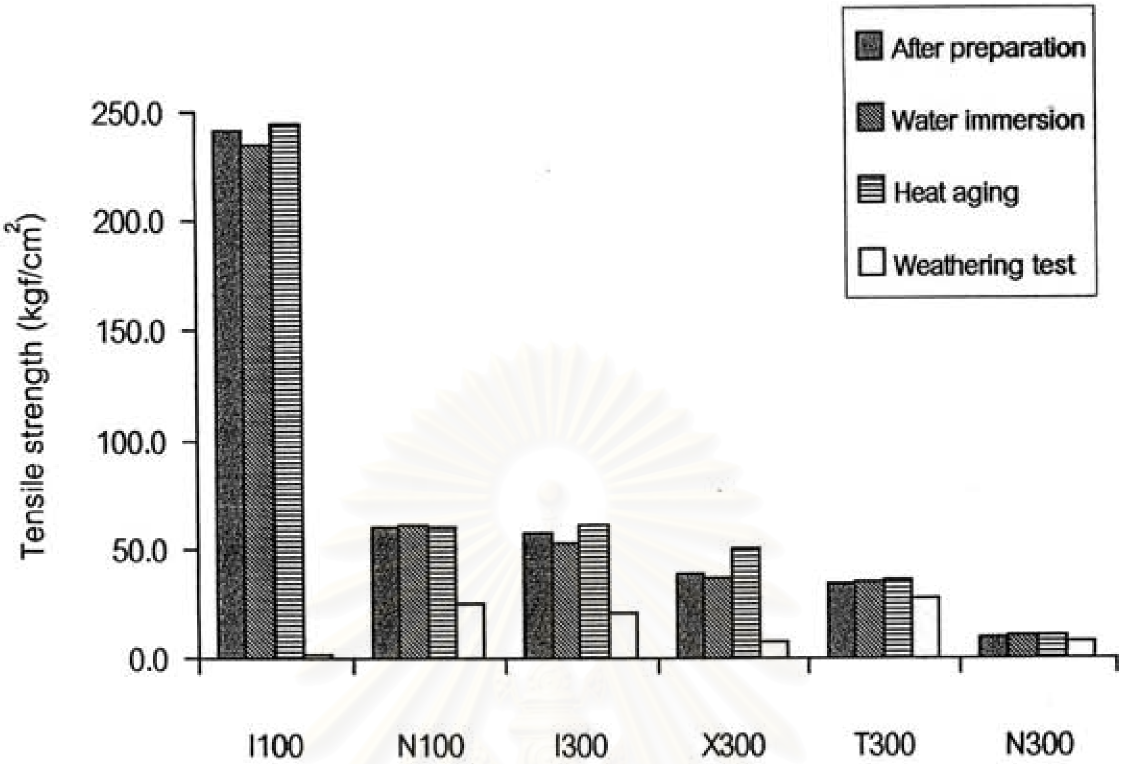

Figure 5.33 Tensile strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

The tensile strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering tests is compared in Fig. 5.33.

Water immersion

It can be seen that the tensile strength of each sample after 1 week of water immersion does not change much from that after preparation.

Heat aging

It is clear that the tensile strength of all samples after 1 week of heat aging is slightly higher than that after preparation.

Weathering test

It is clear that the tensile strength of all samples after 2 months of weathering test is much lower than that after preparation.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the tensile strength of NBDI- and IPDI-based polyurethane elastomer after weathering test is lower than that after preparation by about 58% and 99%, respectively. This shows that the weathering resistance to tensile strength of NBDI-based polyurethane elastomer is better than that of IPDI-based polyurethane elastomer.

Considering ethacure300, the tensile strength of NBDI-, TDI-, IPDI-, and XDI-based polyurethane elastomer is lower than that before weathering test by about 18%, 18%, 64%, and 80% respectively. This shows that NBDI- and TDI-based polyurethane elastomer have higher weathering resistance than those based on the other diisocyanates. Moreover, the weathering resistance of ethacure300-based polyurethane elastomer is higher than that of ethacure100-based polyurethane elastomer.

The results of tensile strength after weathering test might show that the degree of weathering resistance to the tensile strength of these polyurethane elastomer samples is in the order of : NBDI-based and TDI-based > IPDI-based > XDI-based polyurethane elastomers and ethacure300-based > ethacure100-based polyurethane elastomers.

The results on the %elongation after water immersion, heat aging and weathering tests are shown in Table 5.13, comparing to the results after preparation.

Table 5.13 %Elongation of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

Sample	%Elongation (%)			
	After preparation	After 1 week of water immersion	After 1 week of heat aging	After 2 months of weathering test
N100	>1450	>1400	>1438	1171
I100	>842	>880	>860	146
N300	521	458	454	400
I300	>984	>1050	>988	>1133
X300	311	482	471	97
T300	492	490	663	344

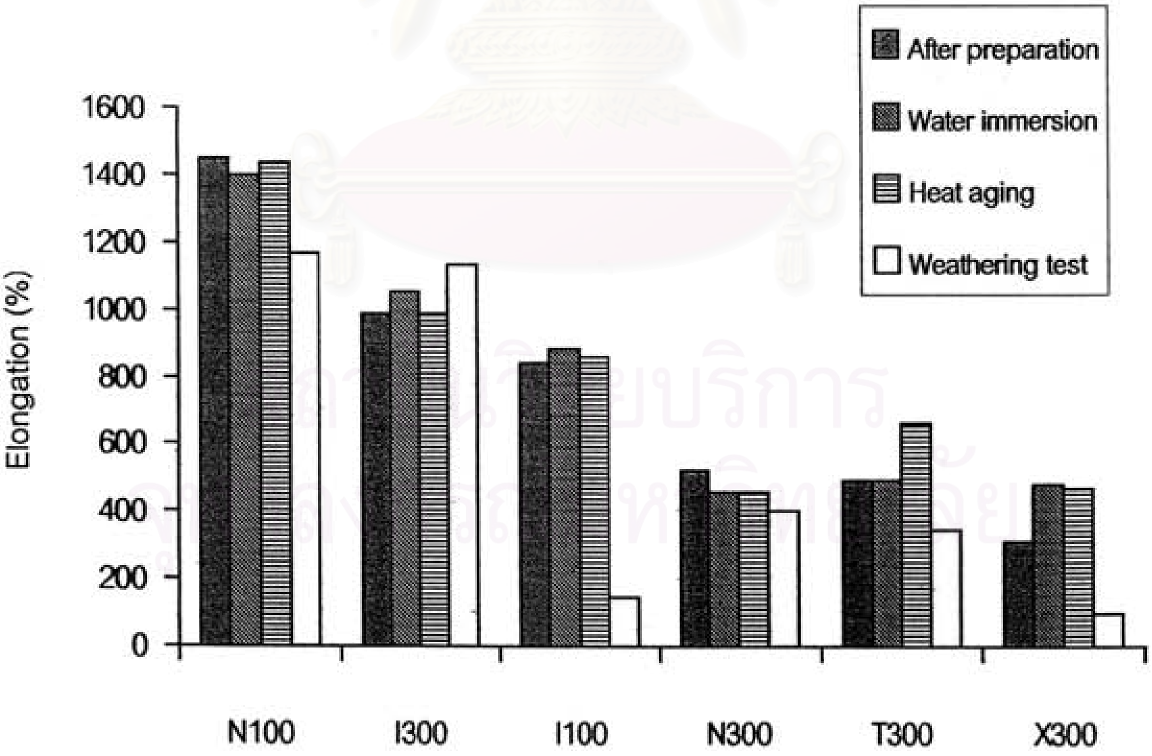

Figure 5.34 %Elongation of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

The %elongation of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering tests is compared in Fig. 5.34.

Water immersion

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that the NBDI-based polyurethane elastomer has lower %elongation than that after preparation, while the IPDI-based polyurethane elastomer has higher %elongation than that after preparation. Considering ethacure300, it is noticed that XDI- and IPDI-based polyurethane elastomer has higher %elongation than those after preparation. NBDI-based polyurethane elastomer has lower %elongation than those after preparation. The %elongation of TDI-based polyurethane elastomer after water immersion is approximately the same as that after preparation.

Heat aging

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that the %elongation of NBDI-based polyurethane elastomer is little lower than that after preparation, while the %elongation of IPDI-based polyurethane elastomer is little higher than that after preparation. Considering ethacure300, it is clear that XDI- , TDI-based polyurethane elastomer has higher %elongation than those after preparation. NBDI-based polyurethane elastomer has lower %elongation than those after preparation. The %elongation of IPDI-based polyurethane elastomer is similar to that after preparation.

Weathering test

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the %elongation of NBDI- and IPDI-based polyurethane elastomer is lower than that after preparation by 19% and 94%, respectively. The elongation at break is very sensitive to structure changes in the polymer backbone caused by UV radiation [RABEK, J. F., 1995]. This shows that NBDI-based polyurethane elastomer has higher weathering resistance to the elongation at break than IPDI-based polyurethane elastomer.

Considering ethacure300, the %elongation of IPDI-based polyurethane elastomer, which is the %elongation at the maximum elongation, is higher than that before 2 months of weathering test by about 15%. This might be explained by the surface appearance. The surface appearance of IPDI-based polyurethane elastomer after weathering test is sticker than that after preparation. NBDI-, TDI- and XDI-based polyurethane elastomers have lower %elongation than those after preparation by about 26%, 30% and 69%, respectively. For TDI and XDI, the decreasing of %elongation of both polyurethane elastomers caused by the surface cracking.

The results on the tear strength after water immersion, heat aging and weathering tests are shown in Table 5.14, comparing to the results after preparation.

Table 5.14 Tear strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

Sample	Tear strength (kgf/cm)			
	After preparation	After 1 week of water immersion	After 1 week of heat aging	After 2 months of weathering test
N100	36.0	33.5	37.5	23.2
I100	53.1	48.7	56.1	2.5
N300	3.0	5.4	3.8	6.0
I300	16.7	16.6	16.2	>13.6
X300	27.3	36.0	29.6	1.5
T300	27.6	25.6	28.5	25.9

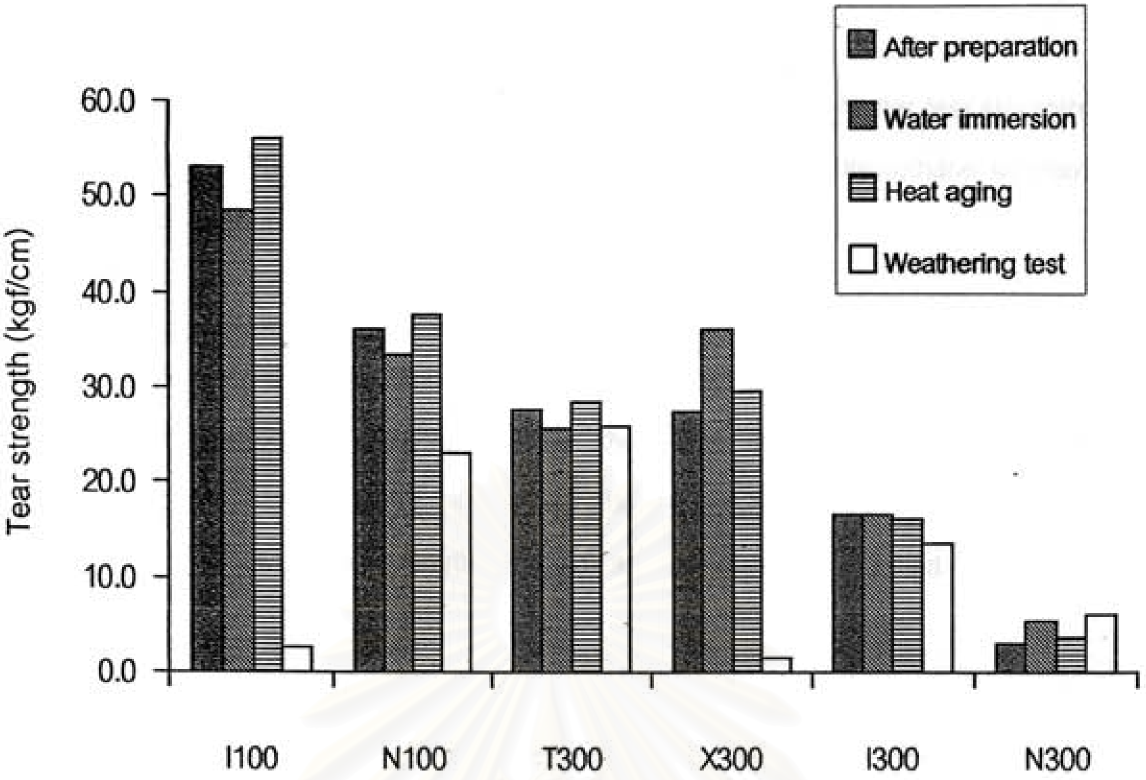

Figure 5.35 Tear strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

The tear strength of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering tests is compared in Fig. 5.35.

Water immersion

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that the tear strength of both NBDI- and IPDI-based polyurethane elastomers is lower than that after preparation. Considering ethacure300, it is clear that XDI- and NBDI-based polyurethane elastomers have higher tear strength than those after preparation. TDI- and IPDI-based polyurethane elastomers have lower tear strength than those after preparation.

Heat aging

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that NBDI- and IPDI-based polyurethane elastomer has higher tear strength than that after preparation. Considering ethacure300, it is clear that

NBDI-, XDI- and TDI-based polyurethane elastomers have slightly higher tear strength than those after preparation, while the tear strength of IPDI-based polyurethane elastomer is about the same as that after preparation.

Weathering test

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the NBDI- and IPDI-based polyurethane elastomers have lower tear strength than that after preparation by about 36% and 95%, respectively

Considering ethacure300, the tear strength of TDI-, IPDI- and XDI- based polyurethane elastomer is lower than that before weathering test by about 6%, 19%, and 94%, respectively. NBDI-based polyurethane elastomer has higher tear strength than that after preparation about 97%. This might be explained that the stiffness of NBDI-based polyurethane elastomer after weathering test is increased.

The results on the modulus at 100% elongation (M100) after water immersion, heat aging and weathering test are shown in Table 5.15, comparing to the results after preparation.

