

EFFECTS OF CALCIUM CARBONATE FILLERS ON MECHANICAL PROPERTIES OF
FLEXIBLE POLYURETHANE FOAM

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2008

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นางสาววิรงรอง ศรีโง๊ะ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2551

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title EFFECTS OF CALCIUM CARBONATE FILLERS ON
 MECHANICAL PROPERTIES OF FLEXIBLE
 POLYURETHANE FOAM

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Field of Study Chemical Engineering

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wirong ศรีโง๊ะ : ผลของสารตัวเติมแคลเซียมคาร์บอเนตต่อสมบัติเชิงกลของพอลิยูรีเทน โฟมแบบยืดหยุ่น. (EFFECTS OF CALCIUM CARBONATE FILLERS ON MECHANICAL PROPERTIES OF FLEXIBLE POLYURETHANE FOAM) อ. ที่ปริกษาวิทยานิพนธ์หลัก : อ.ดร. อนงค์นาฏ สมหวังชน โรจน์, 83 หน้า.

งานวิจัยนี้เป็นการศึกษาเกี่ยวกับคุณสมบัติของพอลิยูรีเทน โฟมแบบยืดหยุ่น โดยปรับเปลี่ยนดัชนีไอโซไซยานาต (Isocyanate Index) ของโฟมซึ่งมีการเติมสารตัวเติมแคลเซียมคาร์บอเนตที่มีขนาดอนุภาคประมาณ 1 ไมโครเมตร ปริมาณร้อยละ 0, 3, 5, 7 และ 10 โดยน้ำหนักของพอลิออล เมื่อนำโฟมไปวิเคราะห์โดยใช้เครื่องฟูรีเออร์ทรานสฟอร์มอินฟราเรดสเปกโตรมิเตอร์เพื่อตรวจสอบหมู่ฟังก์ชันของพอลิยูรีเทน โฟม จะพบว่าตำแหน่งพีคเกิดขึ้นที่ความถี่เดียวกันโดยมีหมู่ฟังก์ชันอีเธอร์เพิ่มขึ้นแต่หมู่ฟังก์ชันยูรีเทนลดลงเมื่อเพิ่มปริมาณสารตัวเติมแคลเซียมคาร์บอเนต โดยโครงสร้างของพอลิยูรีเทน โฟมแบบยืดหยุ่นเมื่อใช้กล้องจุลทรรศน์แบบส่องกราดจะสังเกตเห็นว่าเมื่อเพิ่มสารตัวเติมแคลเซียมคาร์บอเนตลักษณะของเซลล์จะเปิดเหมือนกันทุกดัชนีการฉีด โฟม

นอกจากนี้เมื่อนำพอลิยูรีเทนคอมโพสิตไปทดสอบคุณสมบัติจะพบว่าความแข็งแรง, ค่าความแข็งและความหนืดของพอลิออลที่ผสมกับสารตัวเติมแคลเซียมคาร์บอเนตมีค่าสูงขึ้น แต่คุณสมบัติการดึงยืดและการกระดอนกลับของพอลิยูรีเทนมีค่าลดลง เนื่องจากพอลิยูรีเทนที่มีดัชนีการฉีด โฟมสูงขึ้นจะมีการสร้างพันธะเพิ่มขึ้นอีกทั้งยังมีผลจากการเติมสารตัวเติม จึงทำให้พอลิยูรีเทนมีคุณสมบัติความแข็งแรงและความแข็งเพิ่มขึ้น แต่คุณสมบัติการดึงยืดและการกระดอนกลับลดลง

ภาควิชา....วิศวกรรมเคมี.....
สาขาวิชา....วิศวกรรมเคมี.....
ปีการศึกษา....2551.....

ลายมือชื่อนิสิต.....
ลายมือชื่อ อ.ที่ปริกษาวิทยานิพนธ์หลัก.....

4971470921 : MAJOR CHEMICAL ENGINEERING

KEY WORD: POLYURETHANE / FOAM / FILLER

WIRONGRONG SRI-NGO : EFFECTS OF CALCIUM CARBONATE FILLERS
ON MECHANICAL PROPERTIES OF FLEXIBLE POLYURETHANE FOAM.

THESIS PRINCIPAL ADVISOR : ANONGNAT SOMWANGTHANAROJ, Ph.D.,
83 pp.

The flexible polyurethane foam was prepared with adding a small amount of calcium carbonate fillers whose average size of $1\ \mu\text{m}$. The content of fillers in polyurethane foam is varied from 0, 3, 5, 7 and 10 %wt of polyol. The isocyanate index was also varied from 90, 100 and 110. The FTIR spectrum of polyurethane composite foams showed the similar peaks in the observed range. It was shown that the content of urethane linkage group decreased with an increase of calcium carbonate content. However, ether groups are increased with the increase of calcium carbonate content. Scanning Electron Microscopy (SEM) was shown the cell structure of the flexible polyurethane that the open cell structure was similar at all isocyanate index.

Furthermore, the tensile strength, hardness and density of polyurethane composite foam tended to increase with increase of calcium carbonate filler but the elongation and resilience decreased with increase of the fillers. Although the soft segment was increased with of calcium carbonate filler, the hardness properties of polyurethane foam increased which could be due to the presence of the fillers. In addition, when the isocyanate index in the foam, the hardness properties also increased. In addition, increasing the isocyanate index would increase the intermolecular interaction between filler and matrix thus the tensile strength and hardness of polyurethane foam composites increased but the elongation at break decreased.

Department :Chemical Engineering..... Student's signature.....
Field of study :Chemical Engineering..... Principal Advisor's signature.....
Academic year :2008.....

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to Dr. Anongnat Somwangthanaroj, my supervisor, for initiating this project, for her tremendous encouragement and endless support during my Master of Engineering study.

I am also grateful to my committee members, who provided constructive and scientific advices for the completion of this thesis. These include Assoc. Prof. Dr. Sarawut Rimdusit, Asst. Prof. Montree Wongsri and Dr. Varun Taepaisitphongse from the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Dr. Sawitree Petchuay from the Department of Science and Technology, Faculty of Science, Nakhon Sawan Rajabhat University. I like to thank Miss Sevita Inthapichai a student of Master's Degree from the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. Moreover, I would like to thank TRF-MAG for scholarship during my study at Chulalongkorn University.

To the persons who mean the most in my life, I would like to dedicate this paragraph to my beloved family, especially my mother and my father for their eternal care and endless support. There has never been a single day gone by without them standing by me.

Finally, I have tried to make the acknowledgment list as complete as possible, nevertheless I do apologize if I have unintentionally missed out. Those who feel that their names should have been here, please accept my unwritten but sincere thanks.

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Polyurethane is best known to the public in the form of flexible foams such as upholstery and mattresses. It also came in the rigid foams for insulation of building, water heaters and refrigerated transport. Polyurethanes are formed by reacted a polyol that has an alcohol with more than two reactive hydroxyl groups per molecule, with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives.

The origin of polyurethane dated back to the beginning of World War II where it was first developed as a replacement for rubber. Otto Bayer and co-workers discovered and patented the chemistry of polyurethanes in 1937. The versatility of this new organic polymer and its ability to substitute for scarce materials spurred numerous applications. During World War II, polyurethane coatings were used for the impregnation of paper and the manufacture of mustard gas resistant garments, high-gloss airplane finishes and chemical and corrosion resistant coatings to protect metal, wood and masonry.

By the end of the World War II, polyurethane coatings were being manufactured and used on an industrial scale and could be custom-formulated for specific applications. By the mid-50s polyurethane could be found in coatings and adhesives, elastomers and rigid foams. It was not until the late-50s that comfortable cushioning flexible foams were commercially available. With the development of a low-cost polyether polyol, flexible foams opened the door to the upholstery and automotive applications.

Formulations, additives and processing techniques continuously such as reinforced and structural mouldings for exterior automotive parts and one-component systems.

The polyurethane is used in many industries such as automobile, furniture, construction, thermal insulation and footwear. There are many types of polyurethane that can be choosed. Rigid polyurethane foam is the most produced insulation materials and flexible polyurethane foam is produced for seating cushions for many types of seats and chairs. Polyurethane foam is made by mixing chemicals together, i.e., isocyanate, polyol, catalyst, blowing agent and other additives.

Polyurethane foam is a very important material used for automotive parts such as bumpers, steering wheel and all of the car seat. Competitive quality and price influences the innovation of new materials in order to compete with other suppliers. Filler is added to improve properties of polyurethane foam such as stiffness, resistance to compression and light weight of seat cushions.

In this study, the effects of filler and isocyanate index on cream time, gel time and rising time for polymerization of polyurethane reaction, viscosity, solid-state mechanical properties and processibility as well as cost reduction of flexible polyurethane foam by adding filler were investigated.

1.2 Objectives of the research

This study was aimed primarily at the following objectives.

1. Evaluate the effect of filler loading on the mechanical properties and processibility of flexible polyurethane foam.
2. Improve properties of polyurethane foam in order to reduce cost.

1.3 Scope of the research

1. Calcium carbonate was used as filler 0, 3, 5, 7 and 10% by weight of polyol and isocyanate index of polyurethane at 90, 100 and 110 were used and their effects on mechanical properties of polyurethane foam was evaluated.
2. Study the effect of filler on cream time, gel time and rising time for polymerization of polyurethane reaction.

CHAPTER II

THEORY

2.1 Introduction to polyurethanes

Polyurethanes are based on the exothermic reaction of polyisocyanate, polyol and additives [1]. Composition of chemical mixtures and processing conditions affect the properties of polyurethane foams. There are two types of polyurethane foam, i.e. rigid and flexible foams. For automotive industry, the flexible polyurethane foams are used to make several types of seating cushions. These can be produced easily by moulding flexible polyurethane foams into variety of shapes.

2.2 Types of polyurethane foam

The greatest advantage offered by polyurethane is their versatility, both in finished product properties and ease of production and application. The choice of polyol and isocyanate can be made with properties ranging from the softness of low density flexible foam to the high strength of the high density flexible foam. There are three types of flexible polyurethane foams, i.e. low density flexible foam, low density rigid foam and high density flexible foams.

2.2.1 Low density flexible foam

They are lightly cross-linked polymers with a open-cell structure. Density of material is about 10-80 kg/m³, composition of lightly cross-linked, open-cells. Air flow through the structure is very easily. Application is used to make cushions and pads.

2.2.2 Low density rigid foam

They are highly cross-linked polymers with a closed-cell structure. Density of material is more than 30 kg/m^3 . It is used to make insulation part.

2.2.3 High density flexible foam

Density of material is more than 100 kg/m^3 and they are mostly close-cells. Application of self-skinning foams and microcellular elastomers is for making upholstery, vehicle trim and shoe-soling.

2.3 Raw Materials for polyurethane

Polyurethane is produced from the reaction between alcohol with two or more reactive hydroxyl groups per molecule (diols or polyols) and isocyanates that have more than one reactive isocyanate group per molecule (diisocyanate or polyisocyanate). This type of polymerization is called condensation polymerization.

Raw materials which are used to produce polyurethane are summarized as follows.

2.3.1 Isocyanates

Reactive group of isocyanate is -NCO and there are at least 2 groups per molecule. Polyurethane is made by varying the types of isocyanate used, ie, toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Isocyanate used to make flexible polyurethanes is TDI and MDI and most important commercial product are produced with 80:20 ratios (mole) [1]. TDI is used to make cushion and sometimes is mixed with MDI. Structures of isocyanate are shown in Figure 2.1.