Table 5.15 M100 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

Sample	M100 (kgf/cm^2)			
	After preparation	After 1 week of water immersion	After 1 week of heat aging	After 2 months of weathering test
N100	10.3	9.5	9.3	5.7
I100	18.5	18.4	19.0	1.8
N300	1.6	2.0	2.0	1.7
I300	2.2	3.9	3.9	1.2
X300	22.8	21.6	20.6	8.6
T300	21.1	20.5	21.8	16.7

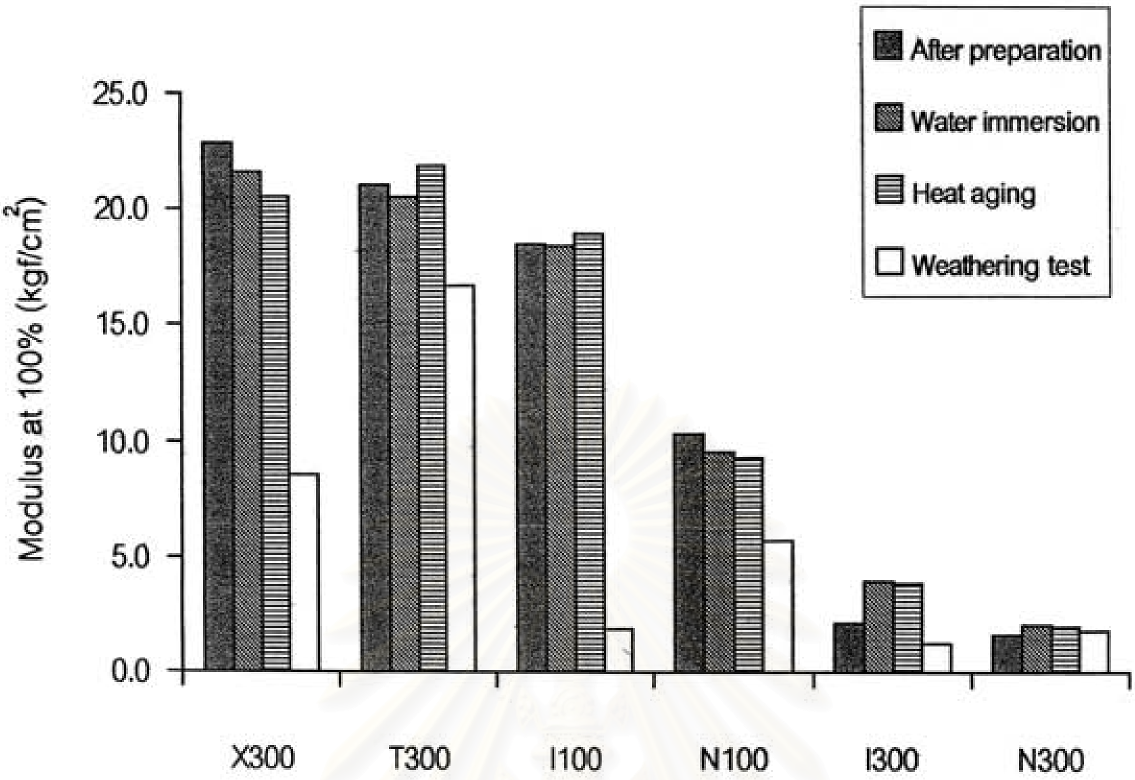

Figure 5.36 M100 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

The M100 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering tests is compared in Fig. 5.36.

Water immersion

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clear that the M100 of NBDI-based polyurethane elastomers is lower than that after preparation, while the M100 of IPDI-based polyurethane elastomer is similar to that after preparation. Considering ethacure300, it is clear that the M100 of XDI- and TDI-based polyurethane elastomer is lower than those after preparation, while IPDI- and NBDI-based polyurethane elastomers have higher M100 than those after preparation.

Heat aging

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it is clearly noticed that the M100 of IPDI-based polyurethane elastomers is slightly higher than that after preparation, while the M100 of NBDI-based polyurethane elastomer is lower than that after preparation. Considering ethacure300, it is clear that XDI-based polyurethane elastomer has lower M100 than that after preparation. The M100 of TDI-, IPDI- and NBDI-based polyurethane elastomers is higher than that after preparation.

Weathering test

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the M100 of both NBDI- and IPDI-based polyurethane elastomers is lower than that after preparation by about 44% and 90%, respectively. For ethacure300, it is clear that the M100 of NBDI-based polyurethane elastomer is similar to that after preparation. The M100 of XDI-, IPDI- and TDI-based polyurethane elastomers is lower than those after preparation by 63%, 44% and 21%, respectively.

The results on the modulus at 300% elongation (M300) after water immersion, heat aging and weathering tests are shown in Table 5.16, comparing to the results after preparation.

Table 5.16 M300 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

Sample	M300 (kgf/cm^2)			
	After preparation	After 1 week of water immersion	After 1 week of heat aging	After 2 months of weathering test
N100	6.1	5.9	5.9	3.6
I100	11.1	10.5	10.7	"None"
N300	1.3	1.6	1.6	1.3
I300	2.1	2.5	2.6	1.1
X300	11.6	10.9	11.2	"None"
T300	10.6	10.9	11.5	9.1

"None" means that M300 values could not be measured.

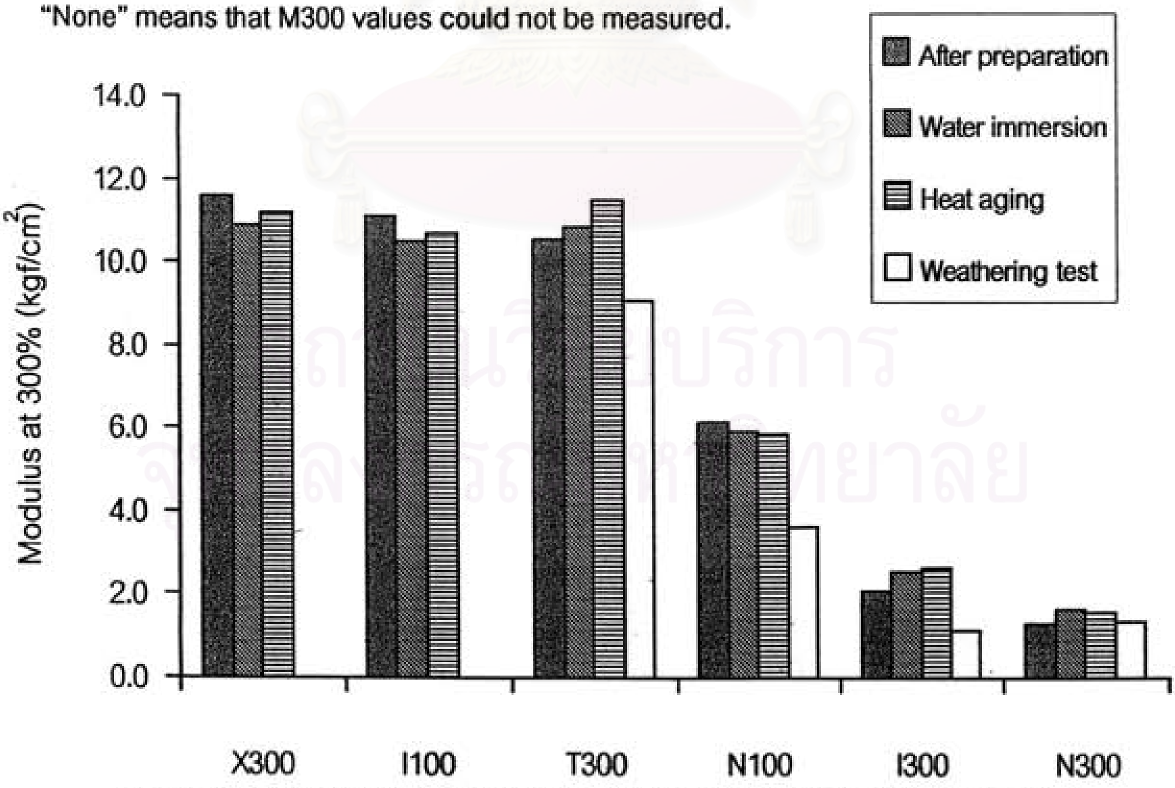

Figure 5.37 M300 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering test.

The M300 of two-component polyurethane elastomers after preparation, water immersion, heat aging and weathering tests is compared in Fig. 5.37.

Water immersion

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, both NBDI- and IPDI-based polyurethane elastomers have lower M300 than those after preparation. For ethacure300, the results are in the same trend as the results of M100 except the M300 of TDI-based polyurethane elastomer, which is higher than that after preparation.

Heat aging

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, the M300 of both NBDI- and IPDI-based polyurethane elastomers is lower than that after preparation. For ethacure300, the results are similar to the results of M100.

Weathering test

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, NBDI-based polyurethane elastomer has lower M300 than that after preparation by 41%, while IPDI-based polyurethane elastomer is broken before %elongation reaches 300%. For ethacure300, the M300 of NBDI-based polyurethane elastomer is approximately the same as that after preparation. The M300 of IPDI- and TDI-based polyurethane elastomers is lower than that after preparation about 45% and 14%, respectively, while the M300 of XDI-based polyurethane elastomer cannot be measured because the specimen is broken before 300% elongation.

From these results, the effects of water immersion, heat aging and weathering test on the mechanical properties of two-component polyurethane elastomers were studied. The effect of water immersion is less pronounced on the mechanical properties of two-component polyurethane elastomers and it does not show a clear trend. One week of water immersion might not be long enough to affect the mechanical properties of the polyurethane elastomers. The heat aging has less pronounced effects on the mechanical properties of two-component polyurethane elastomers. The mechanical properties after heat aging trend to increase slightly. The weathering test has strong effects on the mechanical properties of two-component polyurethane elastomers. All mechanical properties after 2 months of weathering test trend to decrease from those after preparation. The results of mechanical properties after weathering test might show that the degree of weathering resistance of these polyurethane elastomer samples is in the order of : NBDI-based and TDI-based > IPDI-based > XDI-based polyurethane elastomers and ethacure300-based > ethacure100-based polyurethane elastomers.

These results show that weathering test has more effects on mechanical properties of two-component polyurethane elastomers than the other two effects.

5.2.6 Infrared absorption of two-component polyurethane elastomers

In this work, two-component polyurethane elastomers were synthesized by the reaction of polyether polyol (Diol-2000), diisocyanate (NBDI, IPDI, m-XDI or TDI) and curing agent (ethacure300 or ethacure100). The basic structures and the reaction of the two-component polyurethane elastomers were studied by FT-IR spectroscopic technique. IR spectra for each polyurethane elastomer sample (N100, I100, N300, I300, X300, and T300) are shown in Fig. 5.38, Fig. 5.39, Fig. 5.40, Fig. 5.41, Fig. 5.42 and Fig. 5.43, respectively.

Considering the IR spectrum of the NBDI-ethacure100-based polyurethane elastomer, shown in Fig. 5.38, several important bands are labeled and the details of each absorption peak can be analyzed as follows.

The N-H absorption is usually located between 3500 and 3200 cm^{-1}. This consists of amine and amide group such as primary, secondary and tertiary N-H stretching. The strong peak observed at 3338 cm^{-1} could be assigned to hydrogen-bonded N-H group while the free N-H stretching appears as a small shoulder at 3586 cm^{-1}.

The carbonyl absorption (C=O) is usually located between 1730 and 1700 cm^{-1}. These consist of free urethane, hydrogen-bonded urethane, free urea and hydrogen-bonded urea carbonyl groups. The peak observed at 1720 cm^{-1} could be assigned to the free urethane carbonyl group and hydrogen-bonded urethane carbonyl group, which looks to be a single peak. The peak observed at 1632 cm^{-1} could be attributed to hydrogen-bonded urea carbonyl group while the free urea carbonyl peak near 1695 cm^{-1} is not observed.

The N-H bending absorption (amide II, mainly δN-H, mixed with νC-N) is usually located between 1560 and 1500 cm^{-1}. The peak observed at 1538 cm^{-1}, which overlap with C=C aromatic ring stretching peak could be assigned to amide II. In addition, another peak observed at 1247 cm^{-1} could be assigned to amide III.

The C=C aromatic ring stretching absorption is usually located at 1600 and 1475 cm^{-1}. The peak observed at 1562 cm^{-1} could be assigned to C=C aromatic ring stretching but the peak at 1475 cm^{-1} is not observed.

The C-O absorption is located between 1150 and 1070 cm^{-1}. The broad peak observed at 1109 cm^{-1} could be assigned to an asymmetry C-O group.

Several C-H stretching bands are located between 3000 and 2800 cm^{-1}. The four peaks observed at 2972, 2932, 2898 and 2871 cm^{-1} could be assigned to the asymmetric C-H stretching of CH_3, asymmetric C-H stretching of CH_2, symmetric C-H stretching of CH_3 and symmetric C-H stretching of CH_2, respectively.

The asymmetric C-H bending of CH_3 and CH_2 could be observed at 1456 cm^{-1}. And the symmetric C-H bending for CH_3 could be indicated at 1375 cm^{-1}.

C-N stretching absorption is usually located between 1230 to 1030 cm^{-1}. The peak observed at 1018 cm^{-1} could be assigned to C-N stretching.

Considering the IR spectrum of the others, the spectrum is very much the same as that of NBDI-ethacure100-based polyurethane elastomer (Fig. 5.38). However, TDI-ethacure300-based polyurethane elastomer (Fig. 5.43) has a few differences, which can be observed at the peak at 1601 cm^{-1} and 1475 cm^{-1} (marked * and ** in Fig. 5.43, respectively). These peaks could be assigned to C=C aromatic ring stretching. The peak observed at 1601 cm^{-1} split from amide II while this peak of the others overlap with amide II. The peak at 1475 cm^{-1} of the others is not observed.

Comparing different types of diisocyanates (NBDI- and IPDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), it is clear that the two different points can be observed at hydrogen-bonded urethane and hydrogen-bonded urea carbonyl peak.

Considering %Transmittance of hydrogen-bonded urea carbonyl peak of NBDI- and IPDI-based polyurethane elastomer, it is clear that NBDI-based polyurethane elastomer has lower %Transmittance of hydrogen-bonded urea carbonyl peak than IPDI-based polyurethane elastomer. This might be due to NBDI-based polyurethane elastomer has more amount of hydrogen-bonded urea groups than IPDI-based polyurethane elastomer.

For %Transmittance of hydrogen-bonded urethane carbonyl peak of NBDI- and IPDI-based polyurethane elastomer, it is clearly noticed that NBDI-based polyurethane elastomer has higher %Transmittance of hydrogen-bonded urethane peak than that of IPDI-based polyurethane elastomer. This might be due to NBDI-based polyurethane elastomer has fewer amount of hydrogen-bonded urethane groups than IPDI-based polyurethane elastomer.