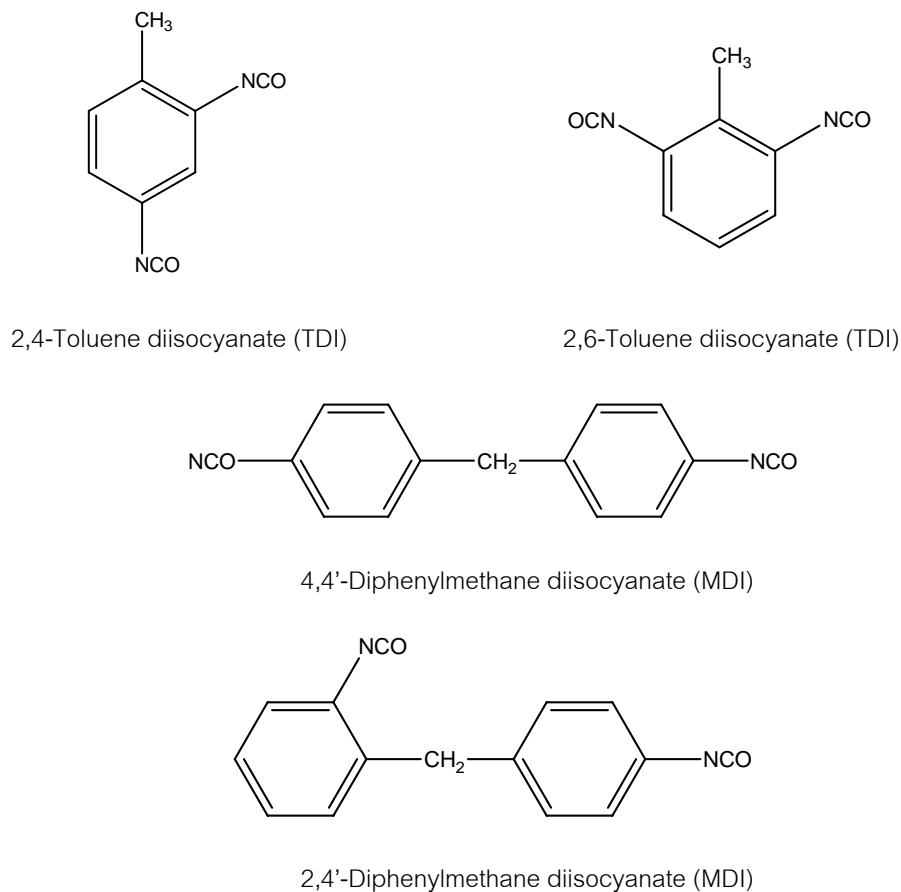


Figure 2.1 Structures of Toluene diisocyanate (TDI) and Diphenylmethane diisocyanate (MDI)

Isocyanate index is molar ratio of isocyanate for reacting with polyol for 1:1 molar ratio of isocyanate reacting with polyol, it is referred to as index 100, which shown in Figure 2.2. Flexible polyurethane foam has isocyanate index about range 90 to 110. Isocyanate index is calculated as shown in Figure 2.3.

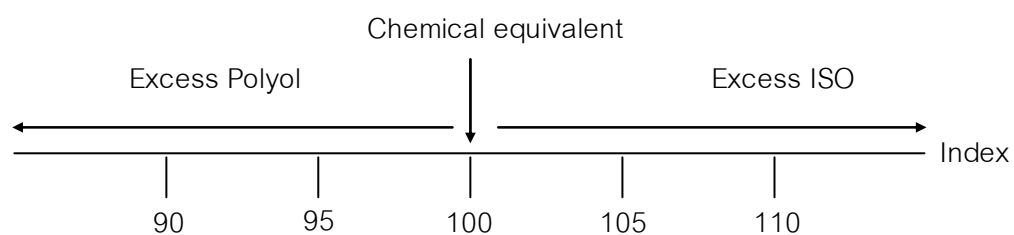


Figure 2.2 Relation of isocyanate index with quantity of isocyanate and polyol

$$\text{Isocyanate Index} = \frac{\text{Actual amount of isocyanate used (mole)}}{\text{Amount of isocyanate required to react in the polyol (mole)}} \times 100$$

Figure 2.3 Calculation of isocyanate index

Increasing the isocyanate index affects the reaction. With increasing index, cream time is reduced. The hardness of polyurethane foam can be adjusted by varying the isocyanate index. The hardness enhancement has been directly related to the increase in isocyanate index.

2.3.2 Polyols

Polyols used to make polyurethane foam are polyethers and polyesters for flexible and rigid polyurethane foams, respectively. They contain hydroxyl group with terminal chain as shown in Figure 2.4

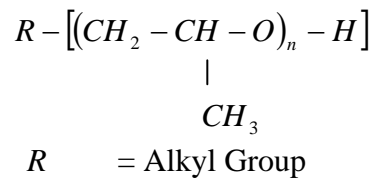


Figure 2.4 Structure of polyol

The properties of polyurethane depends on the choice of polyol; therefore, molecular weight, structure, hydroxyl number and degree of cross-linking of polymer have to be carefully selected. The degree of cross-linking has effect on the stiffness properties. Flexible polyurethane foam has degree of cross-linking less than rigid polyurethane foam.

Hydroxyl value is a measure of the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed as mg KOH/g as shown in Figure 2.5.

$$\text{Hydroxyl value, (mg KOH/g)} = \frac{56.1 \times \text{Functionality}}{\text{Molecular Weight}} \times 1000$$

Figure 2.5 Calculation of hydroxyl value

The structure of the polyol determines the final properties of polyurethane. The characteristic of the polyol for polyurethane manufacture are shown in Table 2.1.

Table 2.1 Polyols for polyurethane manufacture [1]

Characteristic	Flexible foams and elastomers	Rigid foams, rigid plastics and stiff coating
Molecular weight range	1,000 to 6,500	150 to 1,600
Functionality range	2 to 3	3 to 8
Hydroxyl value range (mg KOH/g)	28 to 160	250 to 1,000

2.3.3 Additives

Not only isocyanate and polyol monomers are used to make polyurethane, but additives are also filled to control and modify the polyurethane reaction and its properties. These additives include catalyst, chain extender, cross linking agent, surface-active material, flame-retardants, coloring material and fillers.

1) Catalyst

Catalysts are important for a reaction of polyurethane foam. There are many types of catalyst such as aliphatic and aromatic tertiary amines and organo-metallic compound. Catalyst accelerates the urethane reaction. Examples of catalyst are shown in Table 2.2.

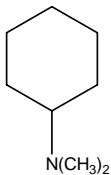

2) Cross-linking agents and chain-extenders

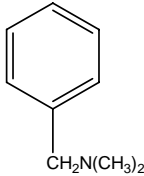
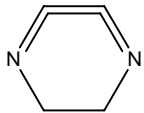
Cross-linking agent and chain extender are used in order to react with diisocyanate to form polyurethane and increase the modulus and hard segment. Low molecular weight polyols and polyamides are examples of these additives.

3) Blowing agents

Reaction of polyurethane foam needs blowing agent to form gas bubbles during polymerization. An example of this additive is water which is formed in the reaction with diisocyanate.

Table 2.2 Example of tertiary-amine catalysts [1]

Catalyst	Application
1. N,N-Dimethylaminoethanol $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$	Inexpensive, low-odour, isocyanate reactive, mobile liquid catalyst used in polyether-based flexible foams.
2. N,N-Dimethylcyclohexylamine. (Catalyst SFC) 	Liquid with an intense odour. Rigid foams, polyester-based flexible foams and some semi-rigid foams.
3. Bis-(2-dimethylaminoethyl)ether $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Low-odour, mobile liquid used in high resilience and cold-cure flexible foams.
4. N,N,N',N',N''-Pentamethyl-diethylene-triamine. $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ 	Flexible with characteristic smell used in polyester-based flexible foams, semi-rigid foams and for prepolymer making.

Catalyst	Application
5. N,N-Dimethylbenzylamine, (Catalyst SFB) 	Liquid with characteristic smell used in polyester-based flexible foams,
6. N,N-Dimethylcetylamine $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{N}(\text{CH}_3)_2$	Viscous liquid with a low odour used in polyester-based flexible foams and some potting compounds.
7. Diaminobicyclooctane (DABCO) 	Solid soluble in water, glycols and polyethers. May be used in most types of polyurethanes.
8. N-Ethylmorpholine	Volatile, low viscosity liquid with characteristic odour. Used as synergistic catalyst in flexible foams and in prepolymer preparation.

4) Surfactants

The function of surfactant in foam is to help in mixing incompatible components. There are many types of surfactant such as nonyl phenols, fatty acid, and ethylene oxide.

5) Coloring materials

Both organic and inorganic pigments are used to color the polyurethane foam product. Pigment pastes are added into the foam reaction mixtures.

6) Fillers

Fillers include many grades of inorganic fillers. The purpose of adding fillers is to increase density, improve compression set, and enhance sound absorption. Depending on the nature of the filler, the overall cost of the final foam product can be reduced. Examples of fillers are shown in Table 2.3.

Table 2.3 Examples of fillers and applications in polyurethane foams [1]

Filler	Typical applications
Calcium carbonate, (Ground chalk, ground limestone, whiting)	Flexible foams, semi-rigid foams, binder compositions, rigid self-skinning mouldings
Barium sulphate, (Barytes)	Flexible foams, semi-rigid foams, especially for sound-absorbing
Clays (China clay, kaolin, etc.)	Flexible systems
Expanded silicas, colloidal silicas	Flexible foams, cast elastomers
Clay balls, vermiculite and expanded mica, etc.	Rigid foams
Glass micro-spheres	Flexible, microcellular foams, RIM
Glass flakes	Elastomer RIM
Silicates, cements	Rigid foams, sealants, grouting compound
Short fibres, milled and chopped glass fibre, Aramid fibres, carbon fibres, conducting fibres, (aluminum, coated glass, steel)	Elastomeric RIM, rigid foams

Filler	Typical applications
Glass cloths and scrim, wire mesh and organic fibres.	Encapsulation in rigid foams, reinforcement low density flexible foam mouldings

7) Flame Retardant

Flame retardant is added into polyurethane foam to reduce flammability because polyurethane is active to burn when oxygen is presented. The most widely used flame retardants are the chlorinated phosphate esters, chlorinated parafins and melamine powders.

2.4 The polymerization reaction of polyurethane

The synthesis of polyurethane is step polymerization as shown in Figure 2.6.

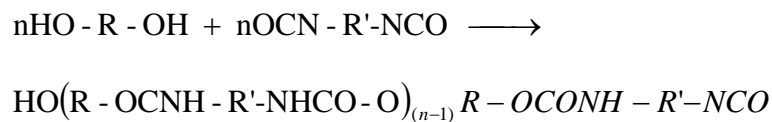


Figure 2.6 Polymerization of polyurethane foam

The polymerization is subjected to many side reactions [2] due to the reactivity of the isocyanate group towards a variety of reagents including water, amines catalyst, and carboxylic acids. Thus, water reacts with isocyanates to yield carbon dioxide and an amine catalyst as shown in Figure 2.7.

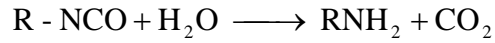


Figure 2.7 Reaction of isocyanate with water

The amine catalyst then reacts further with the isocyanate groups.

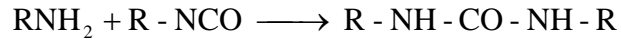


Figure 2.8 Reaction of amine catalyst with the isocyanate

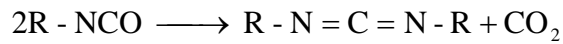


Figure 2.9 Dimerization to carbodiimides

And trimerization.

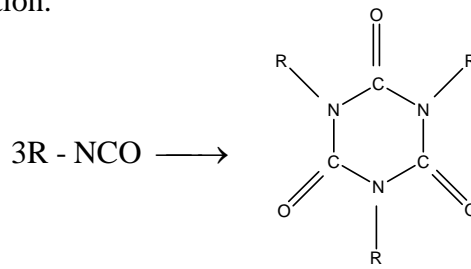


Figure 2.10 Trimerization of isocyanate to isocyanurate

The various side reactions make it difficult to obtain a stoichiometric balance of the diisocyanate and polyol reaction. A slight excess of the diisocyanate is usually needed to overcome the effect of the side reactions and to produce high molecular weight polyurethanes. These side reactions also play a decisive role in determining many of the other process variables. Relatively low temperatures, not higher than 100-120 °C, are usually employed. High reaction temperature are usually avoided because urethane polymers undergo several different types of degradation reactions.

2.5 Calcium carbonate filler

Calcium carbonate is widely used as fillers in plastics, rubber, paper, paints and other fields. Calcium carbonate is a chemical compound with the chemical formula CaCO_3 . It is a common substance found as rock in all parts of the world, and is the main component of shells of marine organisms, snails, and eggshells. Calcium carbonate is the active ingredient in agricultural lime, and is usually the principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but high consumption can be hazardous. Furthermore, it is a very stable mineral, forming entire mountain ranges in addition to portions of seashores composed of coral and mollusk shell. Calcium carbonate has many different are recognized, such as limestone, marble, calcite, chalk, aragonite and dolomite (calcium magnesium carbonate). It is available at favourable pound-volume costs, and is produced in a broad range of particle size distributions. Current commercial grades include surface-modified grades to promote ease of wetting and dispersion, which permit higher loading [3].

2.6 The preparation of flexible foam

Flexible polyurethane foam was prepared by reaction injection moulding. There are three systems for used in industry.

2.6.1 The one shot system

The one shot system is used to prepare flexible polyurethane foam by mixing the component such as polyol, isocyanate, water, surfactant, catalyst and other

additives in the mixing room. This system is suitable for continuous process. The diagram of the system is shown Figure 2.11.

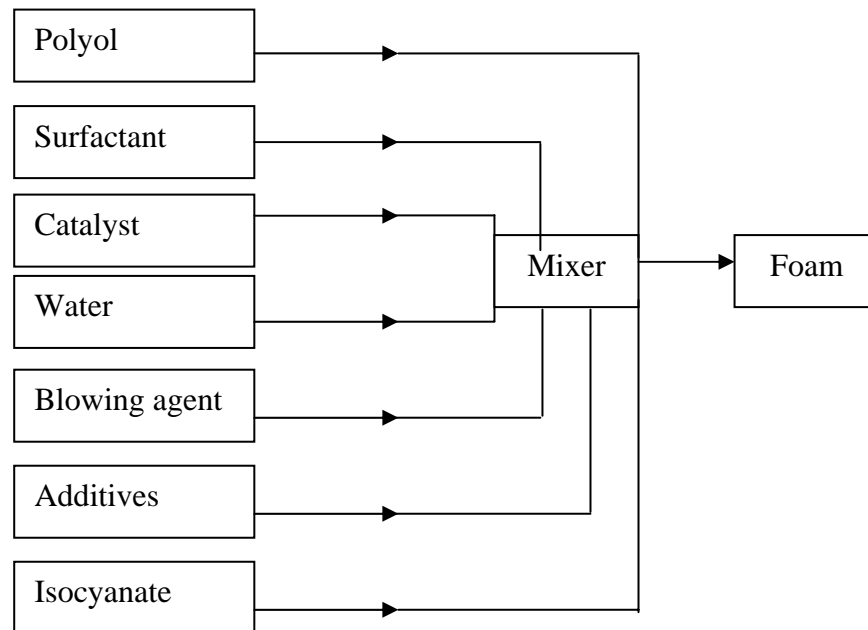


Figure 2.11 Diagram of the one shot system

2.6.2 The two component system

This system is to mix the components such as polyol, water, surfactant, catalyst and other additives in the mixing room. After that, the polyol premix is sent to mix with isocyanate in the mixing room. This system is suitable for both continuous and discontinuous process. The two component system is well mixed than the one shot system. This system can be used in the discontinuous process but materials will be lost the formulation is changed. The diagram of the two component system is shown in Figure 2.12.

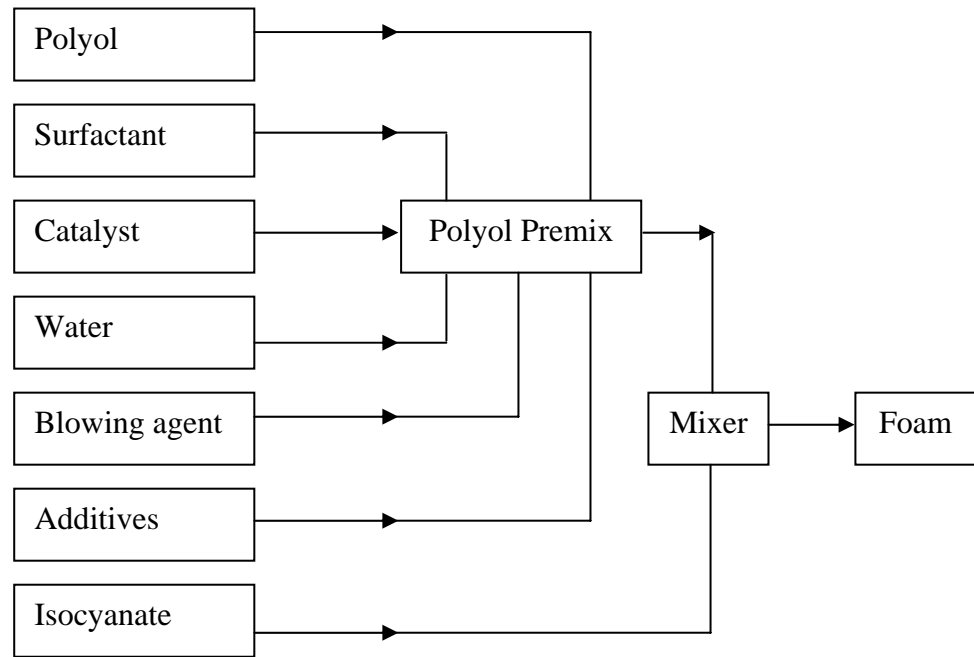


Figure 2.12 Diagram of the two component system

2.6.3 The quasi-prepolymer system

The quasi-prepolymer system separates polyol into two parts. The first part of polyol is mixed with isocyanate and is called prepolymer. The second part of polyol is then mixed with water, surfactant, catalyst and other additives in the mixing room. After that, the prepolymer and the second part components are mixed together in the mixing room. They are then sent to the mould of either continuous or discontinuous process. The mixture in this system is more homogeneous than that in one shot system. However, while changing the formulation in this process, the mixture will be lost more than that in other processes. The diagram is shown in Figure 2.13.

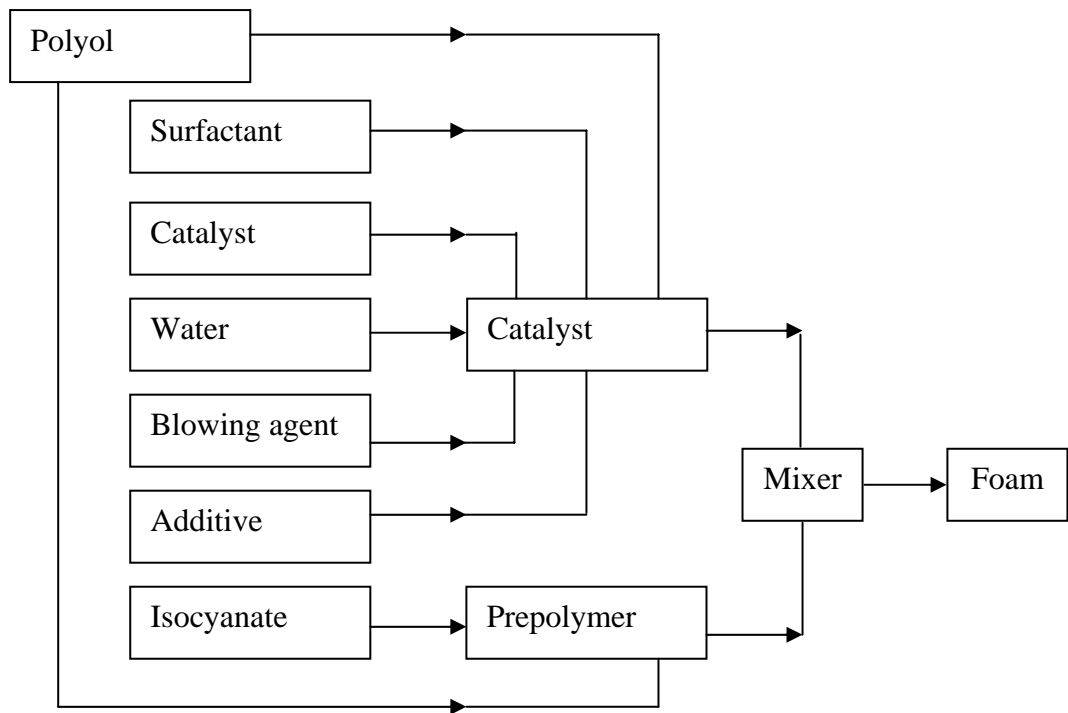


Figure 2.13 Diagram of the quasi prepolymers system

2.7 The formation of flexible foam

Flexible polyurethane foam is characterized by a density that is in the range of 10 kg/m^3 to 60 kg/m^3 , high tensile strength and elongation to break, and high resilience or fast recovery from deformation. The production of low density flexible foam is based upon slightly-branced polyester polyols and 65:35 = TDI:MDI, based upon polyether polyols and 80:20 TDI:MDI. MDI is also used, both alone and in combination with TDI, to make many other special-purpose, mould, low density foams.

Flexible foams are made commercially by a variety of manufacturing process. Detailed descriptions of the process for making slabstock and mould foams are presented as follows.

2.7.1 Flexible foam slabstock or block foam

More than half of the produced flexible polyurethane foam now is in the form of slabstock foam. Slabstock foam is high in demand because of its wide application and large volume usage. Most foams are made on continuous foam machine. Continuous process is proceeded by metering the foam reactant such as polyol, isocyanate, water, catalyst and other additives in the required proportions to a mixing head. The metered materials are then mechanically mixed and immediately distributed on the bottom lining of a continuously moving trough, formed by a horizontal bottom paper or foil and two vertical side papers or foils, carried on a long conveyor at a controlled and adjustable speed.

The distribution of the liquid foam reaction mixture may be assisted by the mixing head or its outlet nozzle across the moving trough. A distribution of the liquid foam reaction mixture over the bottom of the trough dose not result on foam blocks of the most economical rectangular cross-section. The drag and the cooling effect of the side-walls on the rising foam results in a domed section. After that pass trough the cutting or conversion process are foam in sheet of uniform thickness.

The manufacture of low density flexible foam slabstock by moulding individual blocks of foam is usually carried out by mixing a batch of foam reaction mixture and transferring it rapidly into a mould. The process requires that the measured components be thoroughly mixed and poured into the mould within a few seconds before the polymerization reaction has caused defects in the foam structure. The floating lid system and the viscous drag of the four sides of the mould tends to result in foam having a higher density than that made by the continuous process. This can be compensated by formulation adjustment, depending on the foam system and the size of block required. An essential requirement in low density flexible foam

slabstock manufacture is the provision of a separate, vented storage area where freshly made blocks of hot foam must be stored until cool. This area should be monitored and equipped with fire detection. The foam emerging from continuous foaming machines is usually cut into predetermined lengths, weighed, marked to indicate the grade of foam, the size and weight of the block, and the date of manufacture, and transferred to the hot foam store by automatic machinery. Then 12 to 24 hours after manufacture, when the blocks of foam have cooled and cured, they may be cut into sizes required for the final product. The first is usually to trim the sides and top of each block, using vertical and horizontal band knives, to produce a completely usable rectangular block having flat, uniform faces.

2.7.2 Moulded low density flexible foam.

It is estimated that 20 percent of low density flexible polyurethane foam is produced as finished products by moulding in closed moulds. Moulded foam is used for vehicle seating and interior trim, sound absorbing trim. Basically, foam moulding involves pouring the reacting mixture into suitable mould, closing the mould and allowing the foam to fill the mould. Two type of processes are used that are the hot moulding process, which has been established for over twenty years and the more recent one is the cold cure moulding processes.

Hot moulded foam is made by the reaction of TDI with polyether triols similar to those used in slabstock manufacture. External heat is applied to the mould after filling in order to obtain sufficient surface cure of the foam moulding to allow its early release from the mould. Wall of hot moulding is cast aluminum with thickness between 6 mm and 8 mm. The hot cure moulding process is base upon TDI. The amount of the foam reaction mixture is dispersed into mould conditioned at a temperature of about 40°C. The closed mould is then passed through a curing oven at

temperature of 150°C to 250 °C, depending on the mould design. The hot mould then passed, in succession, to stations for cleaning, applying of release agent, cooling, and back to the filling point. The foam density and hardness depends on the level of water and isocyanate used for blowing, the TDI index and the shape of the mould.

Cold cure moulding is used at low temperature and nearly constant temperature, so it consumes the less energy. Formulation of the process is two component systems for applications required by foam users in the automotive and furniture industries. The two component foam may be mixed and poured into moulds conditions at 25°C to 60°C, depending on the foam system adopted and on the material used for the mould. The completed moulding may be demoulded a few minute after pouring, without application of external heat to complete the cure.

2.8 The manufacture of polyurethane

Reaction between polyol and isocyanate begins immediately when two components are mixed. Polymerization is exothermic reaction. Basic requirements for polyurethane foam production are as follows.

2.8.1 Controlling temperature

Properties of polyol and isocyanate such as viscosity, density and chemical reactivity are varying with temperature. Controlling the temperature of the component is essential to processing of polyurethane foam. The effect of temperature variation on the polyurethane may change its physical properties.

2.8.2 Accurate metering or weighing

Polyurethane preparation, the formulation must be accurately controlled when the chemical are mixed together. Weighing the chemical component is potentially the

most accurate method of obtaining the correct proportions. The usual methods of polyurethane manufacturing, both continuous and discontinuous ones, require the use of metering pumps to transfer chemical components to a mixer in the correct proportions and at the required rate.

2.8.3 Effective mixing

Effective mixing is important for production polyurethane foam. Completely mixing can produce foam that has the best chemical dispersion.

CHAPTER III

LITERATURE REVIEW

Polymer composite are widely used in automotive industry because they provide improved mechanical properties (hardness and strength) and other physical properties. Micron-sized particulates and long fibers are most widely used in traditional polymer composites. Small size of composite was new class of materials providing superior properties when compared to their large size of composite. An addition of small-sized filler in polymer matrix can improve a variety of properties without sacrificing the lightweight of polymer matrices.

3.1 Methods for preparing polyurethane foam by adding filler

The chemical reaction between polyol and isocyanate starts spontaneously when they are blended together in the presence of suitable catalysts. Many polyurethane may be made on small scale by simply mixing the required ratios of the chemicals in a cup, using a suitable stirrer and hand pouring into a mould.