In general, the strength of hydrogen-bonded urea group is higher than that of hydrogen-bonded urethane group. This might imply that NBDI-based polyurethane elastomer should has higher strength than IPDI-based polyurethane elastomer but the results on mechanical properties of NBDI- and IPDI-based polyurethane elastomers are in opposite direction. Therefore, in this case, the amount of hydrogen-bonded urethane and hydrogen-bonded urea groups is not responded for the mechanical properties of NBDI- and IPDI-based polyurethane elastomers. The difference on the strength of NBDI- and IPDI-based polyurethane elastomer should be responded by the configuration of NCO groups as discussed in the mechanical properties part.

Considering the IR spectra of NBDI- and IPDI-based polyurethane elastomers prepared from two different types of curing agent (ethacure100 and ethacure300), it is clear that the spectra of NBDI- and IPDI-ethacure100-based polyurethane elastomers are similar to those of NBDI- and IPDI-ethacure300-based polyurethane elastomers. A few differences can be observed at hydrogen-bonded urethane and hydrogen-bonded urea carbonyl peak.

Considering %Transmittance of hydrogen-bonded urea carbonyl peak of ethacure100- and ethacure300-based polyurethane elastomer, it is clear that ethacure100-based polyurethane elastomer has lower %Transmittance of hydrogen-bonded urea carbonyl peak than ethacure300-based polyurethane elastomer. This might be due to ethacure100-based polyurethane elastomer has more amount of hydrogen-bonded urea groups than ethacure300-based polyurethane elastomer.

For %Transmittance of hydrogen-bonded urethane carbonyl peak of ethacure100- and ethacure300-based polyurethane elastomer, it is clearly noticed that ethacure100-based polyurethane elastomer has higher %Transmittance of hydrogen-bonded urethane peak than that of ethacure300-based polyurethane elastomer. This might be due to ethacure100-based polyurethane elastomer has fewer amount of hydrogen-bonded urethane groups than ethacure300-based polyurethane elastomer.

In general, the strength of hydrogen-bonded urea group is higher than that of hydrogen-bonded urethane group. Thus ethacure100-based polyurethane elastomer has higher strength than ethacure300-based polyurethane elastomer. This could be a reasonable support why the strength of ethacure100-based polyurethane elastomer is higher than that of ethacure300-based polyurethane elastomer.

However, another factor mainly affects the difference in %Transmittance is the sample thickness which might not be exactly the same for every sample.

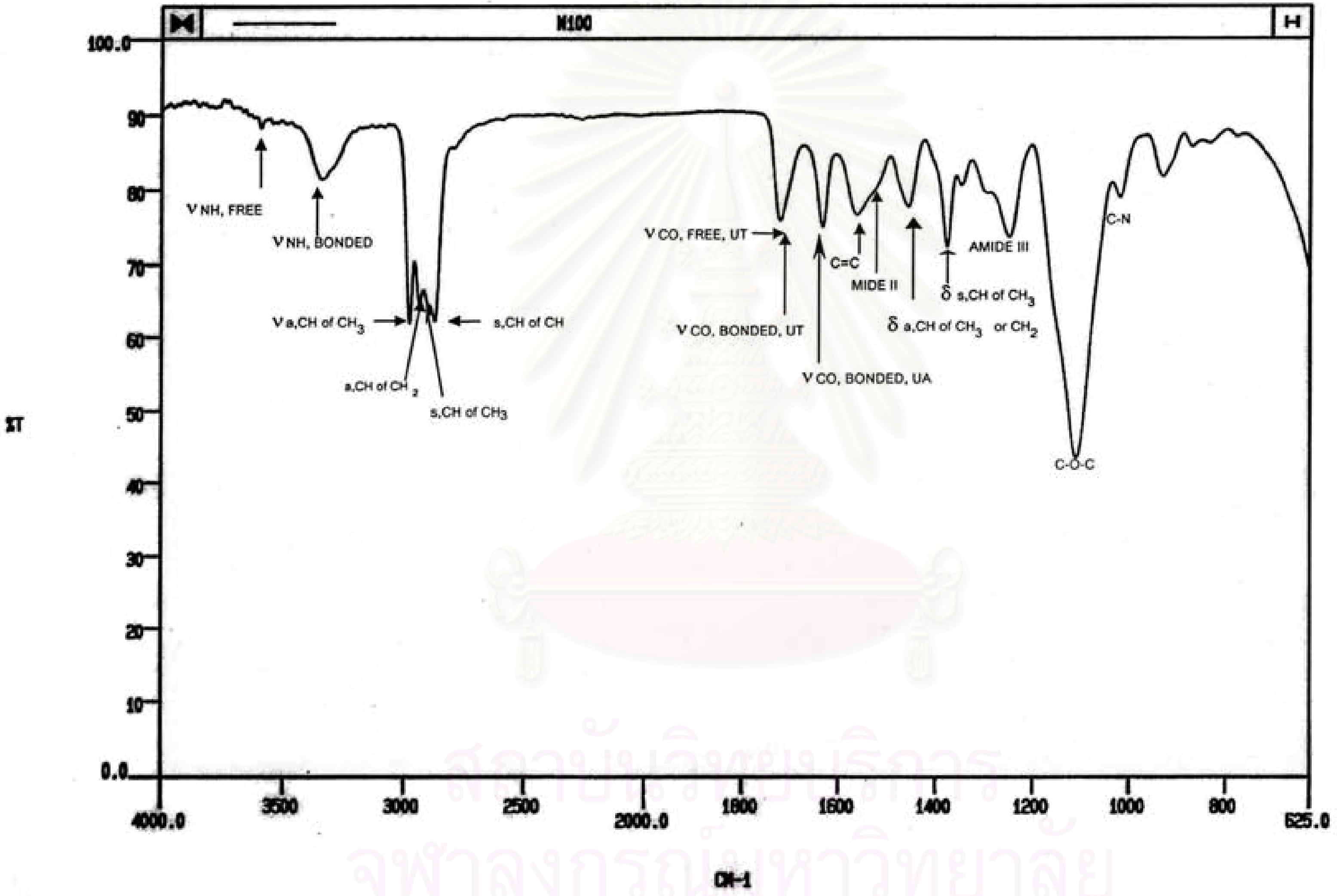

Figure 5.38 Infrared absorption of NBDI-ethacure100-based polyurethane elastomer.

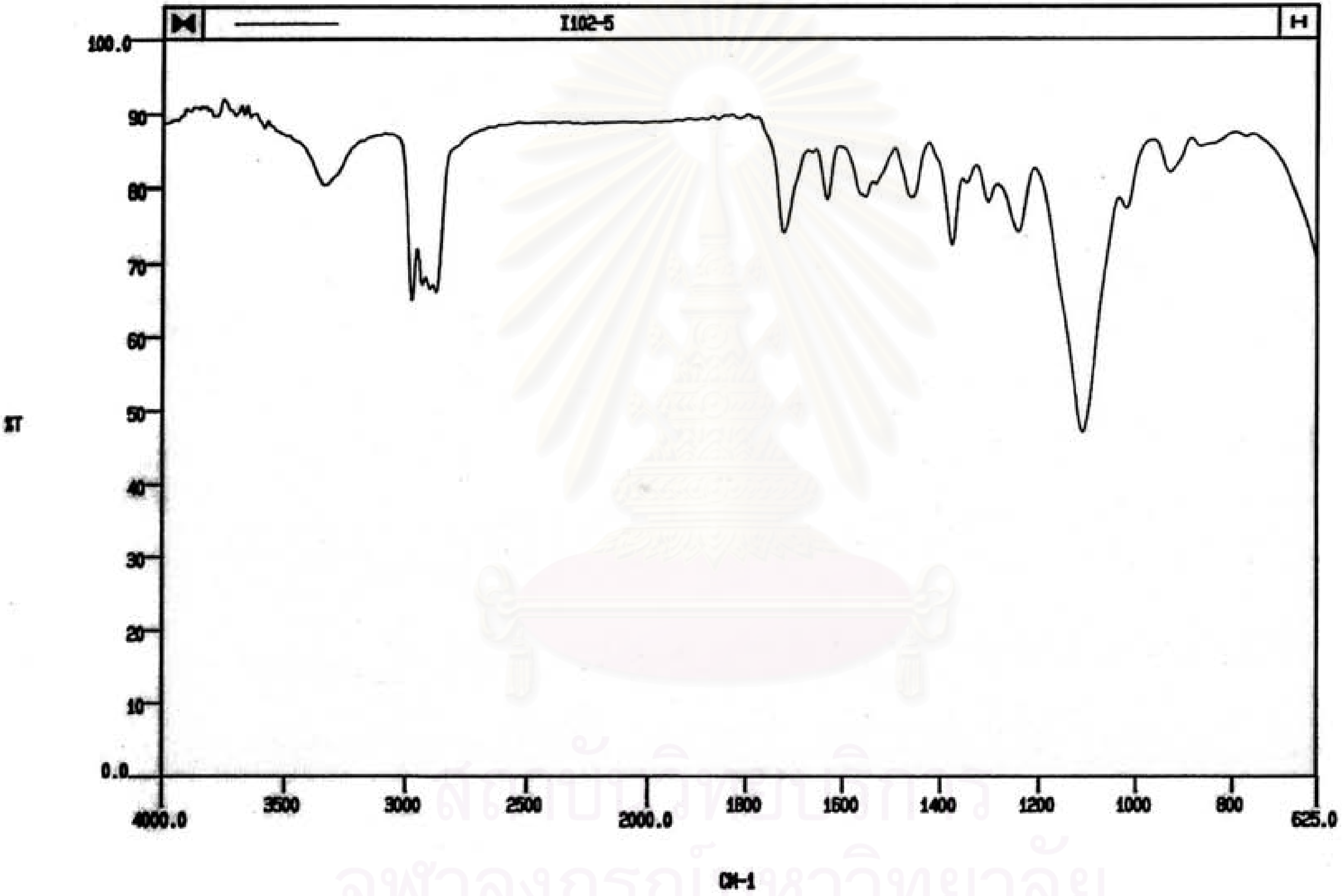

Figure 5.39 Infrared absorption of IPDI-ethacure100-based polyurethane elastomer.

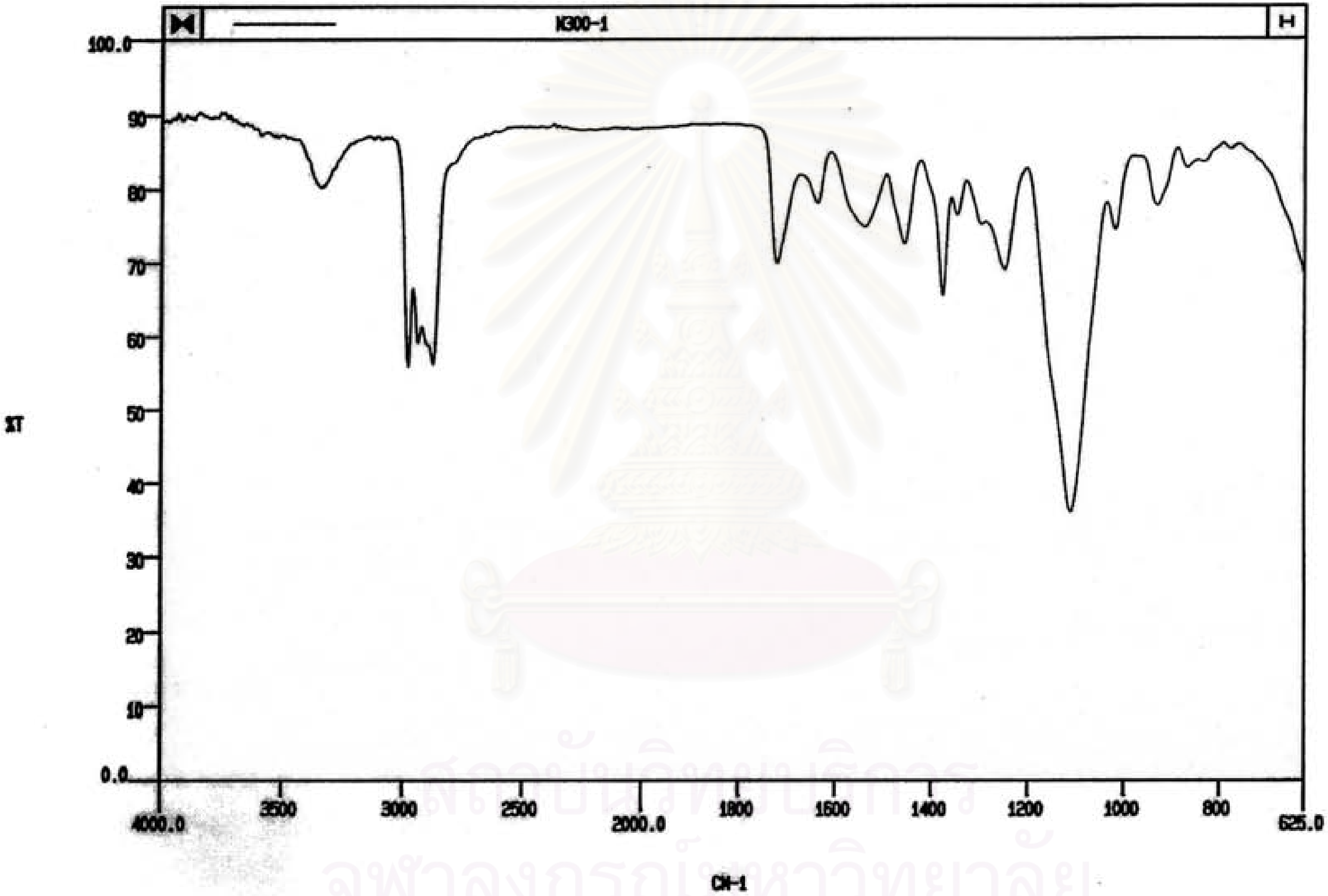

Figure 5.40 Infrared absorption of NBDI-ethacure300-based polyurethane elastomer.