Polyurethane foam is prepared by mixing polyol and isocyanate components with a mechanical stirrer. The fillers are mixed with the polyol, after that additives such as surfactant, water and catalyst are added to premix in the polyol. They are then mixed with isocyanate and are poured into the mould [4-7]. The fillers were dried in an oven before using in order to eliminate water. Temperature of drying was 200 °C for calcium carbonate and 100°C for silica [7].

3.2 Properties of polyurethane composites

The fillers are sometimes used to reinforce polymeric materials [4,8]. For polyurethane foam, the system was much more complicated. They could affect the chemical reaction of the polyurethane formation and macroscopic cell geometry. High concentration of the fillers has increased the viscosity of the reaction mixture, affected the cell growth process and changed the cell geometry [4]. The effect of fillers on the properties of composites depends on their concentration, size, and shape. The nano-fillers have a small number of atoms per particles, therefore they may have different properties like optical, electrical, and magnetic properties than the bulk material. Apart from these, they have an extremely large surface area to volume ratio, and may have considerably stronger interaction with the matrix [9]. The correlation of the foam properties with the material structure is believed to be important but it has always been difficult to identify the individual contributions of the cellular structure and of the polymer to the foam physical properties [10].

The micro-silica fillers have average particle size of $1.5 \mu\text{m}$, concentration of fillers vary from 0-20% by weight of polyol. That has no effect to density of flexible and rigid polyurethane foam. However, it increases rebound resilience but decrease hardness and compression strength of flexible polyurethane foam. The average particle size of micro-silica fillers could be larger than the thinner part of the cell struts of polyurethane. During the rising of the foam, the fillers were probably in the plateau border area [4]. This was an area or space between several cells and it was formed as a result of the redistribution of the reacting polymer during the cell growth. This could cause thinning of the cell struts that would decrease the hardness and compression strength and increase rebound resilience.

The nano-silica fillers have average particle size of 12 nm, concentration of fillers vary from 0-20% by weight of polyol. The hardness and compression strength in flexible polyurethane foams with nano-silica was increased and the rebound resilience decreased. Reduced density of foams was not changed by nano-silica concentrations up to 20%. It was assumed that the nano-fillers, as an additional physical crosslinker, increased modulus in the polyurethane matrix [4], resulting in increasing hardness and compression strength.

For the nano-clay fillers, they could increase cell density, reduce cell size compared to pure polyurethane foam, show 6.5 times larger the polyurethane foam with high molecular weight polyol containing 5% of nano-clay, reduced compression strength and 7.8 times larger reduced modulus than pure polyurethane foam [6].

3.3 Effect of hard and soft segment of polyurethane foam

The polyurethane foam have two segment were consist hard segment and soft segment are shown in Figure 3.1. The literatures have been studied by several approaches effect of hard and soft segment to mechanical properties with the polyurethane foam. Foam properties are affected by the presence of crystalline structure with the soft segment phase. The soft segment was effect to result in increased hardness properties [11]. In addition, increasing the isocyanate index was increased the intermolecular [12-14]. Furthermore, there are in accordance with the soft segment increased, the tensile strength increased and the elongation at break decreased [15].

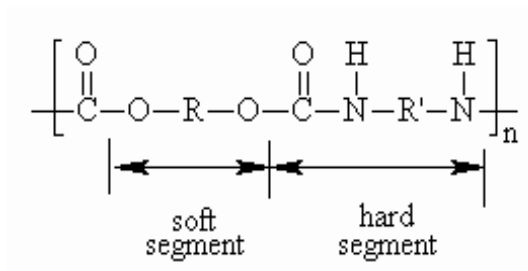


Figure 3.1 Structure of polyurethane foam with hard and soft segments

3.4 Effect of diisocyanate of polyurethane foam

Toluene diisocyanate (TDI) was effect to mechanical properties with polyurethane foam that it was increased tensile strength and decreased elongation properties compared to Diphenylmethane diisocyanate (MDI). Both TDI and MDI being aromatic the stiffness impacted by the aromatic ring cannot explain this observation. However, the difference in the structure of the diisocyanate can account for the difference in the mechanical properties. MDI has a linear symmetric structure consisting of two aromatic rings, imparting lower tensile strength due to the lack of rigidity in the backbone. But in the case of TDI a higher rigidity is imparted due to the direct association of the two isocyanate groups with the same phenyl ring. In addition, higher reactivity of TDI resulting from delocalization of negative charge on $-\text{NCO}$ by aromatic structure, also is responsible for greater tensile strength [13].

3.5 Effect of NCO/OH ratio of polyurethane foam

The NCO/OH ratio was effects to mechanical properties of polyurethane foam have be studied by several approaches. The ratio was greater than 1 or isocyanate index more than 100, the polyurethanes formed will be NCO terminated. These free

NCO group will react further to form three-dimensional allophanate or biuret crosslinks or polar urea structure thus increasing the number of urethane groups. The increased chemical crosslinking leads to a change in morphology and affects the mechanical properties and hardness are shown in Figure 3.2 and 3.3. The increase in NCO/OH ratio increase the intermolecular attraction of hard to hard segments which in turn increases the tensile strength and decreased the elongation [13].

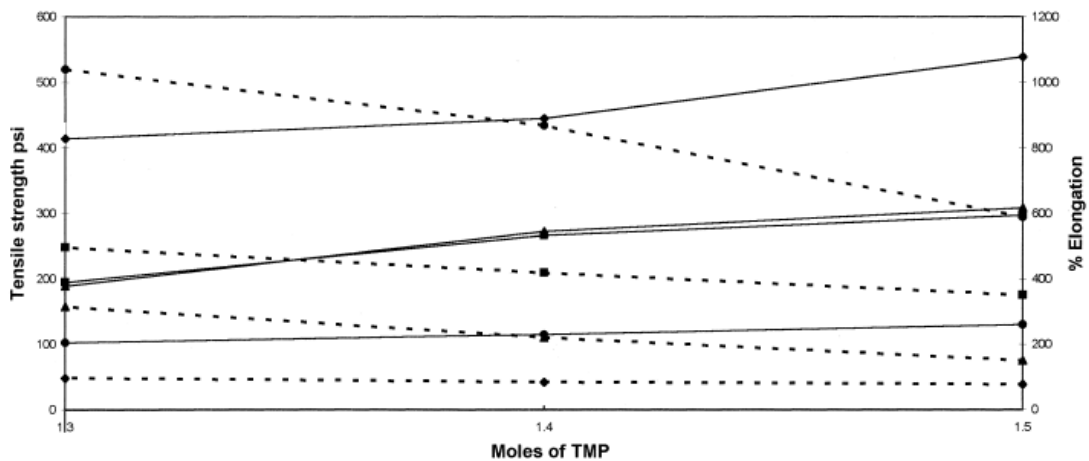


Figure 3.2 Effect of trimethylpropane concentration on tensile strength and elongation of polyurethanes with NCO : OH equivalent ratio 1.3. ◆ : H/T, ■ : H/M,

▲ : P/T, ● : P/M [13]

- Remark :
1. H/T : Hydroxy terminated polybutadiene/TDI/Trimethylpropane
 2. H/M : Hydroxy terminated polybutadiene/MDI/ Trimethylpropane
 3. P/T : Polypropylene glycol/TDI/ Trimethylpropane
 4. P/M : Polypropylene glycol/MDI/ Trimethylpropane

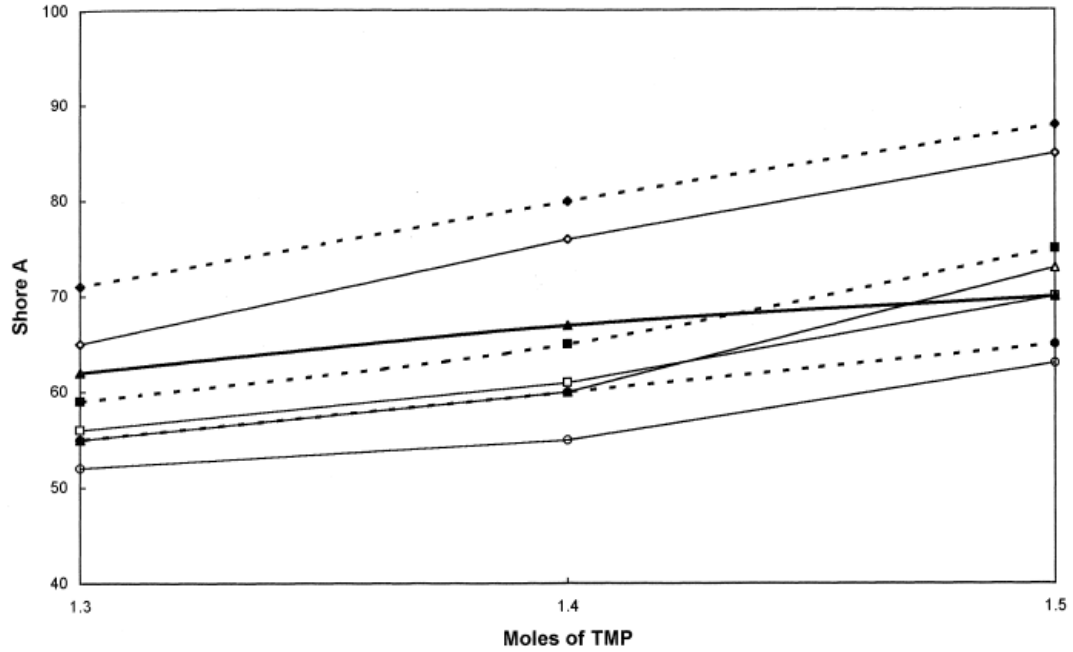


Fig. 3.3 Effect of TMP concentration on shore hardness of PUs with NCO : OH equivalent ratio. 1.3; \blacklozenge : H/T, \blacksquare : H/M, \blacktriangle : P/T, \bullet : P/M, and 1.2; \diamond : H/T, \square : H/M, \triangle : P/T, \circ : P/M [13]

3.6 Technique used for the characterization of composites

3.6.1 Infrared spectroscopy (IR)

Fourier transform infrared spectrometer (FT-IR) was determined the chemical bonding between the filler particles and polymer chains [15]. The functional group of the polyurethane foam have shown in various frequencies are shown in Table 3.1 and FT-IR spectra of composite of polytherpolyol are shown in Figure 3.4.

Table 3.1 Infrared band assignments observed in polyurethane foams [17,18]

Frequency (cm ⁻¹)	Band assignment
3305-3361	-NH
2277	Isocyanate
1730	Free urethane
1715-1710	Soluble urea
1697-1695	Free urea
1661	Intermediate urea
1645-1640	H-bonded urea
1625-1655	Carbonyl
1710-1700	H-bonded urethane
1697	Soluble D-urea
1638	Associated D-urea
1595	Phenyl
1415	Isocyanurate
1220	Urethane (-C-O-)

Two main regions are of interest, -NH absorption and -C-O- stretching. It is seen in Figure 3.4 that the -NH absorption peak at 3320 cm⁻¹ was due to hydrogen-bonded -NH groups of urethane linkages. In this case, such hydrogen bonding can be formed with hard segment carbonyl and with soft segment ether linkages. A small shoulder, seen at ~3420 cm⁻¹ is characteristic of stretching of free -NH groups.

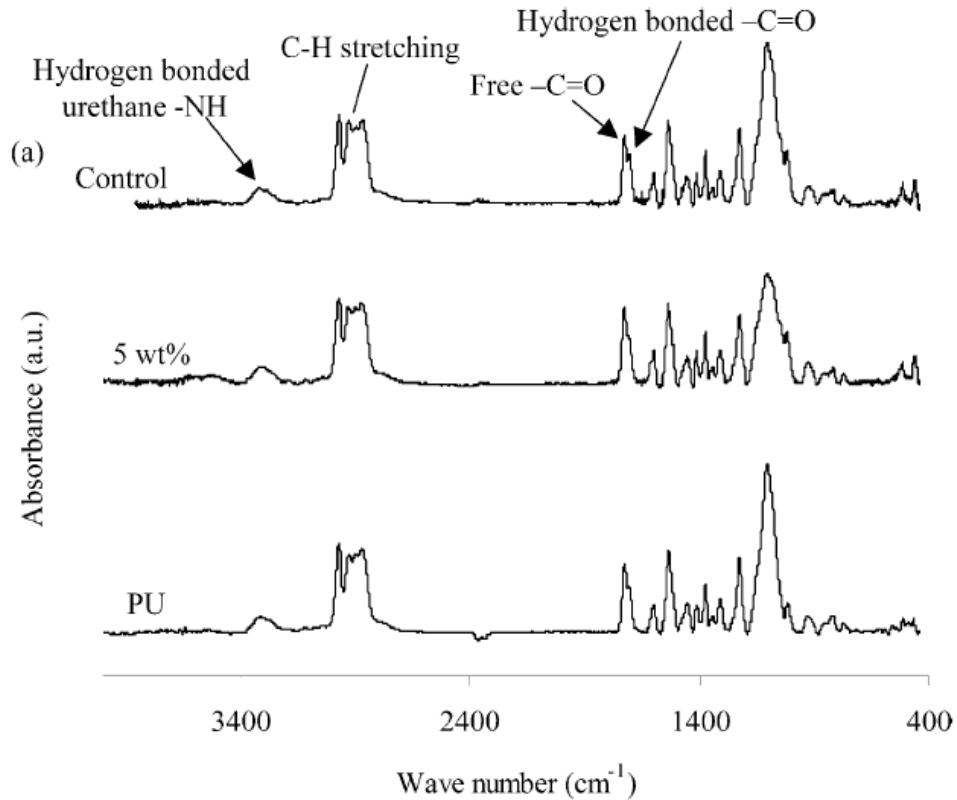


Figure 3.4 FT-IR spectra of composites of polyetherpolyol [19]

3.6.2 Scanning electron microscope (SEM)

Microstructures of nanoparticles was investigate by emission scanning electron microscope (SEM). Small amount of nanoparticles are placed on one side of a double-sided tape (opposite side is attached to the sample holder) for taking SEM pictures. Small samples from both neat and nanophased polyurethane foam are cooled to freeze in liquid nitrogen which are cut with a sharp razor blade and are placed on a sample holder with a silver paint. Both nanoparticles and foam samples are coated with gold palladium to prevent charge build-up by the electron to be absorbed by the specimen. All foam pictures are taken perpendicular to the rise direction. SEM micrographs of different nanoparticles are shown in Figure 3.5.

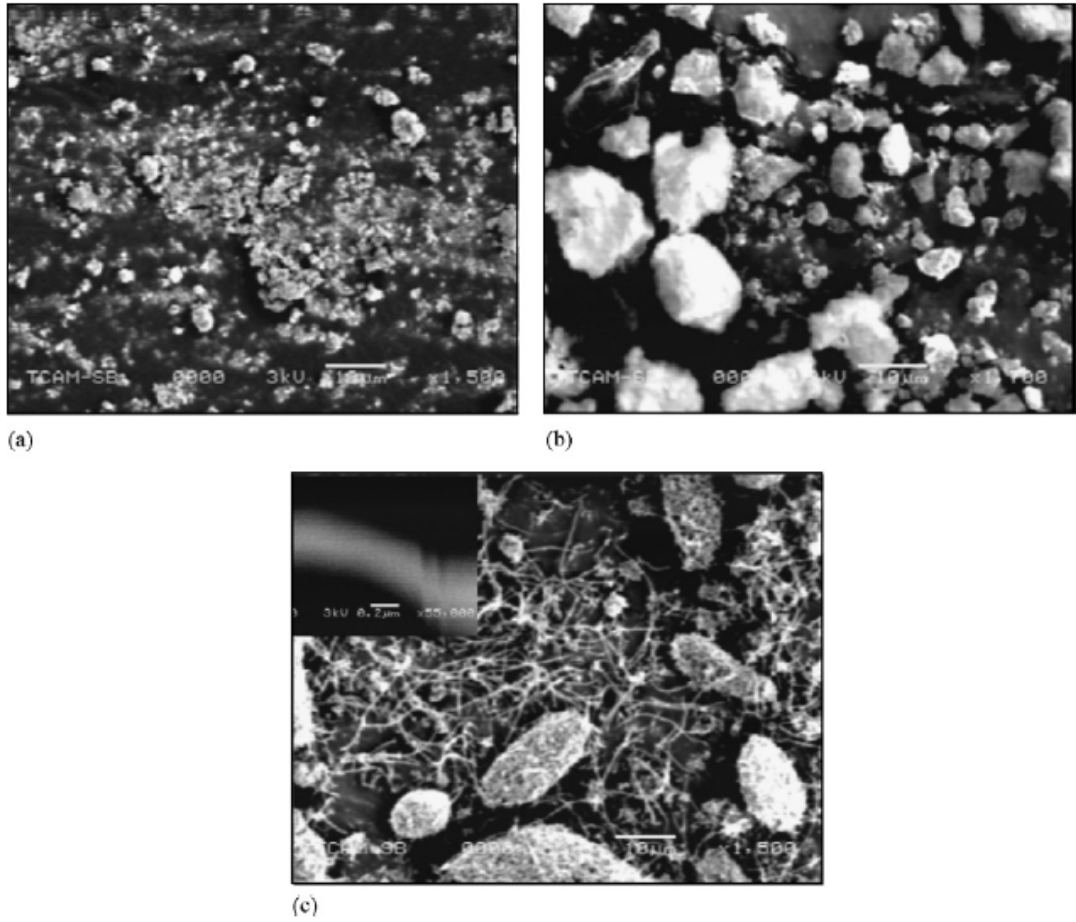


Figure 3.5 SEM micrographs of different nanoparticles used : (a) TiO₂ (1500x), (b) nanoclay (1100), and (c) carbon nanofibers (1500x) [16]

CHAPTER IV

EXPERIMENT

4.1 Materials

The flexible polyurethane foam material consists of isocyanate, polyol and calcium carbonate filler. The isocyanate used in this study was a polymeric aromatic isocyanate based on toluene diisocyanate (TDI) with diphenylmethane diisocyanate (MDI) (TDI:MDI = 80:20) from Bayer Group with NCO content of 44.8 % by weight. Polyol from Bayer Polyurethane Taiwan Company, a ready-for-use polyether polyol formulation for the production of the flexible polyurethane foam with hydroxyl number of 30 mg.KOH/g, was used in this study. Calcium carbonate particles from Behn Meyer having an average diameter of 1 μm and density range of 2.3 – 2.6 g/cm^3 was used in this study.

4.2 Method

Polyurethane foam was prepared by mixing polyol and isocyanate component with a mechanical stirrer. The isocyanate, polyol and calcium carbonate filler was weight out into a suitable mechanical stirrer. The mechanical stirrer was used to prepare a mixture of calcium carbonate filler and polyol, as shown in table 4.1, mixed thoroughly for 60 second using speed is 6,000 rpm. The temperature of the chemical was controlled in the range of 21 ± 1 °C using dry ice. Isocyanate add was added to the mixture and mix again for 8 second depending on cream time. After that the mixture

was poured into a suitable box or mould and cream time, gel time and rise time were record.

Table 4.1 Isocyanate index and quantity of calcium carbonate filler

Isocyanate index	CaCO ₃ filler into polyol
90	} Add filler 0, 3, 5, 7 and 10% by weight
100	
110	

4.3 Characterisation

4.3.1 Infrared Spectrometer (IR)

Infrared Spectrometer (IR) was used to determine the chemical bonding between the fillers and polymer chains. Infrared light was sent onto or through the sample. The substance was identified by comparing its IR spectra from known reference peak.

4.3.2 Scanning Electron Microscopy (SEM)

The characterisation of the cellular structure and the cell size of the polyurethane foam were performed with a Scanning Electron Microscopy (SEM). First, the samples were freeze-fractured in liquid nitrogen. Then the fracture surface were gold coated to make them conducting. The micrographs obtained were estimated by image analysis with the software.

4.4 Mechanical properties test

4.4.1 Tensile strength

The specimens for tensile strength tests follow as dumbbell No.1 of JIS K6301 were shown in Figure 4.1. Tensile strength was apply at the rate of 200 mm./min. Tensile strength was measurement shall be performed by reading the maximum load up to the time of cutting of the test pieces. Tensile properties were the average of at 5 pieces specimens. Calculation

$$T = \frac{F}{A}$$

Where ; T : Tensile strength (Kgf/cm²)
 F : Maximum load (Kgf)
 A : Section area of the test piece (cm²)

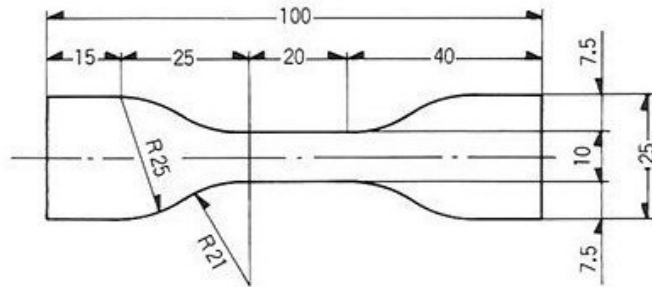


Figure 4.1 Dumbbell No.1 Under JIS K 6301

4.4.2 Elongation test

Elongation test was performed according to JIS K6301 using specimen dumbbell No.1. The dumb-shaped was test piece measure the gauge length to with mm. by the rate of 200 mm./min at the time of cutting. Elongation properties were the average of at 5 piece specimen.

Calculation

$$E = \frac{L_1 - L_0}{L_0}$$

Where ; E : Elongation (%)

L₀ : Gauge length (mm.)

L₁ : Length between indicators at the time of cutting

(mm.)

4.4.3 Resilience test

Resilience tests were performed according to ASTM D3574. The foam sample was cut in size of thickness = 50 mm, width = 100 mm, length = 100 mm. After that, the foam sample was crush by hand 40 times before take it to a position A, which shown in figure 4.2. The zero percentage's line was move to a top of foam by turning a knob at the side of the equipment. The switch bottom was press to plumb the ball and simultaneously observe the ball at highest rebounding point. The results were record and take the ball at highest rebounding point. There were record the result and take the ball back to the top gap. There were repeat 3-5 times, maximum percentage result is reported the ball rebound test.

4.4.4 Hardness test

Hardness tests was performed according to JIS K6301 using specimen with dimension is thickness = 25 mm, width = 50 mm, length = 50 mm. The specimen was compress downwards with a preload of 0.392 N using a plate 100 mm in diameter. It was measure the thickness under this condition (initial thickness). The specimen was compress 75% of its initial thickness at the speed of 50 mm/min. It was remove the load immediately and compress again 25% of its initial thickness at the speed of 50

mm/min, maintain this condition and measure the load 20 second later. It was report the measurement as the hardness (expressed in N).



Figure 4.2 Resilience Tester



Figure 4.3 Auto Urethane H/N Tester

4.5 Physical properties test

Density test was performed according to ASM D3574. Foam sample was cut in size of thickness = 50 mm, width = 100 mm, length = 100 mm and measure actual dimension of foam by vernier again. After that it was weight to calculate density of foam.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Effect of filler on polyol blend

Polyurethane foams were prepared by mixing both the polyol and isocyanate component with a mechanical stirrer. The calcium carbonate which was used as filler must be dried before mixing. This content of filler loading was varied as 0, 3, 5, 7 and 10% by weight of polyol. Then the polyol was mixed with isocyanate and poured into the mold to produce the free rise foam.

The viscosities of polyol blend with different fillers loading were measured with viscometer. The results were shown in Figure 5.1. At any filler loading, the viscosity of polyol blend decreased with increasing temperature. At any temperatures, the higher the CaCO_3 loading, the higher the viscosity of the polyol blend. Hence, filler loading obviously affected the viscosity of the polyol blends. This could be due to CaCO_3 filler dispersion into the polyol therefore there were increased the CaCO_3 loading with an increased the viscosity of the polyol blend. It should be noted that there was a cell collapse of polyurethane foam at CaCO_3 loading of 7-10 wt% and isocyanate index 110.

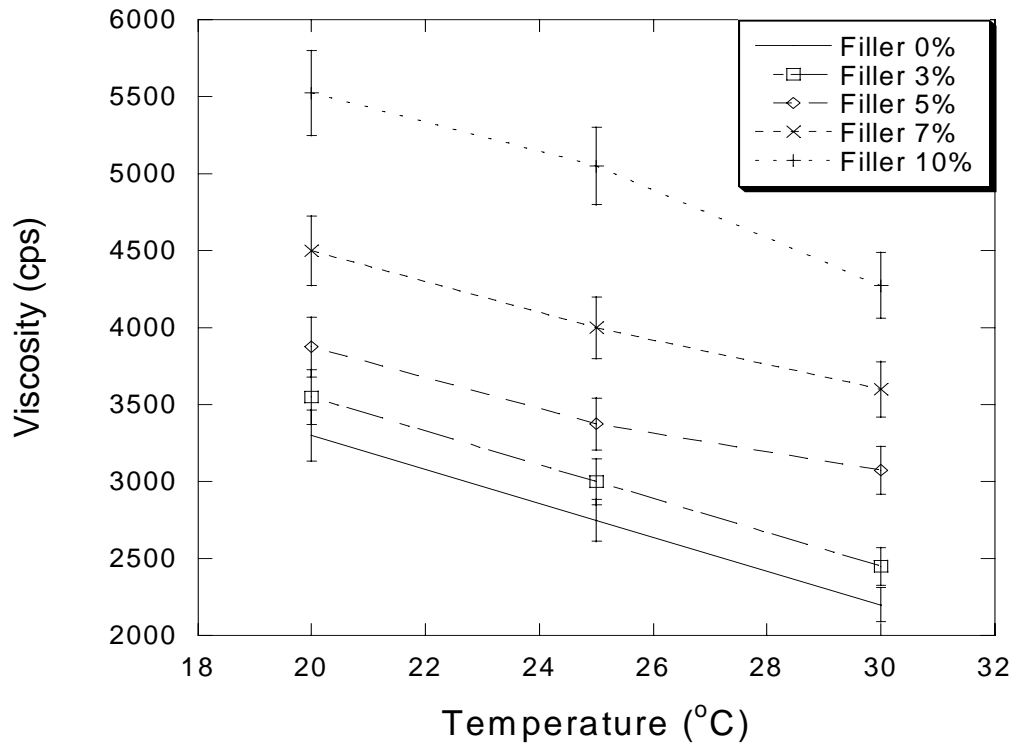


Figure 5.1 Effect of filler on the viscosity of polyol blend at isocyanate index 100

5.2 Cream time, gel time and rise time of polyurethane foam

Cream time is the time between the discharge of the foam ingredients from the mixing head and the beginning of the foam rise. At this point, the color of surface of the liquid is changed, usually turning lighter as a result of saturation of the liquid with evolving gas. Gel time is the time between the discharge of the foam ingredients from the mixing head and the point at which the foam has developed enough gel strength to resist light impressions and is dimensionally stable. Furthermore, rise time is the time between discharge of the foam ingredient from the mixing head and the point at which the foam rise is complete. In this study the effect of the calcium carbonate filler on cream time, gel time and rise time was investigated for polymerization of polyurethane reaction.