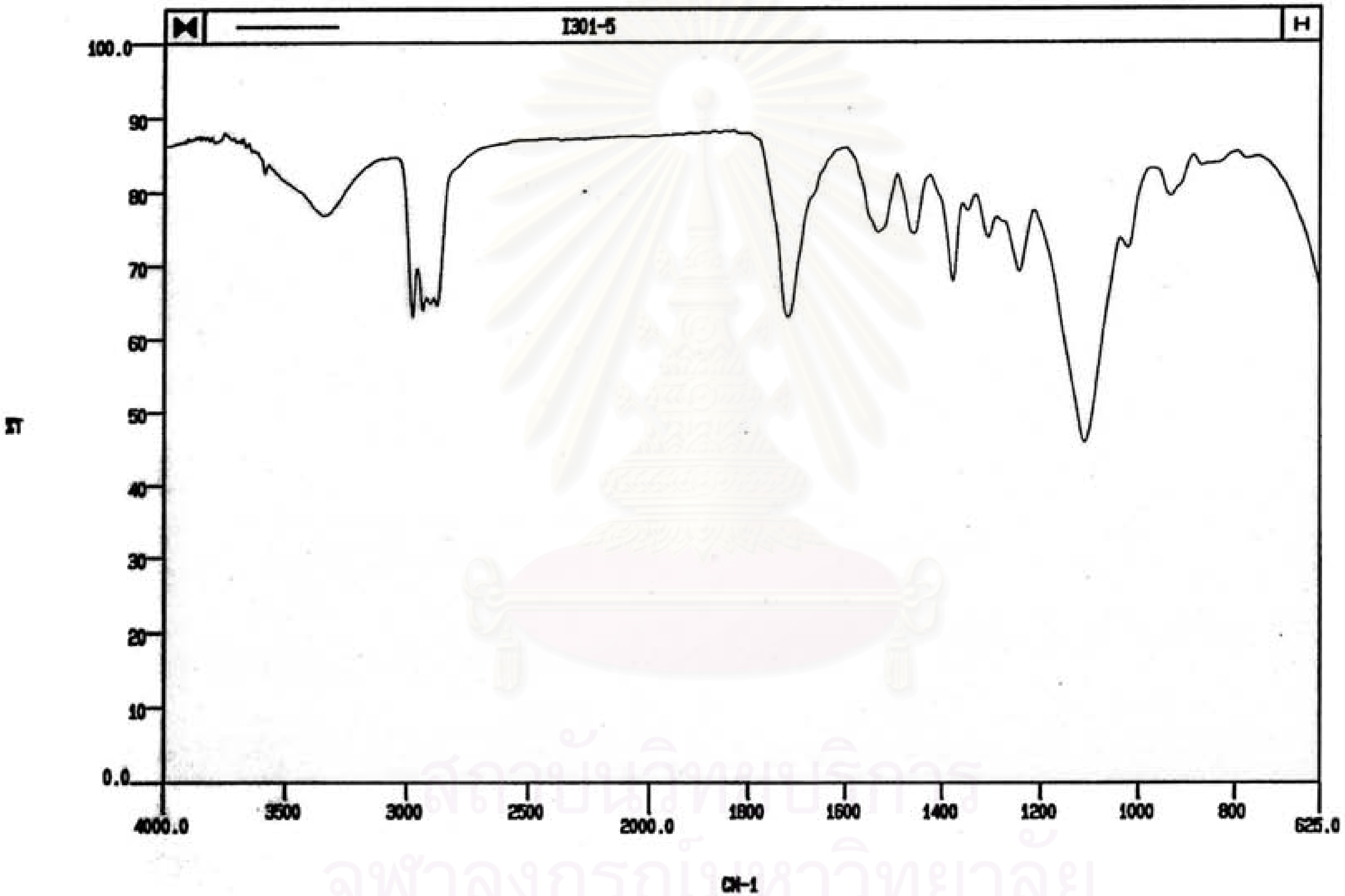

Figure 5.41 Infrared absorption of IPDI-ethacure300-based polyurethane elastomer.

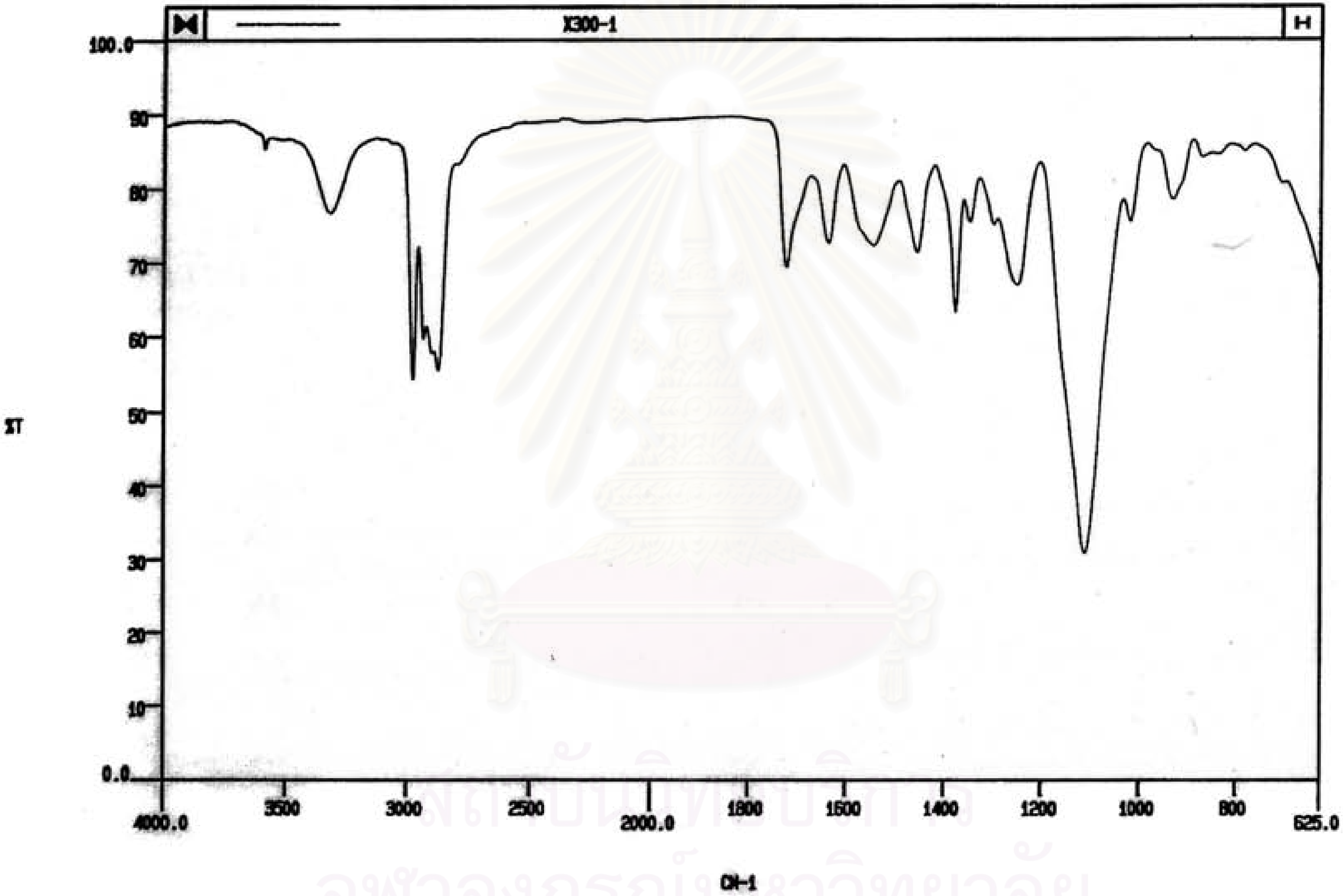

Figure 5.42 Infrared absorption of XDI-ethacure300-based polyurethane elastomer.

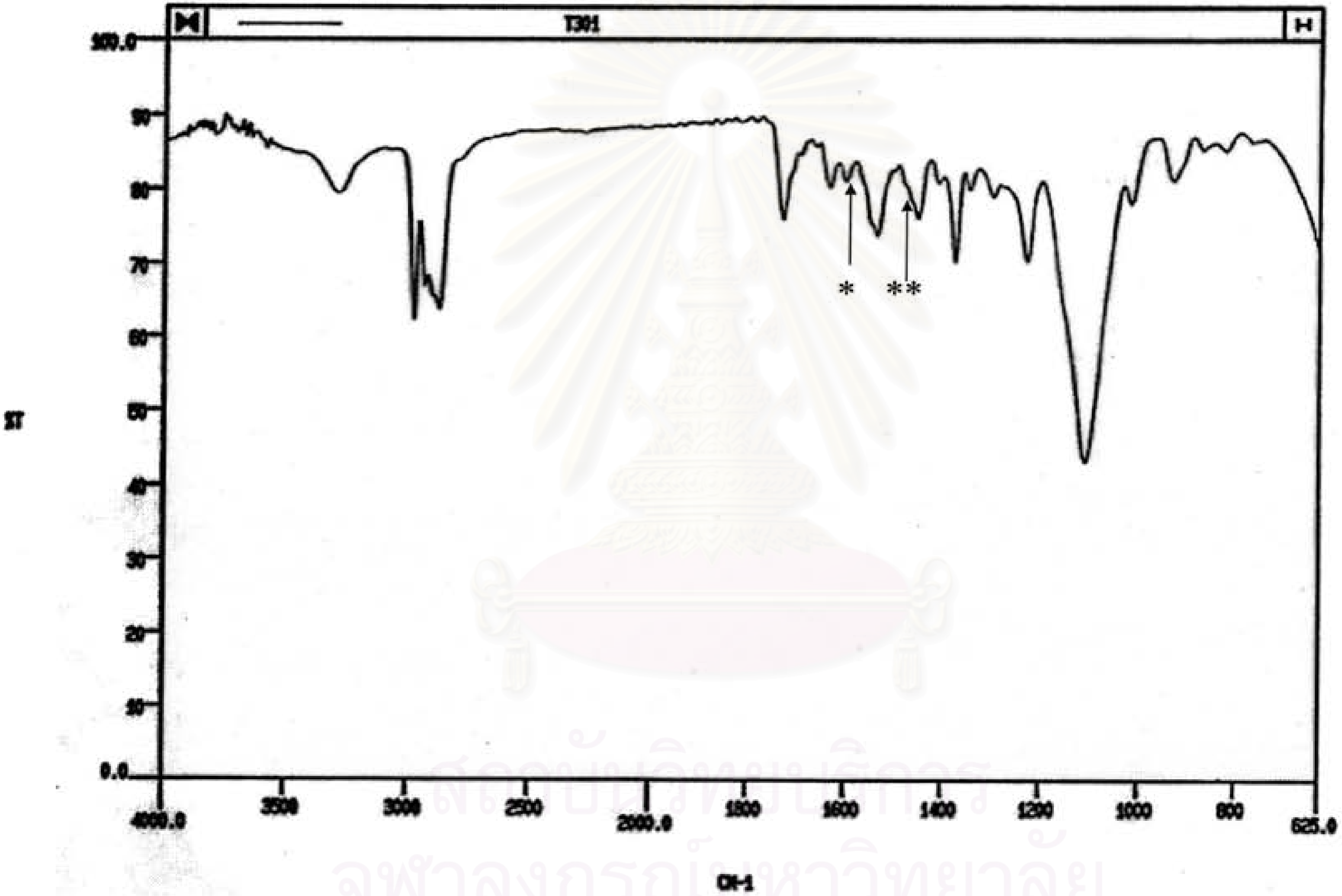

Figure 5.43 Infrared absorption of TDI-ethacure300-based polyurethane elastomer.

Reactivity of two-component polyurethane elastomers

FT-IR spectroscopic technique could be used to study the reaction between isocyanate group (NCO) and active hydrogen group (NH or OH). The reaction between NCO group of prepolymers and NH group of curing agents can be observed from the changes of %Transmittance of NCO absorption peak (at around 2270 cm^{-1}) in the IR spectrum of two-component polyurethane elastomers at various reaction time.

Considering relationship between %Transmittance of NCO absorption peak and reaction time (heating time in the oven) of two-component polyurethane elastomers, shown in Table 5.17, it is clear that increasing in reaction time increases the %Transmittance of NCO absorption peak. This results from decreasing in the amount of NCO groups as the reaction proceeds. When the reaction between NCO groups and NH groups completes, the %Transmittance of NCO absorption peak would disappear.

On the other hand, the absorbance of NCO absorption peak of two-component polyurethane elastomers is plotted against reaction time in Fig. 5.44.

Table 5.17 %Transmittance of NCO absorption peak of two-component polyurethane elastomers and reaction time.

Reaction time	%Transmittance of NCO absorption peak					
(days)	N100	I100	N300	I300	X300	T300
1	"None"	85.9	"None"	78.6	"None"	"None"
2		"N/A"		"N/A"		
3		88.2		"N/A"		
4		88.2		86.7		
5		"None"		"None"		

"None" means that no NCO absorption peak was observed.

"N/A" means that no measurement was performed.

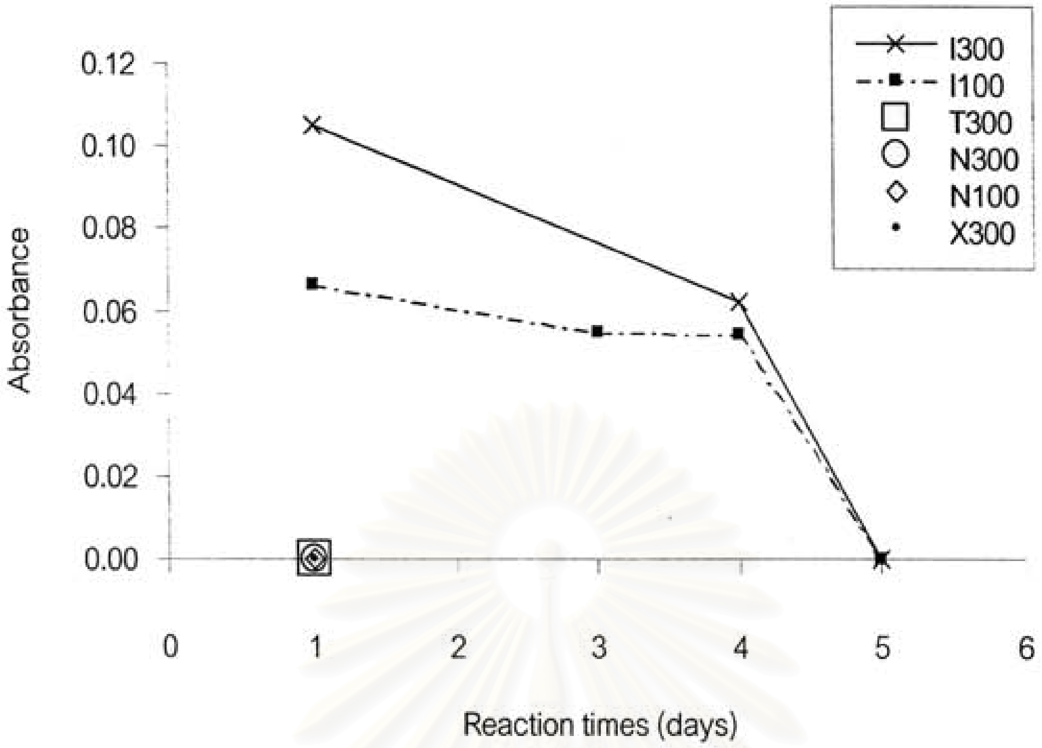

Figure 5.44 Absorbance of NCO absorption peak of two-component polyurethane elastomers vs. reaction time.