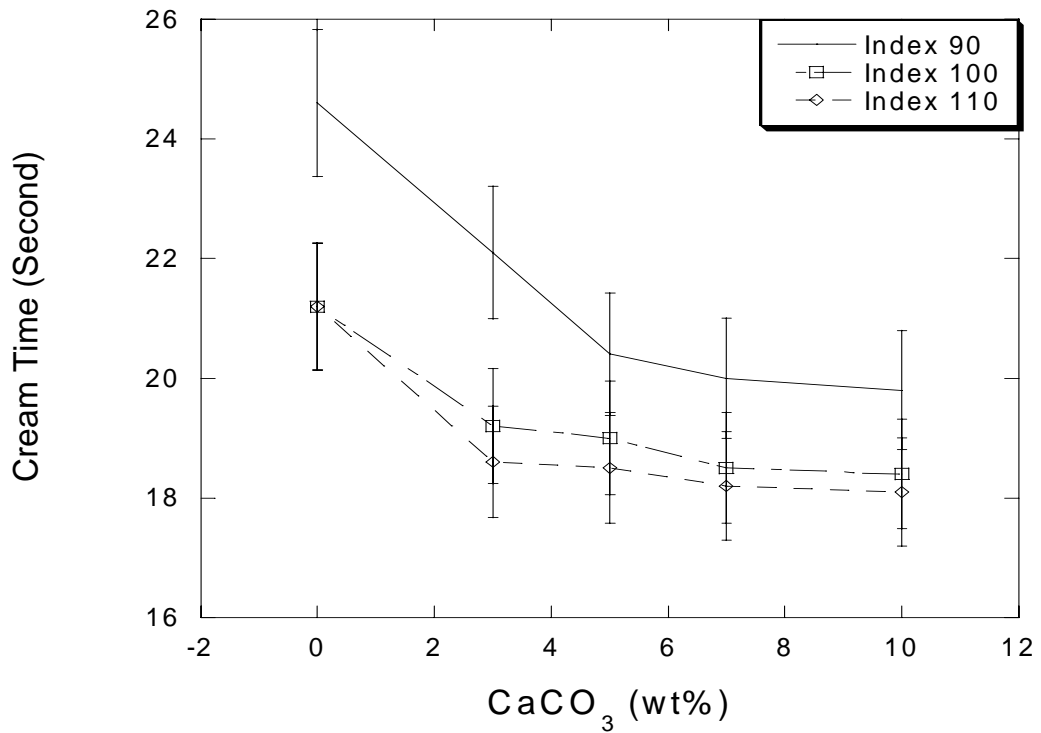


Figure 5.2 Effect of the CaCO₃ filler on cream time of flexible polyurethane foam at 90-110 isocyanate index

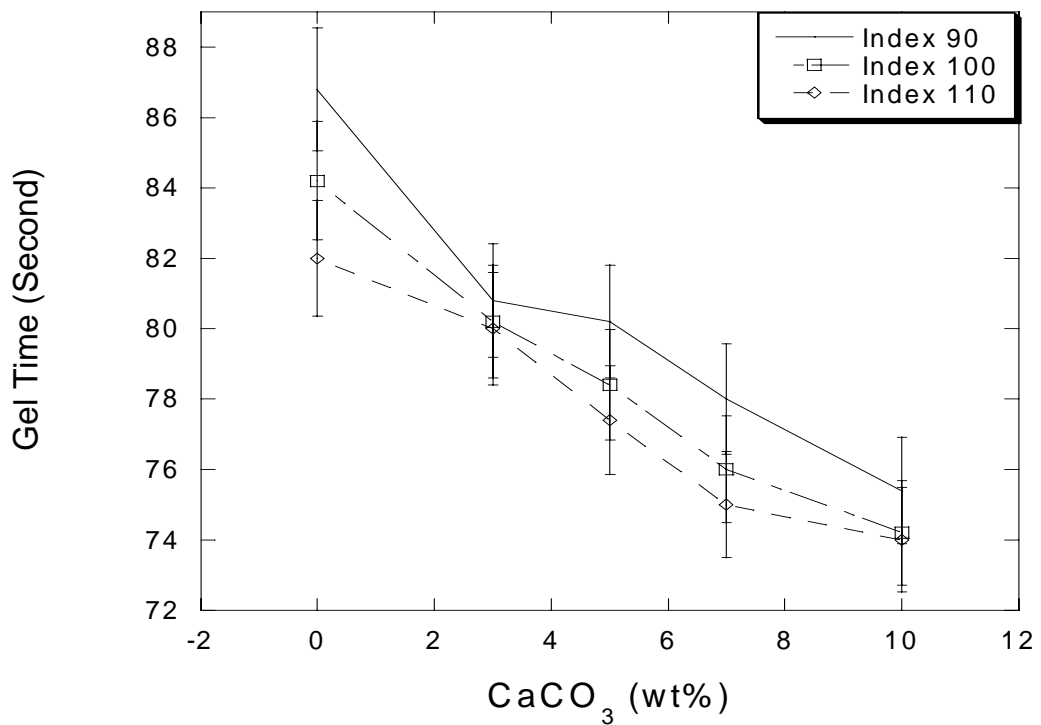


Figure 5.3 Effect of the CaCO₃ filler on gel time of flexible polyurethane foam at 90-110 isocyanate index

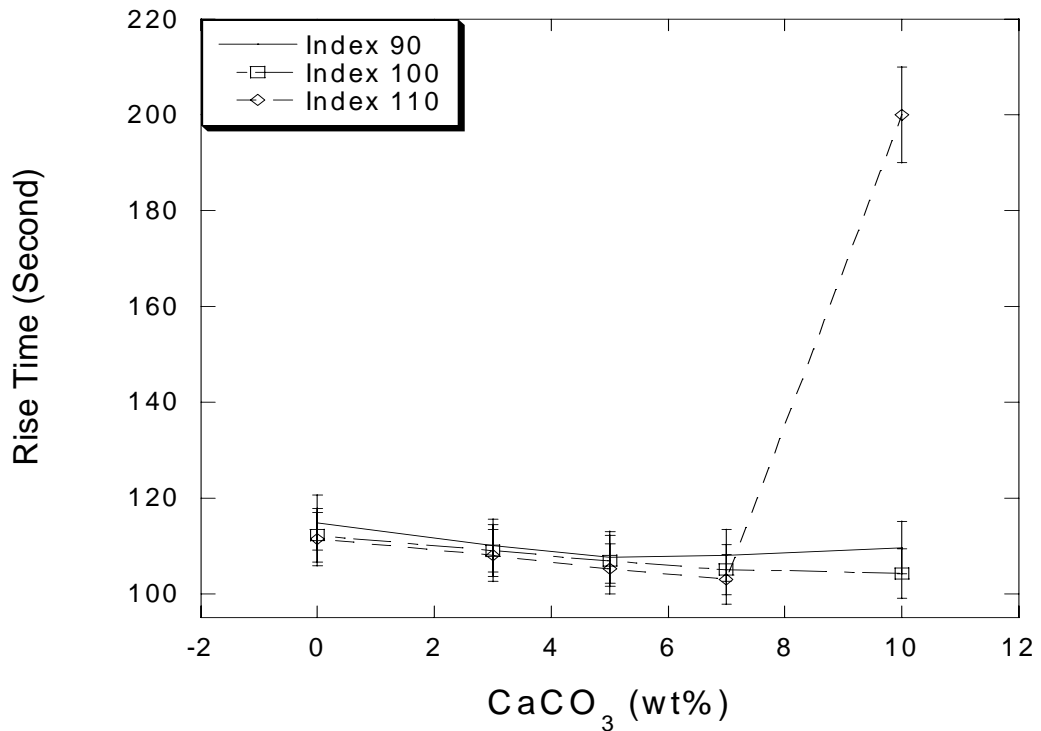


Figure 5.4 Effect of the CaCO₃ filler on rise time of flexible polyurethane foam at 90-110 isocyanate index

The effects of calcium carbonate filler loadings on the cream time, gel time and rise time were shown in Figure 5.2-5.4. It could be observed that cream time, gel time and rise time tended to decrease when there is an increase of calcium carbonate content except 10 wt % of filler for rise time at isocyanate index 110. The filler could reduce the linkages of polyurethane foam; thus, reduce the polyurethane foam reaction's time. In addition, FTIR peak as shown in Figure 5.10-5.12 exhibited the decrease of urethane linkages when calcium carbonate content was increased which is consistent with the reduction of the time of reaction. On the other hand, when 10 wt% of calcium carbonate was added at index 110 the cell foam collapsed which increased rise time of the polyurethane foam reaction.

5.3 Physical property of polyurethane composite

Density test was performed according to the ASTM D3574. The density of polyurethane foam was increased with an increase of isocyanate index. In general, the reaction of polyurethane foam consists of reaction of water with $-NCO$ group (isocyanate) to produce carbon dioxide to make cell foam rise. The amount of carbon dioxide thus affects the density of polyurethane foam. For polyurethane foam with isocyanate index 110, there was an excess of isocyanate in which the amount of polyol was not enough to react with, thus this reaction produced less carbon dioxide than that with isocyanate index 100. In fact, the polyurethane foam with isocyanate index 110 is slightly denser than other foams. In addition, the increase isocyanate index or when NCO/OH ratios were increased chemical cross-linking leads to increase the density of polyurethane foam [13].

Effect of the calcium carbonate filler loading on the density of flexible polyurethane were shown in Figure 5.5. The addition of calcium carbonate filler slightly increased the density of the polyurethane foam at isocyanate index 90-110. Because the fillers were tiny and have high surface area, it could disperse throughout the polyurethane matrix, thus increases the density of polyurethane foam. At the isocyanate index 110, adding 10 wt% of calcium carbonate increased the density of polyurethane remarkably because the calcium carbonate filler caused the cell foam to collapse after very long rise time.

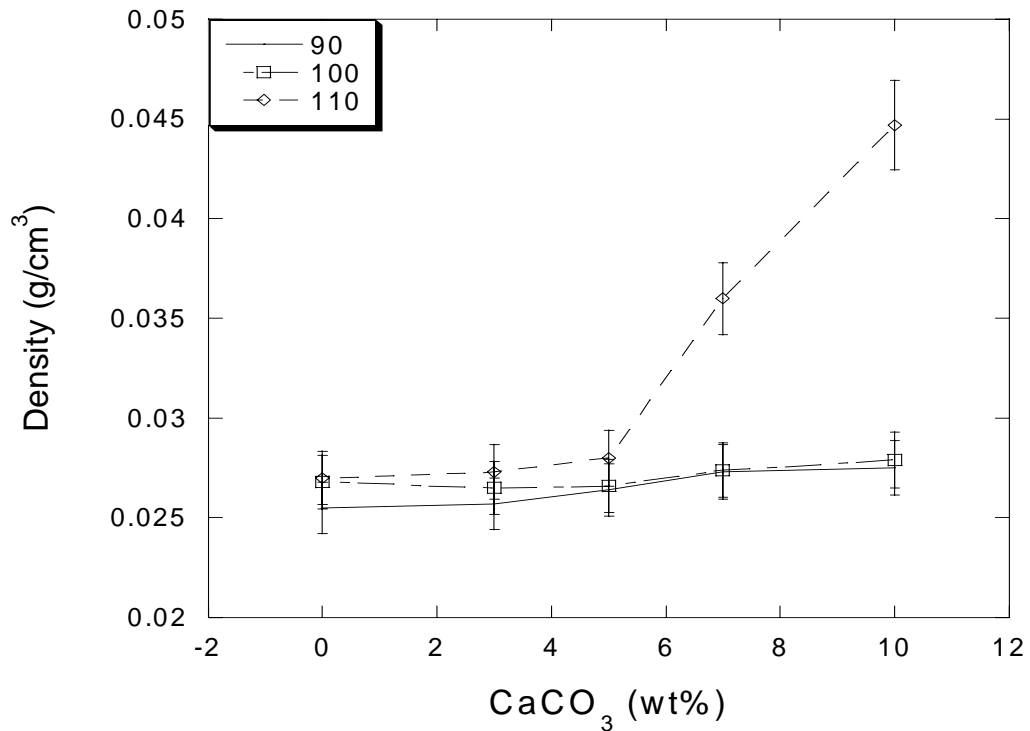


Figure 5.5 Effect of the calcium carbonate filler on density of flexible polyurethane foam at 90-110 isocyanate index

5.4 Chemical reactivity between filler-particles and polyurethane

Fourier Transform Infrared Spectrometer (FTIR) was the method to verify the functional group or the intermolecular interaction of organic substance. FTIR spectra of polyurethane composite foam with isocyanate index 90, 100 and 110 respectively were shown in Figure 5.6, 5.7 and 5.8. It could be observed that spectrum of polyurethane composite foams showed the similar peaks in the observed range. This indicates that the structure of polyurethane foam has not been affected by the presence of calcium carbonate filler, which implies that calcium carbonate filler did not react with the polyurethane molecule. However, the fillers do affect the reaction between isocyanate and polyol as can be seen from FTIR results.

As shown in the Figure 5.6–5.8, two main regions were of interest in this study, i.e., -NH absorption and -C-O stretching. It could be observed that the -NH absorption peak at 3430 cm^{-1} was due to hydrogen-bonded -NH groups of urethane linkages. In this case, such hydrogen bonding could be formed with both hard segment and soft segment, i.e., ether linkages. A small shoulder as seen at $\sim 3420\text{ cm}^{-1}$ was the characteristic of stretching of free -NH groups. The peak at $\sim 1100\text{ cm}^{-1}$ was assigned to free urethane carbonyl, while the peak at $1715\text{-}1725\text{ cm}^{-1}$ was due to hydrogen bonded carbonyl [20] and the peak of -C-O- segment could be seen at 1200 cm^{-1} .

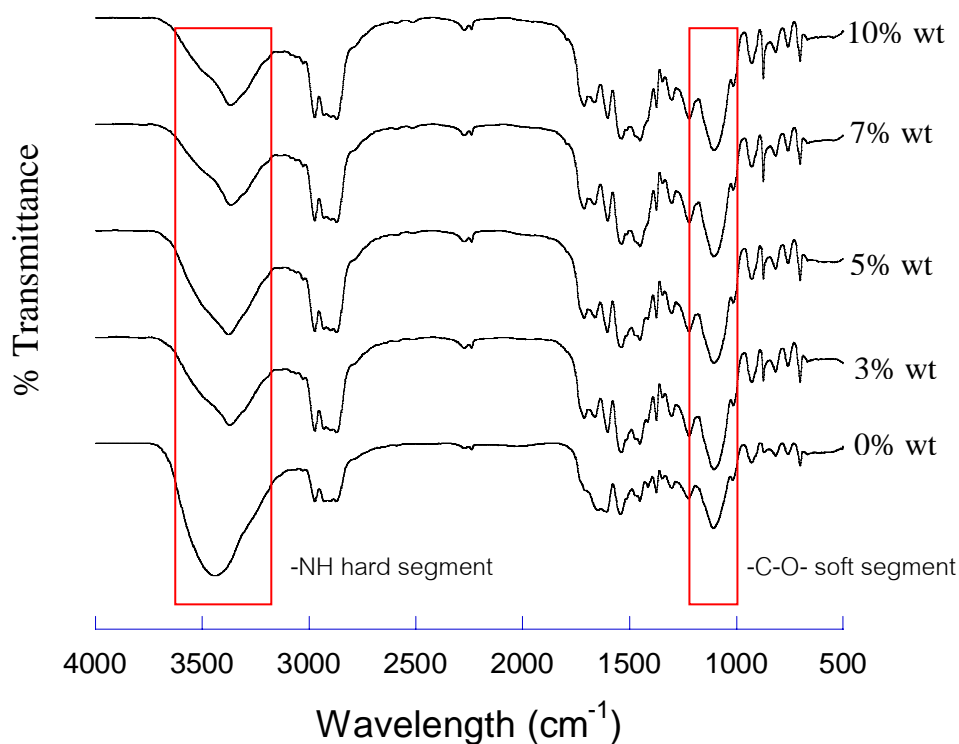


Figure 5.6 FTIR of polyurethane foam at isocyanate index 90

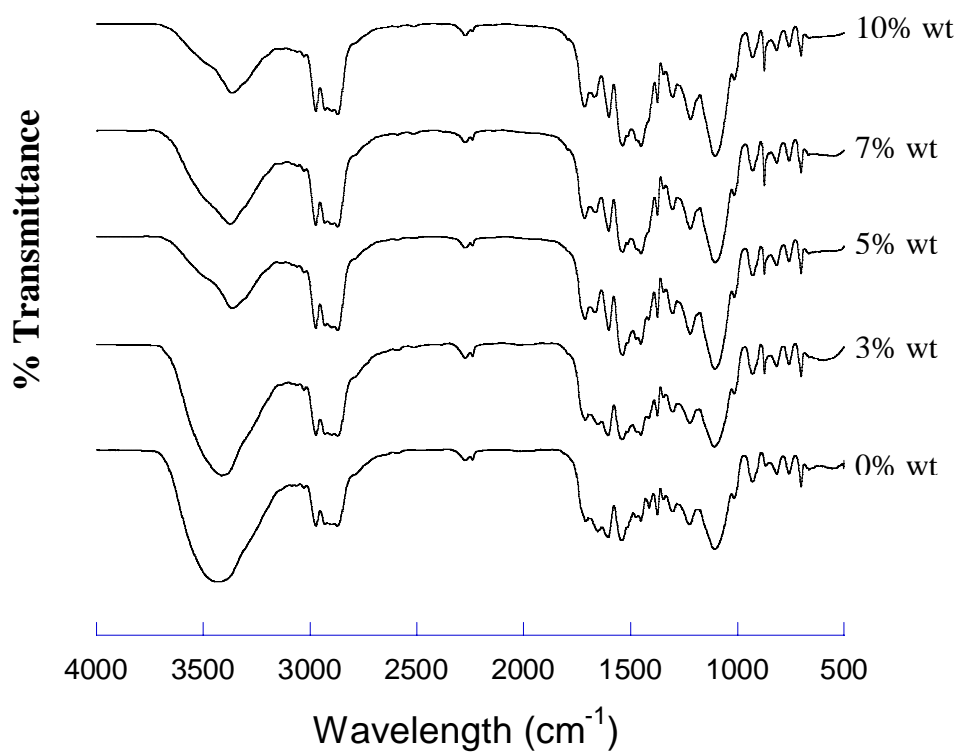


Figure 5.7 FTIR of polyurethane foam at isocyanate index 100

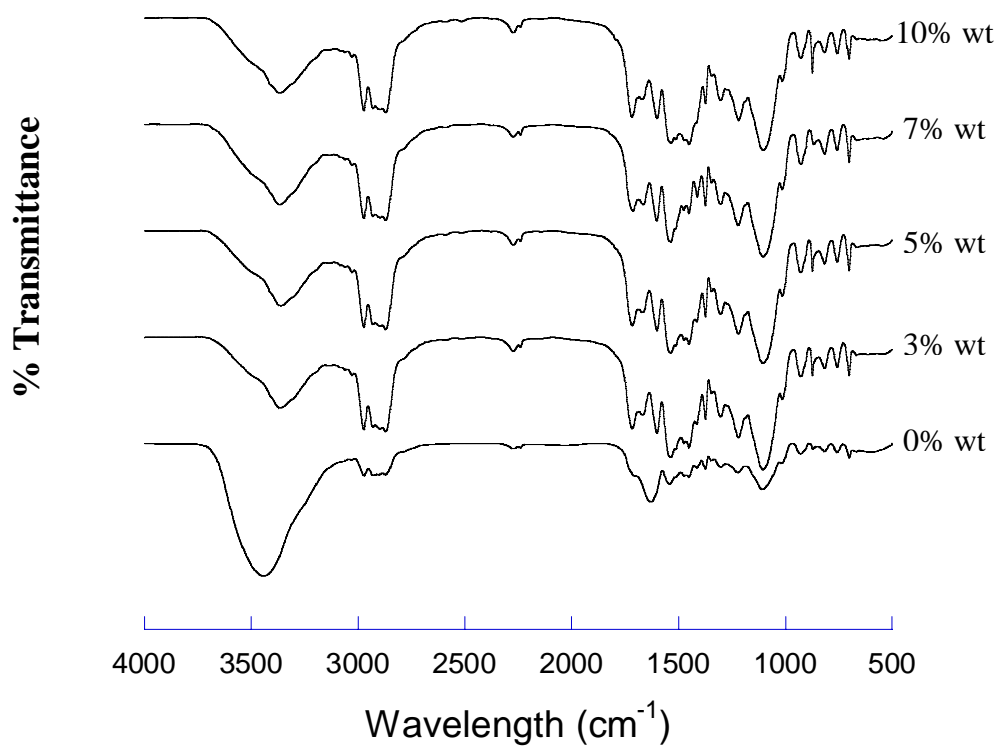


Figure 5.8 FTIR of polyurethane foam at isocyanate index 110

In addition, the functional group of the polyurethane foam was shown in various frequencies as shown in Table 3.1. The transmittance of the different groups was measured by employing a common baseline in order for calculation. It was necessary to choose a functional group that can be use as a reference group to analyze both the -NH and -C=O functional groups quantitatively. In this study, the -C=O (carbonyl) group was used as a reference because this functional group remained constant for all FTIR measurements. The ratios of -NH/C=C functional group and $\text{-C-O-}/\text{C=C}$ functional group segments were plotted as a function of the amount of calcium carbonate filler in Figure 5.9 and 5.10, respectively.

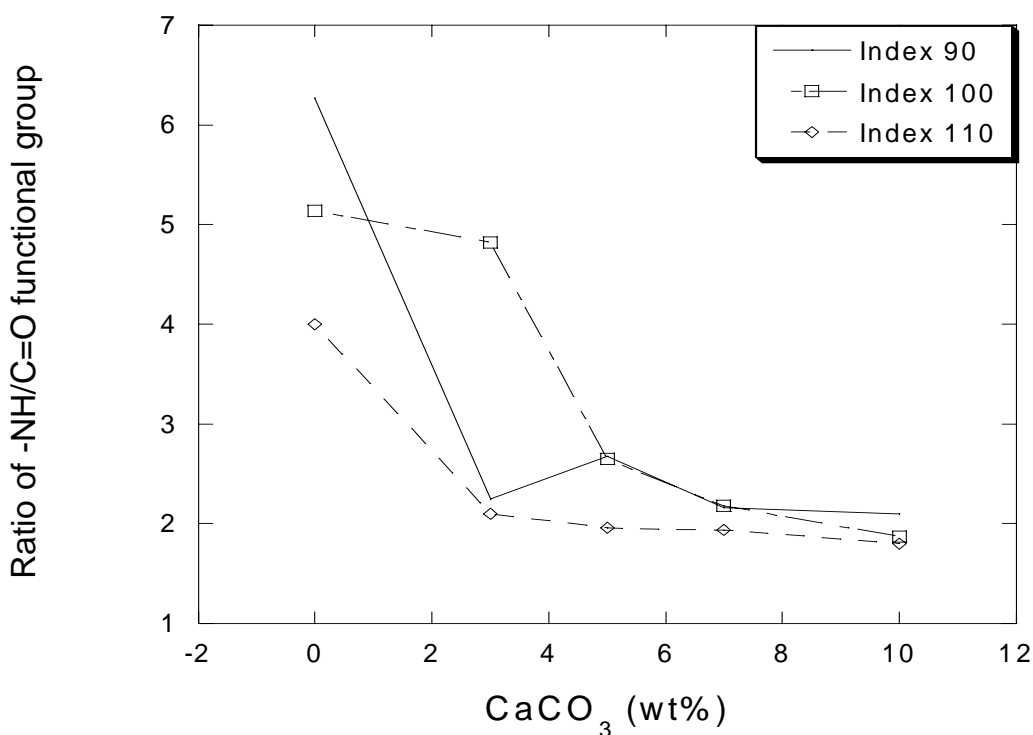


Figure 5.9 The ratio of -NH/C=C functional group of flexible polyurethane composite foam