The reactions of prepolymers and curing agents to from NBDI-ethacure300-, XDI-ethacure300-, TDI-ethacure300- and NBDI-ethacure100-based polyurethane elastomers are very fast as they complete within one day. The IPDI-ethacure100- and IPDI-ethacure300-based polyurethane elastomers are slowly formed and the reaction completes after approximately 5 days.

Considering two different types of curing agent (ethacure100 and ethacure300), the effect of different types of curing agent on the NCO absorption peak cannot be clearly observed.

Comparing different types of diisocyanates (NBDI, IPDI, m-XDI and TDI-based polyurethane elastomers) synthesized with the same curing agent (ethacure100 or ethacure300), for ethacure100, it can be seen that the %Transmittance of NCO absorption peak of NBDI- and IPDI-based polyurethane elastomers disappears within the reaction time of one day and five days, respectively. This shows the reactivity of NBDI is higher than that of IPDI. For ethacure300, it is clearly noticed that the %Transmittance of NCO absorption peak of XDI-, NBDI- and TDI-based polyurethane elastomers disappears within the reaction time of one day, while %Transmittance of NCO absorption peak of IPDI-based polyurethane elastomers disappears within the reaction time of five days. This shows that XDI, NBDI and TDI have much higher reactivity than IPDI. The order of reactivity of diisocyanate is as follows: XDI, NBDI, and TDI >> IPDI. From this results, the difference in reactivity of NBDI, XDI and TDI is not clear. However another way to study the reactivity is the comparison of the gel time of the two-component polyurethane elastomers which can give more details as discussed in section 5.2.1.

5.2.7 Differential scanning calorimetry of two-component polyurethane elastomers

Differential scanning calorimeter (DSC) was used to determine glass transition temperature of polyurethane elastomers. The DSC charts of NBDI- and IPDI-ethacure100-based polyurethane elastomers are shown in Fig. 5.45 and Fig. 5.46, respectively. Polyurethane usually has two glass transition temperatures, which are soft- and hard-segment glass transition temperatures. Soft-segment glass transition temperature locates at low temperature and the other one locates at high temperature.

The DSC chart of NBDI-ethacure100-based polyurethane elastomer shows only soft-segment glass transition temperature at approximately -55°C, which is the same as that of IPDI-ethacure100-based polyurethane elastomer. Unfortunately, no glass transition temperatures at high temperature are observed by this technique. The difference between NBDI- and IPDI-based polyurethane elastomer cannot be seen.

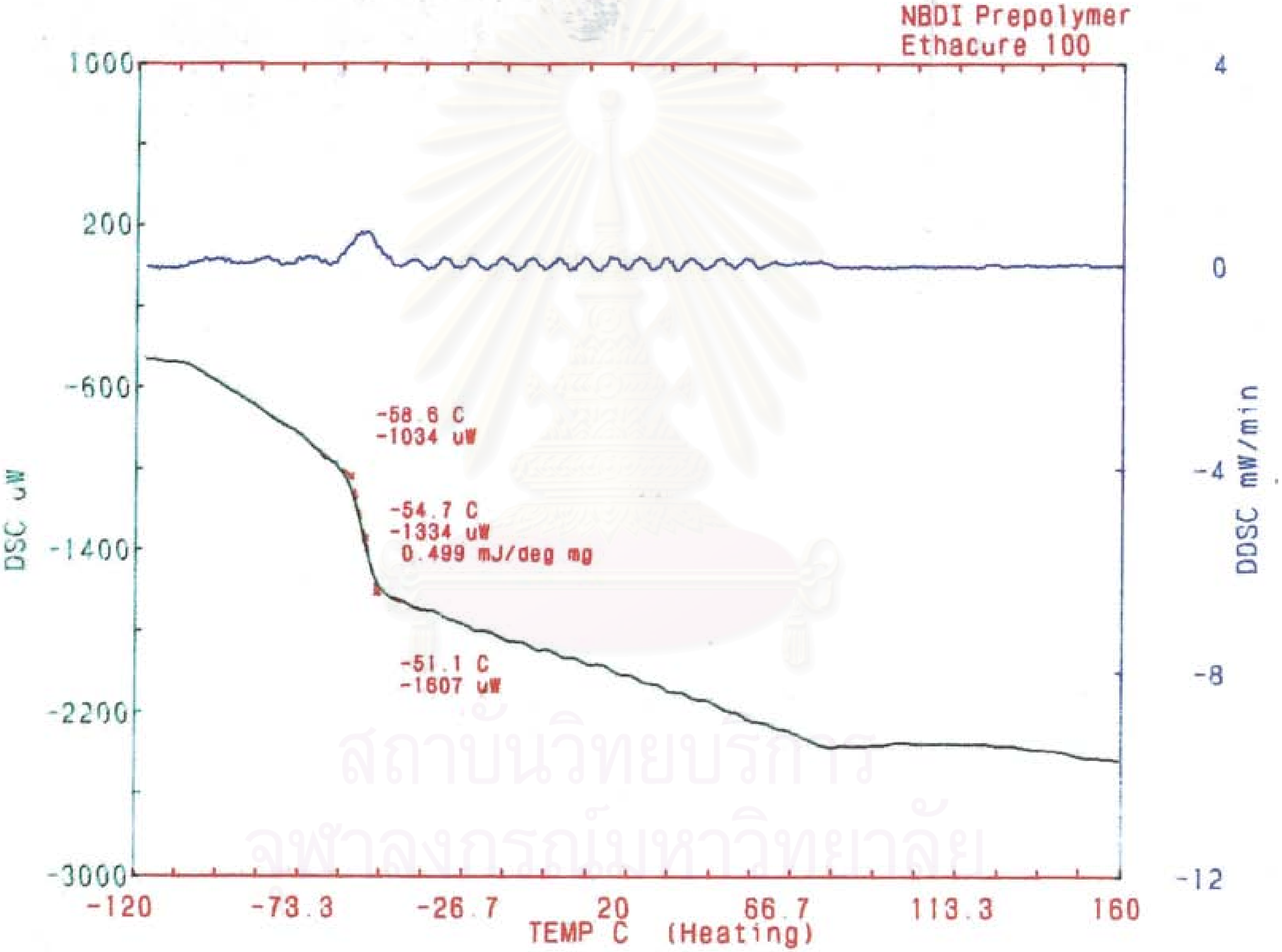

Figure 5.45 The DSC chart of NBDI-ethacure100-based polyurethane elastomer.

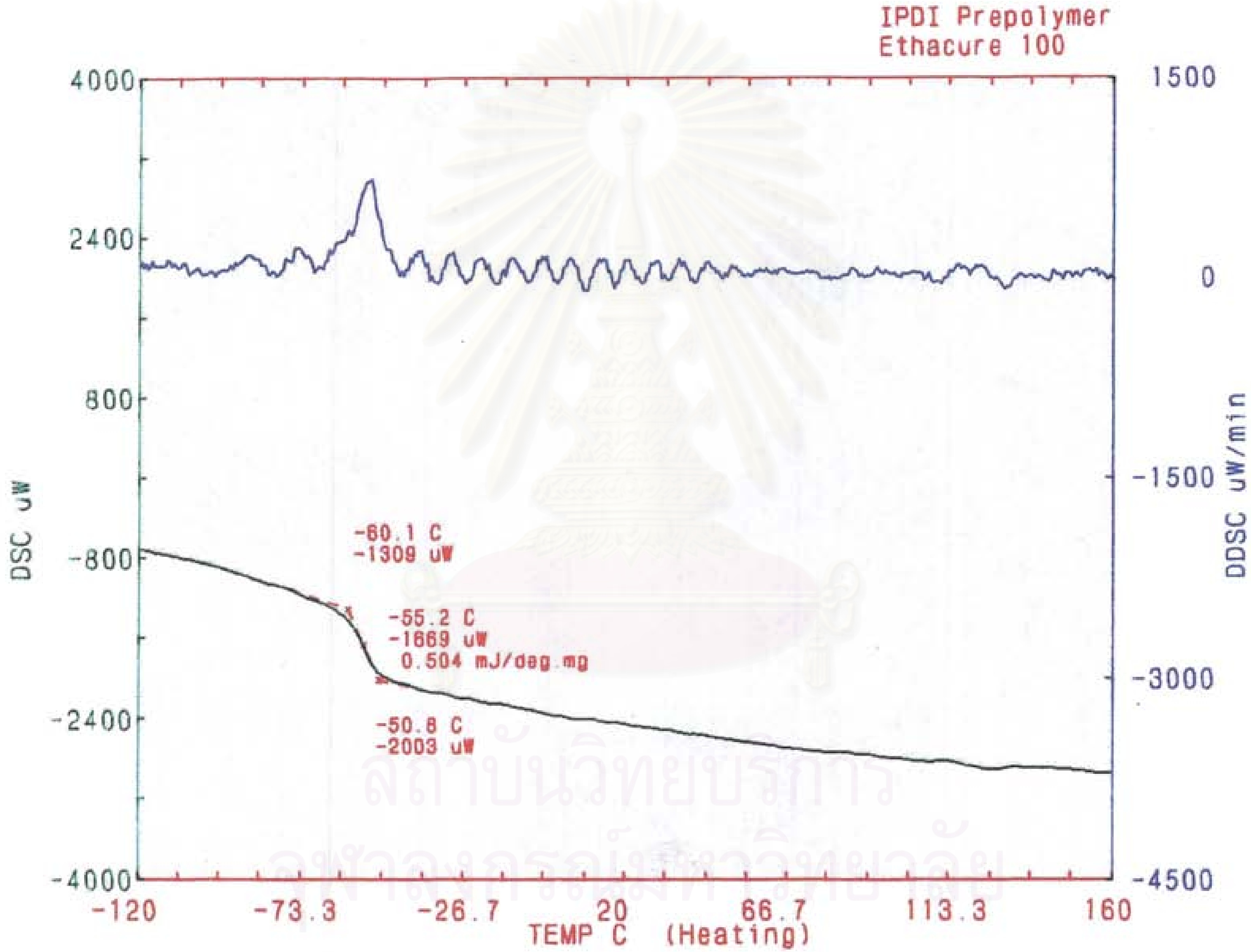

Figure 5.46 The DSC chart of IPDI-ethacure100-based polyurethane elastomer.

5.2.8 Dynamic mechanical properties of two-component polyurethane elastomers

The dynamic mechanical spectrum (DMS) charts of NBDI- and IPDI-ethacure100-based polyurethane elastomers are shown in Fig. 5.47 and Fig. 5.48, respectively.

Considering the tan δ of IPDI-ethacure100-based polyurethane elastomer in Fig. 5.48, two relaxation peaks are obviously observed. The first relaxation process, β_S relaxation, occurs at approximately -45°C that corresponds to the soft-segment glass transition temperature. This exhibits the motion of soft-segment. The second relaxation process, β_H relaxation, occurring at approximately 125°C (marked * in Fig. 5.48), shows the hard-segment glass transition temperature. The tan δ curves for the IPDI-based polyurethane elastomers could indicate that the IPDI-based polyurethane elastomers are an incompatible system. On the other word, The tan δ curve shows that IPDI-based polyurethane elastomer has good phase separation. This result is similar to the result of moisture cured polyurethane elastomer.

For NBDI-ethacure100-based polyurethane elastomer (Fig. 5.47), only one β relaxation peak at approximately -45°C is observed. The peak corresponds to the soft-segment glass transition temperature. The β relaxation corresponds closely to the β_S relaxation in the incompatible system of IPDI-ethacure100-based polyurethane elastomer. The tan δ curves shows that NBDI-ethacure100-based polyurethane elastomer has a poor phase separation.

Comparing different types of diisocyanates (NBDI and IPDI-based polyurethane elastomers) synthesized with ethacure100, it is clear that IPDI-ethacure100-based polyurethane elastomer have two relaxation processes compared with NBDI-ethacure100-based polyurethane elastomer. This might imply that IPDI-ethacure100-based polyurethane elastomer has better phase separation than NBDI-ethacure100-based polyurethane elastomer.

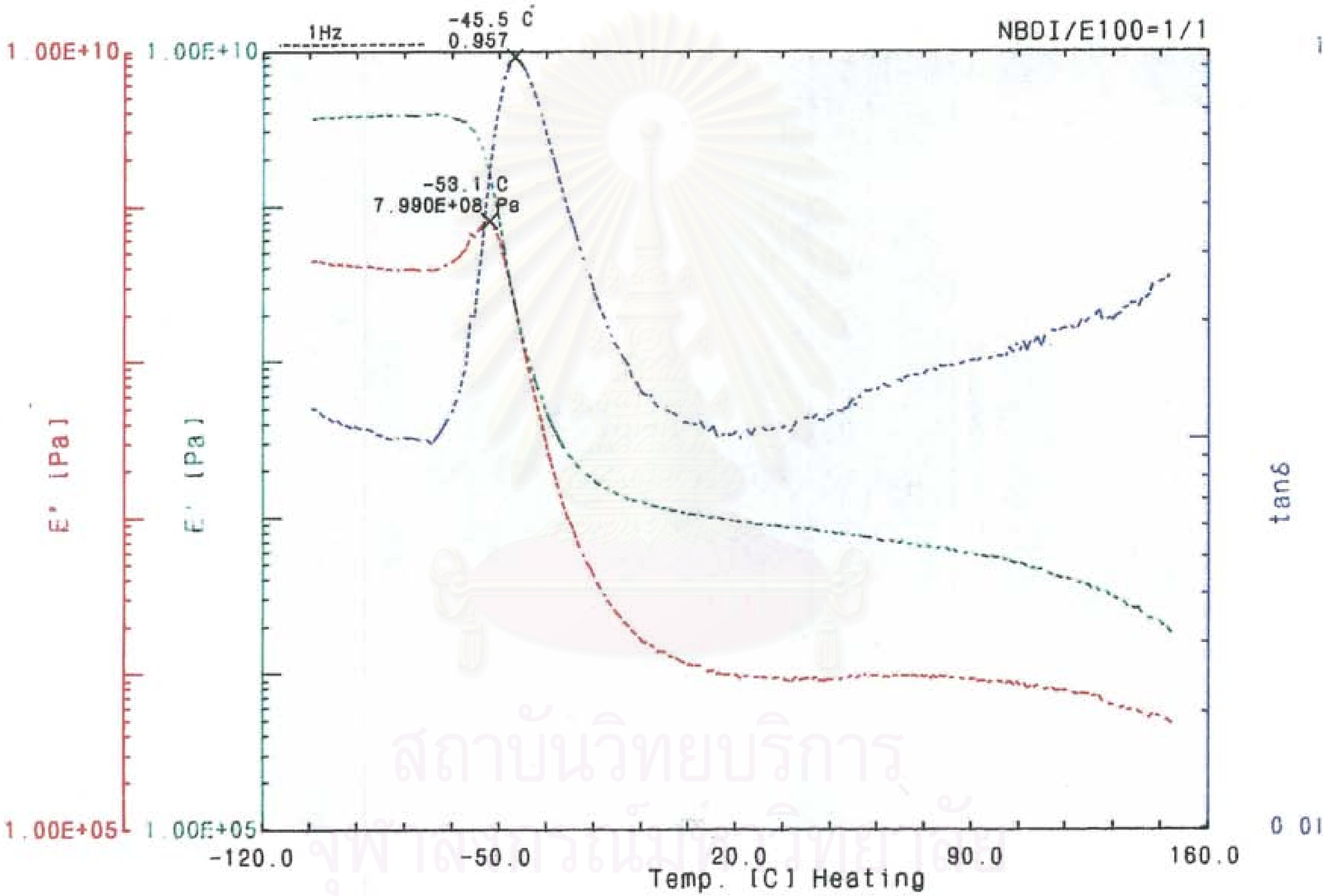

Figure 5.47 The dynamic mechanical spectrum chart of NBDI-ethacure100-based polyurethane elastomer.

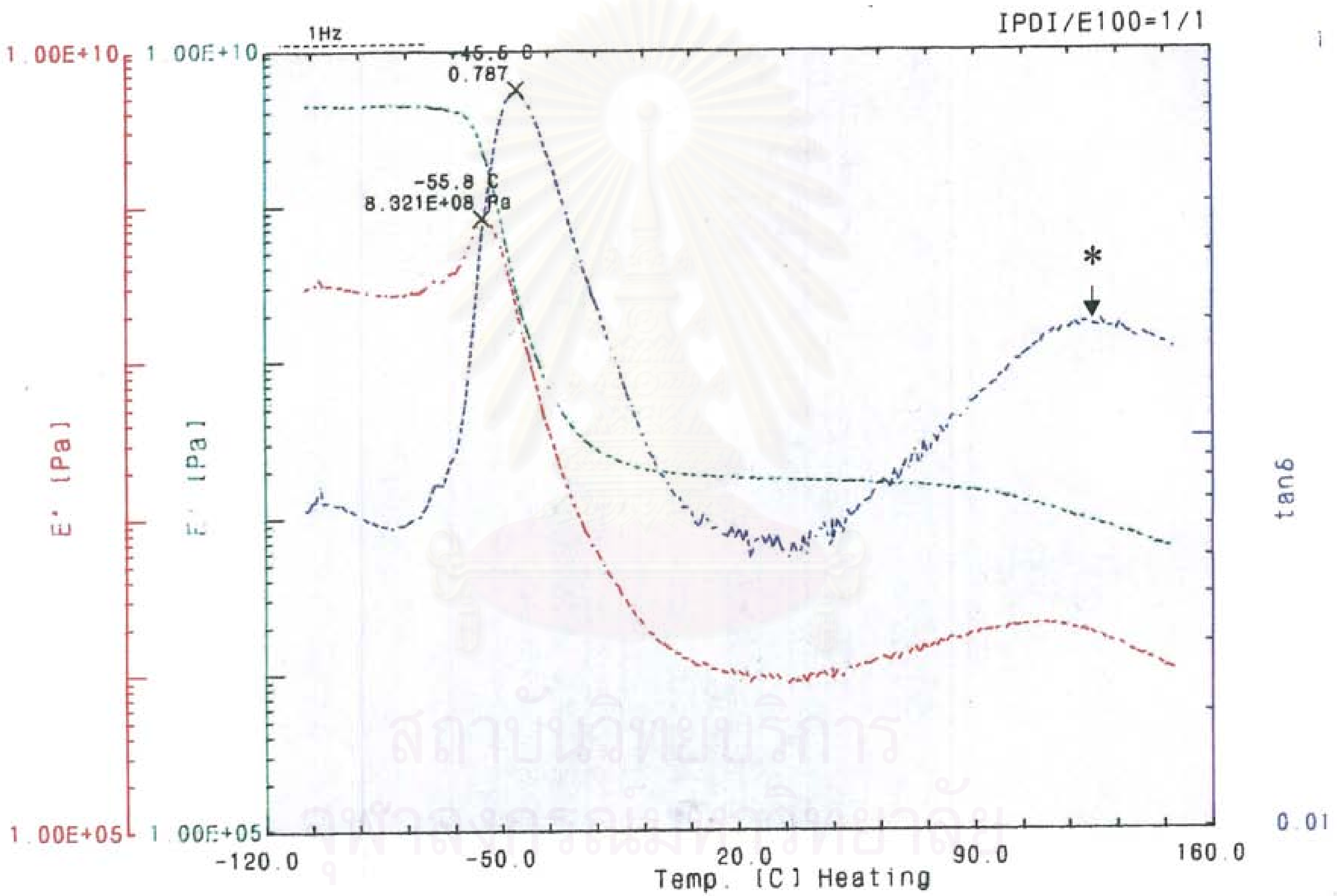

Figure 5.48 The dynamic mechanical spectrum chart of IPDI-ethacure100-based polyurethane elastomer.

CHAPTER VI

CONCLUSIONS

6.1 Moisture cured polyurethane elastomers

From the study of the properties and structure of NBDI-based polyurethane elastomers comparing to those of IPDI-based polyurethane elastomers at the NCO% of 6% and 8%, several points can be summarized as follows.

1. The viscosity of NBDI-based prepolymers is higher than that of IPDI-based prepolymers at equivalent NCO%. Increasing NCO% from 6% to 8% decreases the viscosity of prepolymers.
2. The gel time of NBDI-based polyurethane elastomers is lower than that of IPDI-based polyurethane elastomers. This implies that NBDI has higher reactivity than IPDI.
3. IPDI-based polyurethane elastomers have superior mechanical properties; tensile strength, %elongation, and tear strength, to NBDI-based polyurethane elastomers. This might be because the total hard-segment contents of IPDI-based polyurethane elastomers are more than that of NBDI-based polyurethane elastomers. Increasing NCO% from 6% to 8% increases tensile strength and tear strength of polyurethane elastomers but decreases %elongation.
4. NBDI-based polyurethane elastomers have higher weathering resistance than IPDI-based polyurethane elastomers.
5. IPDI-based polyurethane elastomers have slightly lower %Transmittance of the symmetric C-H stretching of CH_3 than NBDI-based polyurethane elastomers. This is due to the fewer amount of CH_3 groups in NBDI-based polyurethane elastomers than in IPDI-based polyurethane elastomers.
6. IPDI-based polyurethane elastomers have slightly lower %Transmittance of hydrogen-bonded urea carbonyl peak than NBDI-based polyurethane elastomers. This might imply that the hydrogen-bonded urea carbonyl groups of IPDI-based polyurethane

elastomers are more than those of NBDI-based polyurethane elastomers. This implies that the strength of IPDI-based polyurethane elastomers is higher than that of NBDI-based polyurethane elastomers which is in agreement with the tensile strength results.

7. Increasing NCO% decreases %Transmittance of hydrogen-bonded N-H peak, hydrogen-bonded urethane and urea carbonyl peak of polyurethane elastomers. This suggests that there are more hydrogen-bonded N-H groups, hydrogen-bonded urethane and hydrogen-bonded urea groups containing in the polyurethane elastomers when increasing NCO%. This implies that the strength of polyurethane elastomers at NCO% of 8% is higher than that at NCO% of 6%.
8. IPDI-based polyurethane elastomers show two relaxation peaks. The first relaxation process, β_S relaxation, occurring between -60 to -10°C corresponds to the soft-segment glass transition temperature. The second relaxation process, β_H relaxation, occurring between 0 to 70°C shows the hard-segment glass transition temperature. This implies that IPDI has a good phase separation.
9. NBDI-based polyurethane elastomers have only one relaxation process located between -60 to 30°C. NBDI-based polyurethane elastomers could exhibit a nearly compatible system.
10. IPDI-based polyurethane elastomers have better phase separation than NBDI-based polyurethane elastomers.
11. Increasing the NCO% from 6% to 8%, the position of the β_H relaxation peak also moved to higher temperature which resulted from the decreasing of the soft-segment contents, i.e. increasing of the hard-segment contents.

6.2 Two-component polyurethane elastomers

From the study of the properties and structure of NBDI-based polyurethane elastomers comparing to those of conventional isocyanate (IPDI, XDI and TDI)-based polyurethane elastomers synthesized with two curing agents (ethacure100 and ethacure300), several points can be summarized as follows.

1. The degree of prepolymer viscosity is in the order of : NBDI-based > TDI-based > XDI-based > IPDI-based prepolymers.
2. The degree of gel time of two-component polyurethane elastomers is in the order of : XDI-based < TDI-based < NBDI-based << IPDI-based polyurethane elastomers and ethacure100-based < ethacure300-based polyurethane elastomers. Therefore, the degree of reactivity of two-component polyurethane elastomers is in the order of : XDI-based > TDI-based > NBDI-based >> IPDI-based polyurethane elastomers and ethacure100-based > ethacure300-based polyurethane elastomers.
3. IPDI-based polyurethane elastomers are tougher than NBDI-based polyurethane elastomers and the aromatic diisocyanate (XDI and TDI)-based polyurethane elastomers are stiffer than the aliphatic diisocyanate (NBDI and IPDI)-based polyurethane elastomers. Ethacure100-based polyurethane elastomers are stiffer and tougher than ethacure300-based polyurethane elastomers.
4. IPDI-based polyurethane elastomers have superior mechanical properties, such as tensile strength, %elongation, tear strength, modulus at 100% and 300% elongation to other polyurethane elastomers prepared from the other diisocyanates (NBDI, m-XDI, TDI). Ethacure100-based polyurethane elastomers have superior mechanical properties to ethacure300-based polyurethane elastomers. The hard-segment contents are not responded for the differences in the strength of two-component polyurethane elastomers, the differences in the strength of the two-component polyurethane elastomers should be caused by different types of diisocyanate and curing agent. The chemical structure of NBDI-based polyurethane elastomer is more flexible than that of IPDI-based polyurethane elastomer so IPDI-based polyurethane elastomer is more rigid and stiffer than NBDI-based polyurethane elastomer. The chemical structure of

ethacure300 gives steric hindrance effect of the S atom comparing to the C atom in ethacure100.

5. The degree of weathering resistance to surface cracking and mechanical properties of two-component polyurethane elastomer samples is in the order of : NBDI-based and TDI-based > IPDI-based > XDI-based polyurethane elastomers and ethacure300-based > ethacure100-based polyurethane elastomers.
6. IPDI-based polyurethane elastomers have higher discolouration resistance than NBDI-based polyurethane elastomers. Ethacure100-based polyurethane elastomers have higher discolouration resistance than ethacure300-based polyurethane elastomers.
7. Effects of water immersion are less pronounced on the mechanical properties of two-component polyurethane elastomers and it does not show a clear trend. One week of water immersion might not be long enough to affect the mechanical properties of the polyurethane elastomers.
8. The heat aging has less pronounced effect on mechanical properties of two-component polyurethane elastomers. The mechanical properties after heat aging trend to increase slightly.
9. The weathering test has strong effect on mechanical properties of two-component polyurethane elastomers. All mechanical properties after weathering test trend to decrease from those after preparation.
10. The weathering test has more effects on mechanical properties of two-component polyurethane elastomers than water immersion and heat aging.
11. %Transmittance of hydrogen-bonded urethane and hydrogen-bonded urea carbonyl peak of NBDI-based polyurethane elastomers is lower than that of IPDI-based polyurethane elastomers. This might imply that NBDI-based polyurethane elastomer has more amount of hydrogen-bonded urethane and hydrogen-bonded urea groups than IPDI-based polyurethane elastomer.
12. Ethacure100-based polyurethane elastomers have lower %Transmittance of hydrogen-bonded urea carbonyl peak but higher %Transmittance of hydrogen-bonded urethane carbonyl peak than ethacure300-based polyurethane elastomer. This might be due to ethacure100-based polyurethane elastomers have more amount of hydrogen-

bonded urea groups but fewer amount of hydrogen-bonded urethane groups than ethacure300-based polyurethane elastomers.

13. The results on DSC of NBDI-ethacure100-based polyurethane elastomer show only soft-segment glass transition temperature at approximately -55°C, which is the same as that of IPDI-ethacure100-based polyurethane elastomer.
14. IPDI-ethacure100-based polyurethane elastomer has obviously two relaxation peaks. The first relaxation process, β_S relaxation, occurs at approximately -45°C that corresponds to the soft-segment glass transition temperature. The second relaxation process, β_H relaxation, occurring at approximately 125°C shows the hard-segment glass transition temperature. This shows that IPDI-based polyurethane elastomer has good phase separation.
15. NBDI-ethacure100-based polyurethane elastomer has only one β relaxation peak, occurring at approximately -45°C, that corresponds to the soft-segment glass transition temperature. This shows that NBDI-ethacure100-based polyurethane elastomer has a poor phase separation.
16. IPDI-based polyurethane elastomer has better phase separation than NBDI-based polyurethane elastomer.

CHAPTER VII

RECOMMENDATIONS

1. The sample thickness of all polyurethane elastomer used in infrared absorption should be controlled to be exactly the same so the %Transmittance results of infrared absorption can be obviously compared.
2. One week of water immersion and heat aging might not be long enough to affect the mechanical properties of the polyurethane elastomers, therefore, these effects should be studied at longer time.
3. It is also of interest to study the morphology and the phase separation of polyurethane elastomer synthesized from different raw materials in order to give more information on the relationship of structure and properties of polyurethane elastomers.

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APPENDICES

APPENDIX A

RAW DATA OF ELASTOMERS PREPARATION

A.1 Moisture cured polyurethane elastomers

Table A-1 Weight for prepolymer synthesis.

Sample	Diol-2000 (g)	Diisocyanate (g)	10% DBTDL (g)
6N	771.54	229.32	0.4
6I	755.53	245.16	0.46
8N	727.35	273.36	0.4
8I	707.98	292.45	0.41

Table A-2 Weight of prepolymer sample used to determine NCO% of prepolymer.

Sample no.	6N (g)	6I (g)	8N (g)	8I (g)
1	3.3269	3.3526	2.5158	2.5013
2	3.3763	3.337	2.5109	2.497
3	3.3374	3.3593	2.5046	2.5235

Table A-3 Quantities of HCl for prepolymer titration and NCO% of prepolymer.

Prepolymer	Quantity of HCl (ml.)			NCO% of prepolymer			Average NCO%
6N	11.05	10.9	11	5.9703	5.9753	5.9827	5.9761
6I	10.8	10.8	10.9	6.0796	6.1080	6.0056	6.0644
8N	11.2	11.1	11	7.7711	7.8691	7.9719	7.8707
8I	11	11.1	11	7.8993	7.9129	7.9122	7.9081

*Quantity of 0.5 N HCl standard solution required for blank test = 20.6 ml.

Table A-8 Weight of prepolymer and curing agent (ethacure100 and ethacure300) used for polyurethane elastomer sheet preparation.

Sample	Prepolymer (g)	Ethacure100 (g)
NBDI	103.50	6.50
IPDI	103.62	6.38

Sample	Prepolymer (g)	Ethacure300 (g)
NBDI	102.28	7.72
IPDI	102.41	7.59
m-XDI	102.57	7.43
TDI	102.44	7.56

APPENDIX B

RAW DATA OF MECHANICAL PROPERTIES

B.1 Moisture cured polyurethane elastomers

Table B-1 The tensile strength and the %elongation of NBDI-based polyurethane elastomer before weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break	Max. load@break	%Elongation	Tensile strength
	1	2	3	Average	(cm)	(gf)	(%)	(kgf/cm^2)
1	0.115	0.115	0.115	0.115	6.9	146.0	245.0	25.4
2	0.13	0.13	0.13	0.13	7.2	169.5	260.0	26.1
3	0.13	0.13	0.13	0.130	6.8	152.6	237.5	23.5
4	0.128	0.128	0.128	0.128	7.1	152.8	255.0	23.9
5	0.13	0.13	0.13	0.13	6.7	149.5	235.0	23.0
Average					6.9	154.1	246.5	24.4

Table B-2 The tensile strength and the %elongation of IPDI-based polyurethane elastomer before weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break	Max. load@break	%Elongation	Tensile strength
	1	2	3	Average	(cm)	(gf)	(%)	(kgf/cm^2)
1	0.115	0.115	0.115	0.12	8.10	240.7	305.0	41.9
2	0.14	0.138	0.135	0.14	8.35	291.7	317.5	42.4
3	0.128	0.125	0.122	0.13	8.60	271.6	330.0	43.5
4	0.125	0.125	0.125	0.13	8.25	274.0	312.5	43.8
5	0.12	0.12	0.12	0.12	8.10	239.5	305.0	39.9
Average					8.3	263.5	314.0	42.3

Table B-3 The tensile strength and the %elongation of NBDI-based polyurethane elastomer before weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.13	0.13	0.13	0.130	6.4	298.7	220.0	46.0
2	0.13	0.13	0.13	0.130	6.5	335.5	225.0	51.6
3	0.125	0.125	0.125	0.125	6.6	345.0	230.0	55.2
4	0.125	0.125	0.125	0.125	6.7	348.2	235.0	55.7
5	0.12	0.12	0.12	0.120	6.8	343.5	240.0	57.3
Average					6.6	334.2	230.0	53.2

Table B-4 The tensile strength and the %elongation of IPDI-based polyurethane elastomer before weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.135	0.135	0.135	0.135	7.9	667.5	295.0	98.9
2	0.135	0.135	0.135	0.135	8.3	688.0	315.0	101.9
3	0.15	0.15	0.15	0.15	8.0	670.5	300.0	89.4
4	0.135	0.135	0.135	0.135	7.5	557.0	275.0	82.5
Average					7.9	645.8	296.3	93.2

Table B-5 The tear strength of NBDI-based polyurethane elastomer before weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.115	49.7	4.3
2	0.112	54.7	4.9
3	0.11	54.1	4.9
4	0.12	61.7	5.1
5	0.12	57.1	4.8
Average	0.12	55.4	4.8

Table B-6 The tear strength of IPDI-based polyurethane elastomer before weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.090	44.5	4.9
2	0.095	45.5	4.8
3	0.095	42.1	4.4
Average	0.09	44.0	4.7

Table B-7 The tear strength of NBDI-based polyurethane elastomer before weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.140	95.8	6.8
2	0.120	77.6	6.5
3	0.130	80.4	6.2
4	0.120	73.6	6.1
5	0.130	81.2	6.2
Average	0.13	81.7	6.3

Table B-8 The tear strength of IPDI-based polyurethane elastomer before weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.120	117.9	9.8
2	0.120	123.1	10.3
3	0.118	115.4	9.8
4	0.118	123.7	10.5
Average	0.12	120.0	10.1

Table B-9 The tensile strength and the %elongation of NBDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.135	0.135	0.135	0.135	11.3	152.7	465.0	22.6
2	0.13	0.13	0.13	0.13	11.7	154.0	485.0	23.7
3	0.14	0.14	0.14	0.14	10.8	148.0	440.0	21.1
Average					11.3	151.6	463.3	22.5

Table B-10 The tensile strength and the %elongation of IPDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.125	0.125	0.125	0.125	11.8	185.0	490.0	29.6
2	0.125	0.125	0.125	0.125	12.0	188.7	500.0	30.2
3	0.12	0.12	0.12	0.12	11.7	153.2	485.0	25.5
Average					11.8	175.6	491.7	28.4

Table B-11 The tensile strength and the %elongation of NBDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.145	0.145	0.145	0.145	8.6	300.0	330.0	41.4
2	0.14	0.14	0.14	0.14	9.2	341.2	360.0	48.7
3	0.125	0.125	0.125	0.125	9.5	315.5	375.0	50.5
Average					9.1	318.9	355.0	46.9

Table B-12 The tensile strength and the %elongation of IPDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.16	0.16	0.16	0.16	10.4	653.5	420.0	81.7
2	0.16	0.16	0.16	0.16	10.5	664.0	425.0	83.0
3	0.15	0.15	0.15	0.15	10.4	598.0	420.0	79.7
Average					10.4	638.5	421.7	81.5

Table B-13 The tear strength of NBDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.12	44.1	3.7
2	0.122	43.2	3.5
3	0.12	42.2	3.5
4	0.12	41.9	3.5
Average	0.12	42.9	3.6

Table B-14 The tear strength of IPDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.13	62.1	4.8
2	0.13	56.7	4.4
3	0.13	65.3	5.0
Average	0.13	61.4	4.7

Table B-15 The tear strength of NBDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.130	70.5	5.4
2	0.130	73.8	5.7
3	0.125	68.3	5.5
4	0.128	76.3	6.0
Average	0.13	72.2	5.6

Table B-16 The tear strength of IPDI-based polyurethane elastomer after 1 week of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.130	111.1	8.5
2	0.140	118.9	8.5
3	0.140	120.7	8.6
Average	0.14	116.9	8.6

Table B-17 The tensile strength and the %elongation of NBDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.12	0.12	0.12	0.12	13.1	108.5	555.0	18.1
2	0.11	0.11	0.11	0.11	14.5	101.2	625.0	18.4
3	0.11	0.11	0.11	0.11	13.5	105.5	575.0	19.2
4	0.12	0.12	0.12	0.12	13.5	108.7	575.0	18.1
Average					13.7	106.0	582.5	18.4

Table B-18 The tensile strength and the %elongation of IPDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.1	0.1	0.1	0.1	15.0	98.7	650.0	19.7
2	0.1	0.1	0.1	0.1	15.0	97.7	650.0	19.5
3	0.11	0.11	0.11	0.11	13.6	105.7	580.0	19.2
4	0.115	0.115	0.115	0.115	14.7	127.2	635.0	22.1
Average					14.6	107.3	628.8	20.2

Table B-19 The tensile strength and the %elongation of NBDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.13	0.13	0.13	0.13	11.0	234.7	450.0	36.1
2	0.115	0.115	0.115	0.115	10.9	182.7	445.0	31.8
3	0.105	0.105	0.105	0.105	10.6	166.0	430.0	31.6
4	0.14	0.14	0.14	0.14	10.7	260.2	435.0	37.2
5	0.12	0.12	0.12	0.12	9.9	196.7	395.0	32.8
Average					10.6	208.1	431.0	33.9

Table B-20 The tensile strength and the %elongation of IPDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)				Extension@break (cm)	Max. load@break (gf)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	0.12	0.12	0.12	0.12	10.9	303.0	445.0	50.5
2	0.13	0.13	0.13	0.13	11.0	383.2	450.0	59.0
3	0.125	0.125	0.125	0.125	11.2	349.7	460.0	56.0
4	0.14	0.14	0.14	0.14	10.7	378.2	435.0	54.0
5	0.12	0.12	0.12	0.12	11.1	344.0	455.0	57.3
Average					11.0	351.6	449.0	55.4

Table B-21 The tear strength of NBDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.14	42.7	3.1
2	0.12	36.1	3.0
3	0.12	38.9	3.2
Average	0.13	39.2	3.1

Table B-22 The tear strength of IPDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 6%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.12	53.0	4.4
2	0.122	51.2	4.2
3	0.115	52.3	4.5
4	0.11	51.0	4.6
Average	0.12	51.9	4.5

Table B-23 The tear strength of NBDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.120	59.6	5.0
2	0.125	77.8	6.2
3	0.122	69.2	5.7
4	0.11	64.0	5.8
Average	0.12	67.7	5.7

Table B-24 The tear strength of IPDI-based polyurethane elastomer after 2 weeks of weathering test at NCO% of 8%.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	0.142	109.8	7.7
2	0.135	102.7	7.6
3	0.145	113.6	7.8
Average	0.14	108.7	7.7

B.2 Two-component polyurethane elastomers

Table B-25 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure100-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.69	2.61	2.52	2.61	10.5	6.2	1450.0	59.8
2	2.07	2.11	2.16	2.11	10.8	6.3	1450.0	61.8
3	1.63	1.67	1.73	1.68	10.3	6.1	1450.0	63.6
4	1.18	1.12	1.11	1.14	9.5	5.9	1450.0	57.7
5	1.57	1.71	1.89	1.72	10.4	6.2	1450.0	58.4
Average					10.3	6.1	1450.0	60.3

Table B-26 The tensile strength, %elongation, M100 and M300 of IPDI- ethacure100-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.81	2.66	2.39	2.62	19.8	11.0	850.0	221.3
2	2.1	2.17	2.38	2.22	19.0	10.8	900.0	257.1
3	2.28	2.22	2.19	2.23	19.8	11.3	850.0	235.9
4	2.11	2.11	2.14	2.12	20.8	11.7	850.0	231.5
5	2.22	2.26	2.35	2.28	20.6	11.5	850.0	247.5
6	0.98	1.13	1.22	1.11	11.2	10.3	750.0	257.3
Average					18.5	11.1	841.7	241.7

Table B-27 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.25	2.38	2.4	2.34	1.3	1.3	550.0	9.4
2	2.13	2.02	1.91	2.02	1.7	1.3	550.0	9.4
3	1.92	1.79	1.77	1.83	1.5	1.2	575.0	8.7
4	1.56	1.64	1.75	1.65	2.3	1.7	475.0	10.7
5	1.51	1.52	1.56	1.53	1.0	1.0	450.0	7.5
6	1.68	1.61	1.58	1.62	2.1	1.6	550.0	10.9
7	1.17	1.12	1.1	1.13	1.2	0.9	500.0	7.2
Average					1.6	1.3	521.4	9.1

Table B-28 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	3.67	3.63	3.44	3.58	2.8	2.6	800.0	52.8
2	2.56	2.68	2.88	2.71	2.1	2.0	1000.0	51.2
3	2.05	2.1	2.18	2.11	2.4	2.4	1000.0	66.7
4	1.5	1.4	1.28	1.39	2.2	1.9	1000.0	67.0
5	3.27	3.14	2.87	3.09	1.9	1.9	975.0	50.4
6	1.77	1.71	1.65	1.71	1.8	1.8	1000.0	50.2
7	1.3	1.15	1.22	1.22	2.5	1.9	1050.0	60.5
8	1.23	1.16	1.14	1.18	1.7	2.0	1050.0	58.5
Average					2.2	2.1	984	57.2

Table B-29 The tensile strength, %elongation, M100 and M300 of XDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	1.98	2.07	2.18	2.08	21.2	10.9	325.0	35.7
2	2.68	2.62	2.53	2.61	23.4	11.8	300.0	39.3
3	1.84	1.89	1.93	1.89	21.6	10.7	300.0	35.1
4	2.6	2.51	2.42	2.51	23.5	12.0	325.0	40.2
5	2.07	2.22	2.31	2.20	23.5	11.8	300.0	39.3
6	2.1	2.32	2.39	2.27	23.5	11.7	300.0	38.4
7	2.11	2.17	2.23	2.17	23.2	12.0	325.0	40.0
Average					22.8	11.6	310.7	38.3

Table B-30 The tensile strength, %elongation, M100 and M300 of TDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.26	2.17	2.08	2.17	19.9	11.1	450.0	36.7
2	2.29	2.24	2.17	2.23	21.9	11.7	525.0	37.9
3	2.25	2.24	2.19	2.23	30.4	11.4	550.0	37.2
4	1.88	1.81	1.74	1.81	19.9	10.6	575.0	33.5
5	1.1	1.23	1.38	1.24	17.5	9.5	450.0	30.0
6	0.78	0.78	0.95	0.84	17.2	8.9	400.0	27.9
Average					21.1	10.6	491.7	33.9

Table B-31 The tear strength of NBDI-ethacure100-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.61	5.422	33.7
2	2.36	9.056	38.4
3	1.51	5.181	34.3
4	1.23	4.707	38.3
5	2.06	7.274	35.3
Average	1.75	6.328	36.0

Table B-32 The tear strength of IPDI- ethacure100-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.06	11.360	55.1
2	2.46	12.220	49.7
3	2.07	11.620	56.1
4	2.44	12.720	52.1
5	2.4	12.600	52.5
Average	2.29	12.104	53.1

Table B-33 The tear strength of NBDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.32	0.357	2.7
2	2.8	0.824	2.9
3	2.83	1.000	3.5
4	1.34	0.404	3.0
5	1.4	0.420	3.0
Average	1.94	0.601	3.0

Table B-34 The tear strength of IPDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.99	2.910	14.6
2	2.14	4.092	19.1
3	1.79	3.143	17.6
4	2.54	3.610	14.2
5	3.41	6.364	18.7
6	3.53	5.710	16.2
Average	2.57	4.305	16.7

Table B-35 The tear strength of XDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.96	5.236	26.7
2	2.28	6.278	27.5
3	2.21	6.208	28.1
4	2.24	6.605	29.5
5	2.15	5.827	27.1
6	1.89	5.220	27.6
7	2.32	6.644	28.6
8	2.06	5.780	28.1
9	1.77	4.045	22.9
Average	2.10	5.760	27.3

Table B-36 The tear strength of TDI-ethacure300-based polyurethane elastomer after preparation.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.05	5.819	28.4
2	1.41	3.999	28.4
3	1.23	3.719	30.2
4	1.09	2.536	23.3
Average	1.45	4.018	27.6

Table B-37 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure100-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	2.18	2.35	2.39	2.31	10.4	6.2	1350.0	65.6
2	1.45	1.42	1.42	1.43	9.4	6.0	1500.0	57.2
3	1.61	1.68	1.75	1.68	8.9	5.6	1350.0	62.2
4	1.61	1.64	1.63	1.63	9.2	5.8	1400.0	59.8
Average					9.5	5.9	1400.0	61.2

Table B-38 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure100-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	2.22	2.25	2.29	2.25	19.8	11.1	875.0	251.2
2	1.9	2.03	2.09	2.01	17.5	10.5	900.0	229.6
3	2.09	2.14	2.08	2.10	19.6	10.9	850.0	219.9
4	1.56	1.64	1.82	1.67	18.6	10.7	925.0	276.8
5	2.17	2.03	2.89	2.36	16.5	9.3	850.0	199.5
Average					18.4	10.5	880.0	235.4

Table B-39 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	1.95	2.00	2.00	1.98	2.0	1.6	450.0	10.2
2	2.53	2.37	2.14	2.35	2.4	1.9	425.0	11.4
3	1.59	1.71	1.83	1.71	2.0	1.6	475.0	10.4
4	1.89	1.90	1.94	1.91	2.0	1.6	500.0	10.6
5	1.59	1.52	1.45	1.52	2.0	1.6	500.0	10.4
6	1.58	1.38	1.28	1.41	1.8	1.5	400.0	9.5
Average					2.0	1.6	458.3	10.4

Table B-40 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	2.03	2.07	2.02	2.04	4.3	2.6	1050.0	54.1
2	1.79	1.74	1.8	1.78	4.2	2.6	1075.0	52.9
3	1.5	1.53	1.54	1.52	3.7	2.5	1050.0	50.5
4	2.1	2.09	2.1	2.10	3.8	2.5	1050.0	53.4
5	1.78	1.86	1.94	1.86	3.7	2.4	1025.0	50.7
Average					3.9	2.5	1050.0	52.3

Table B-41 The tensile strength, %elongation, M100 and M300 of XDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	1.68	1.59	1.57	1.61	21.7	11.0	425.0	38.0
2	1.87	1.80	1.75	1.81	23.0	11.6	550.0	39.6
3	1.40	1.37	1.40	1.39	21.4	10.8	450.0	36.7
4	1.60	1.60	1.65	1.62	22.4	11.4	600.0	38.5
5	1.11	1.05	1.02	1.06	20.2	10.1	450.0	34.3
6	1.30	1.24	1.27	1.27	22.8	11.5	550.0	39.9
7	0.72	0.73	0.77	0.74	19.5	9.7	350.0	31.1
Average					21.6	10.9	482.1	36.9

Table B-42 The tensile strength, %elongation, M100 and M300 of TDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	1.99	1.97	1.93	1.96	21.4	11.3	600.0	36.5
2	2.33	2.25	2.14	2.24	22.1	11.7	550.0	37.8
3	1.17	1.27	1.42	1.29	20.1	10.6	400.0	32.9
4	1.23	1.27	1.28	1.26	20.3	10.7	475.0	35.8
5	0.7	0.8	0.95	0.82	18.9	10.0	425.0	32.4
Average					20.5	10.9	490.0	35.1

Table B-43 The tear strength of NBDI-ethacure100-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.37	8.643	36.5
2	2.76	6.838	24.8
3	1.67	5.703	34.1
4	1.47	5.695	38.7
Average	2.07	6.720	33.5

Table B-44 The tear strength of IPDI- ethacure100-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.94	10.720	55.3
2	2.32	11.410	49.2
3	2.73	14.520	53.2
4	2.25	9.569	42.5
5	1.22	5.259	43.1
Average	2.09	10.296	48.7

Table B-45 The tear strength of NBDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.26	1.338	5.9
2	1.94	0.933	4.8
3	1.92	1.011	5.3
4	1.90	1.042	5.5
5	2.45	1.307	5.3
Average	2.09	1.126	5.4

Table B-46 The tear strength of IPDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.44	4.808	19.7
2	2.03	3.190	15.7
3	1.62	2.614	16.1
4	1.80	2.738	15.2
5	2.00	3.221	16.1
Average	1.98	3.314	16.6

Table B-47 The tear strength of XDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.73	10.350	37.9
2	2.73	9.149	33.5
3	1.93	7.663	39.7
4	1.89	6.698	35.4
5	1.98	7.297	36.9
6	2.07	6.706	32.4
Average	2.22	7.98	35.97

Table B-48 The tear strength of TDI-ethacure300-based polyurethane elastomer after 1 week of water immersion.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.30	3.812	29.3
2	1.23	3.625	29.5
3	1.38	3.143	22.8
4	0.66	1.369	20.7
Average	1.14	2.987	25.6

Table B-49 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure100-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2	2.13	2.32	2.15	10.3	6.2	1400.0	65.3
2	1.87	1.65	1.52	1.68	10.2	6.1	1400.0	62.0
3	1.49	1.56	1.67	1.57	8.6	5.5	1450.0	59.5
4	1.41	1.24	1.12	1.26	8.0	5.7	1500.0	54.5
Average					9.3	5.9	1437.5	60.3

Table B-50 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure100-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.43	2.31	2.22	2.32	19.4	10.8	900.0	237.8
2	1.92	1.92	1.9	1.91	18.0	10.5	850.0	243.7
3	2.53	2.51	2.45	2.50	19.2	10.7	850.0	240.6
4	2.57	2.42	2.31	2.43	20.2	11.2	850.0	236.1
5	2.06	1.87	1.69	1.87	18.1	10.3	850.0	262.0
Average					19.0	10.7	860.0	244.0

Table B-51 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.4	2.36	2.34	2.37	1.7	1.1	525.0	11.3
2	2.66	2.48	2.37	2.50	3.0	2.2	575.0	12.9
3	2.37	2.07	1.87	2.10	2.4	1.9	400.0	10.8
4	1.11	1.12	1.15	1.13	1.8	1.5	425.0	9.4
5	1.22	1.2	1.17	1.20	1.7	1.4	400.0	9.6
6	1.1	1.07	1.2	1.12	1.4	1.3	400.0	8.8
Average					2.0	1.6	454.2	10.5

Table B-52 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.39	2.43	2.48	2.43	4.6	2.9	975.0	70.0
2	2.12	2.01	2.83	2.32	3.4	2.1	975.0	42.6
3	2.04	2.02	1.94	2.00	4.8	3.0	975.0	67.9
4	1.65	1.57	1.5	1.57	3.2	2.5	1000.0	59.5
5	1.59	1.63	1.62	1.61	4.1	2.6	1000.0	58.4
6	1.17	1.18	1.17	1.17	3.1	2.7	1000.0	70.3
Average					3.9	2.6	987.5	61.5

Table B-53 The tensile strength, %elongation, M100 and M300 of XDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.41	2.59	2.69	2.56	23.6	12.1	450.0	41.6
2	2.1	2.32	2.5	2.31	23.1	11.7	450.0	39.3
3	1.4	1.35	1.36	1.37	21.9	11.5	600.0	32.7
4	1.7	1.72	1.75	1.72	21.1	10.9	450.0	38.1
5	1.68	1.51	1.33	1.51	20.8	10.8	400.0	55.8
6	0.93	0.9	0.92	0.92	10.9	9.5	500.0	81.1
7	1.27	1.35	1.4	1.34	22.5	11.7	450.0	60.6
Average					20.6	11.2	471.4	49.9

Table B-54 The tensile strength, %elongation, M100 and M300 of TDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.35	2.2	2.1	2.22	22.9	12.0	650.0	36.4
2	2.2	2.11	2.03	2.11	23.4	12.3	800.0	37.8
3	1.27	1.39	1.43	1.36	21.6	11.5	550.0	35.4
4	1.59	1.6	1.61	1.60	21.8	11.3	650.0	37.9
5	1.4	1.08	1.2	1.23	20.2	10.5	700.0	31.5
6	1.16	1.25	1.2	1.20	21.3	11.2	625.0	37.5
Average					21.8	11.5	662.5	36.1

Table B-55 The tear strength of NBDI-ethacure100-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.30	8.698	37.8
2	1.30	4.466	34.4
3	1.60	6.815	42.6
4	1.24	4.372	35.3
Average	1.61	6.088	37.5

Table B-56 The tear strength of IPDI- ethacure100-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.56	13.890	54.3
2	2.41	14.410	59.8
3	2.39	13.430	56.2
4	1.67	9.133	54.7
5	1.48	8.246	55.7
Average	2.10	11.822	56.1

Table B-57 The tear strength of NBDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.31	0.995	4.3
2	1.80	0.606	3.4
3	1.77	0.560	3.2
4	1.42	0.606	4.3
Average	1.83	0.692	3.8

Table B-58 The tear strength of IPDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.23	3.221	14.4
2	2.13	3.143	14.8
3	1.99	3.796	19.1
4	1.87	2.972	15.9
5	1.56	2.598	16.7
Average	1.96	3.146	16.2

Table B-59 The tear strength of XDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.90	5.469	28.8
2	2.64	9.616	36.4
3	2.17	6.846	31.5
4	1.81	5.049	27.9
5	1.19	2.770	23.3
Average	1.94	5.950	29.6

Table B-60 The tear strength of TDI-ethacure300-based polyurethane elastomer after 1 week of heat aging.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.90	6.519	34.3
2	1.68	5.594	33.3
3	2.19	6.138	28.0
4	0.81	1.914	23.6
5	0.73	1.680	23.0
Average	1.46	4.369	28.5

Table B-61 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure100-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	1.95	2.05	2.21	2.07	5.9	3.7	1200.0	24.2
2	2.28	2.19	2.17	2.21	6.3	4.0	1400.0	32.8
3	2.33	2.15	2.1	2.19	5.7	3.6	1050.0	24.8
4	2.35	2.08	1.9	2.11	5.3	3.3	950.0	22.1
5	2.07	2.03	2.07	2.06	5.5	3.5	1175.0	22.8
6	1.79	1.78	1.8	1.79	5.7	3.6	1250.0	23.8
Average					5.74	3.6	1170.8	25.1

Table B-62 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure100-based polyurethane elastomer after 2 months of weathering test.

.No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	2.75	2.26	2.22	2.41	1.8	-	146.5	2.1
Average					1.8	-	146.5	2.1

Table B-63 The tensile strength, %elongation, M100 and M300 of NBDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	1.82	1.97	2.09	1.96	1.3	1.0	325.0	5.6
2	3.14	3.04	3.04	3.07	2.0	1.5	425.0	8.9
3	3.2	3.17	3.08	3.15	1.9	1.4	450.0	8.3
Average					1.7	1.3	400.0	7.6

Table B-64 The tensile strength, %elongation, M100 and M300 of IPDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)				M100	M300	%Elongation	Tensile strength
	1	2	3	Average	(kgf/cm^2)	(kgf/cm^2)	(%)	(kgf/cm^2)
1	3.00	3.00	2.88	2.96	1.6	1.5	1150.0	25.4
2	2.02	2.02	2.02	2.02	0.8	0.8	1150.0	16.0
3	2.35	2.43	2.62	2.47	1.2	1.2	1100.0	20.7
Average					1.2	1.1	1133.3	20.7

Table B-65 The tensile strength, %elongation, M100 and M300 of XDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	3.25	3.29	3.35	3.30	8.6	-	111.6	8.0
2	2.94	3.04	3.13	3.04	-	-	97.1	7.4
3	2.88	2.85	2.63	2.79	-	-	85.8	6.7
4	3.47	3.68	3.37	3.51	-	-	94.2	8.2
Average					8.6	-	97.2	7.6

Table B-66 The tensile strength, %elongation, M100 and M300 of TDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)				M100 (kgf/cm^2)	M300 (kgf/cm^2)	%Elongation (%)	Tensile strength (kgf/cm^2)
	1	2	3	Average				
1	1.99	2.02	2.03	2.01	16.5	9.4	350.0	29.2
2	2.14	2.04	1.89	2.02	17.0	9.0	350.0	27.7
3	2.13	2.12	2.05	2.10	17.4	9.3	375.0	27.9
4	1.61	1.73	1.81	1.72	15.8	8.5	300.0	25.9
Average					16.7	9.1	343.8	27.7

Table B-67 The tear strength of NBDI-ethacure100-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.78	4.217	23.7
2	2.00	5.391	27.0
3	1.56	3.408	21.8
4	1.32	2.614	19.8
5	1.78	4.185	23.5
Average	1.69	3.963	23.2

Table B-68 The tear strength of IPDI- ethacure100-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.72	0.684	2.5
Average	2.72	0.684	2.5

Table B-69 The tear strength of NBDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.76	1.730	6.3
2	2.81	1.867	6.6
3	2.34	1.183	5.1
Average	2.64	1.593	6.0

Table B-70 The tear strength of IPDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.96	4.279	14.5
2	2.44	3.345	13.7
3	2.81	3.563	12.7
Average	2.74	3.729	13.6

Table B-71 The tear strength of XDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	1.95	0.155	0.8
2	3.17	0.933	2.9
3	1.85	0.233	1.3
4	1.97	0.233	1.2
Average	2.24	0.389	1.5

Table B-72 The tear strength of TDI-ethacure300-based polyurethane elastomer after 2 months of weathering test.

No. of sample	Thickness (mm)	Max. load (gf)	Tear strength (kgf/cm)
1	2.06	5.601	27.2
2	1.65	4.045	24.5
Average	1.86	4.823	25.9

VITA

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