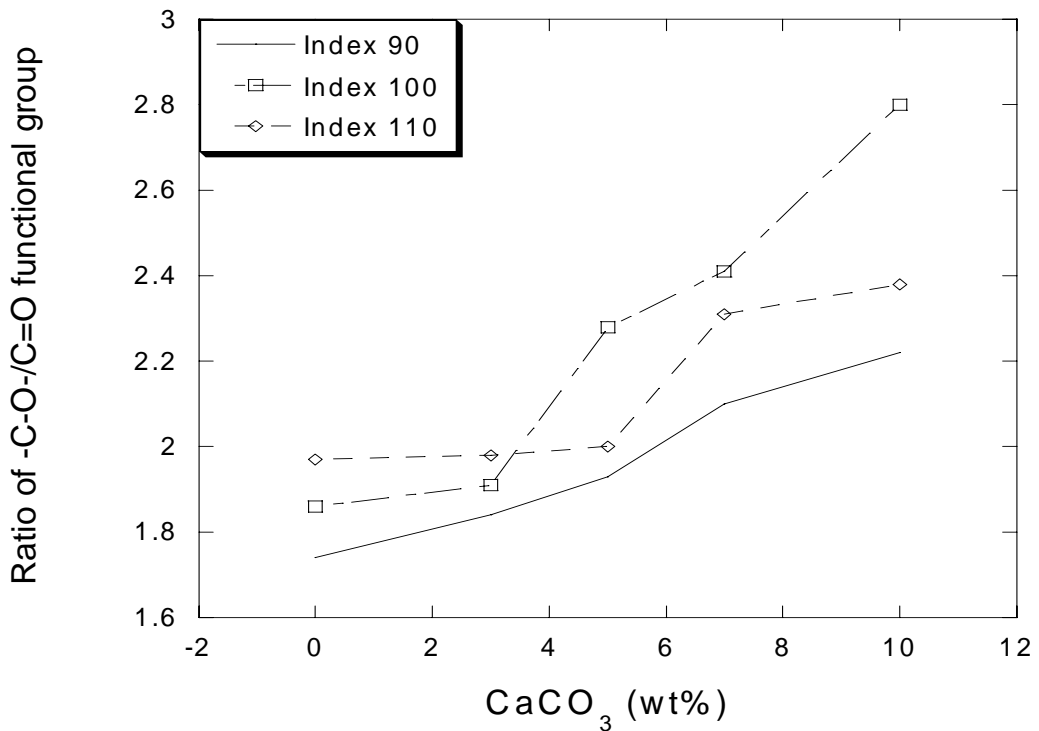
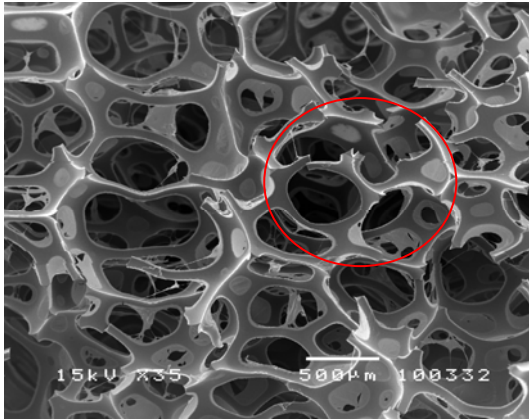


Figure 5.10 The ratio of $-C-O-/C=C$ functional group of flexible polyurethane composite foam

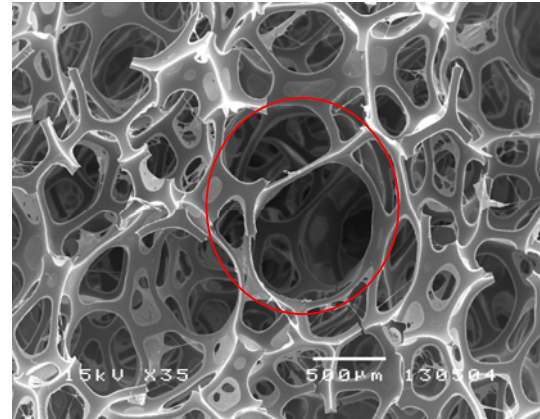
It could be observed that the ratio of $-NH$ segment was decreased with an increase the isocyanate index. In contrast, the ratio of $-C-O-$ segment was increased with an increased the isocyanate index. Although, calcium carbonate filler has not reacted with both polyol and isocyanate in order to hinder the reaction of polyurethane foam but it shifted the reaction by increasing the $-C-O-$ group or soft segment. From FTIR results, it could be assumed that amount of calcium carbonate would increase the soft segment of ether linkage but decrease the urethane linkage.

5.5 Structure of polyurethane composite foam

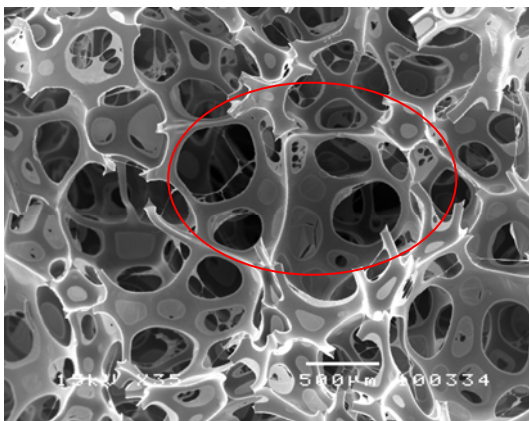
The cell structure of the polyurethane foam was investigated by Scanning Electron Microscopy (SEM). The SEM micrograph of pure flexible polyurethane foam was shown in Figure 5.11(a). It can be compared to the cell structure of the composite foams with calcium carbonate 3, 5, 7 and 10% by weight of polyol as shown in Figure 5.11(b-e). Generally, polyurethane foams can also be defined as either closed cell or open cell foams. For closed cell foams, the foam cells were isolated from each other and cavities were surrounded by complete cell walls that have effect on lower permeability, leading to better insulation properties. However, in open cell foams, cell walls were broken and the structure consists of mainly ribs. In this study, open cell type could be observed from SEM micrographs of all flexible polyurethane foam. When the amount of calcium carbonate increased, the SEM micrographs look similar, thus showing open cells. However, adding filler into polyurethane foam would increase closed cells which could inherently alter the foam properties such as air flow [21]. In addition, adding filler would make the cell struts was much thicker thereby giving rise to somewhat higher density foam which was consistent with the density of composite foams.



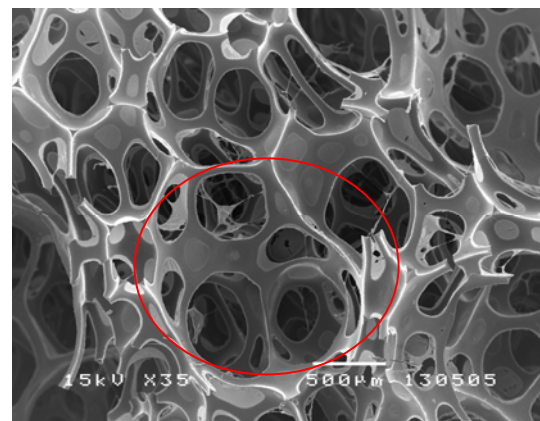
(a) Index 90, CaCO₃ 0%



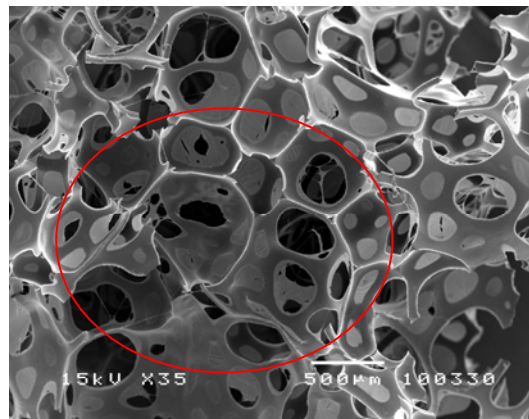
(b) Index 90, CaCO₃ 3%



(c) Index 90, CaCO₃ 5%



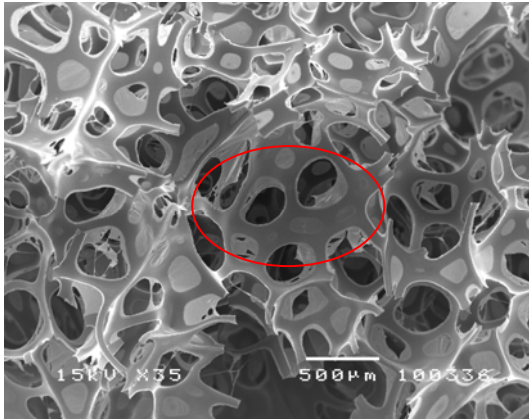
(d) Index 90, CaCO₃ 7%



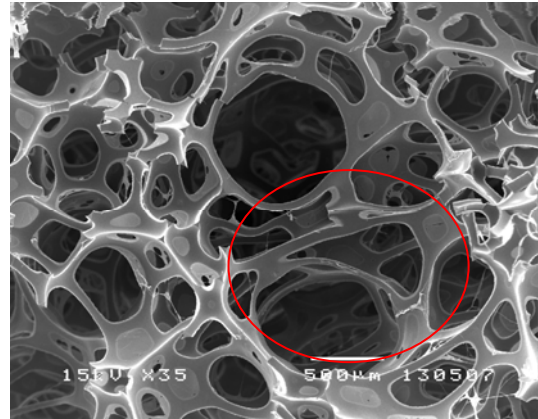
(e) Index 90, CaCO₃ 10%

Figure 5.11 SEM micrographs of cell structure of flexible polyurethane foam

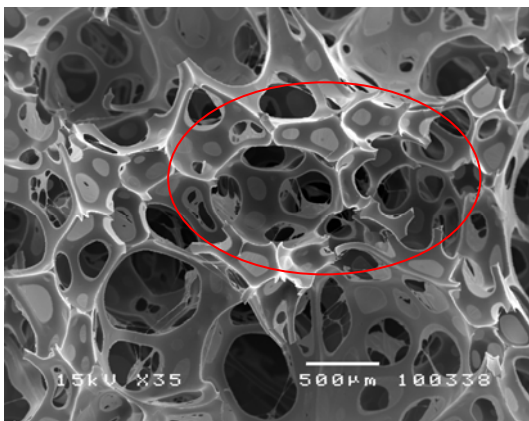
Index 90 with CaCO₃ 0, 3, 5, 7 and 10wt%



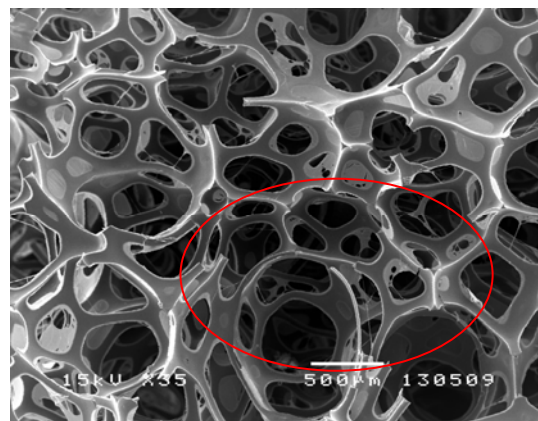
(a) Index 100, CaCO₃ 0%



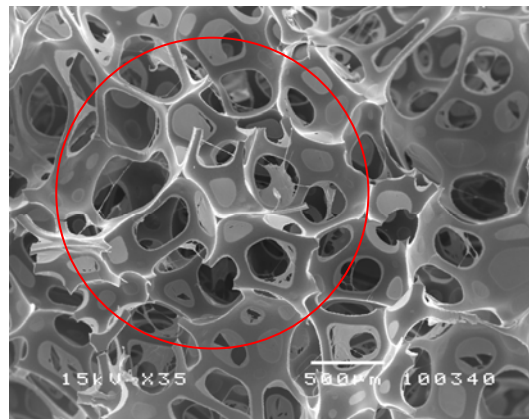
(b) Index 100, CaCO₃ 3%



(c) Index 100, CaCO₃ 5%



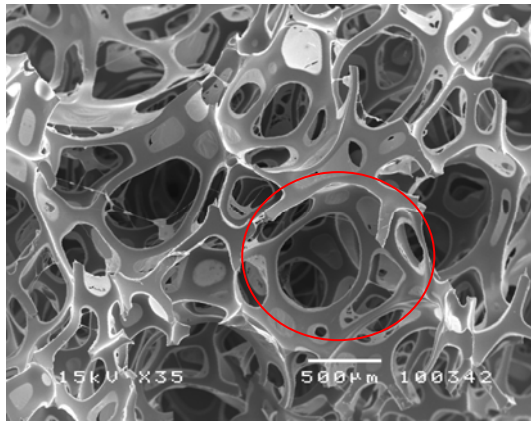
(d) Index 100, CaCO₃ 7%



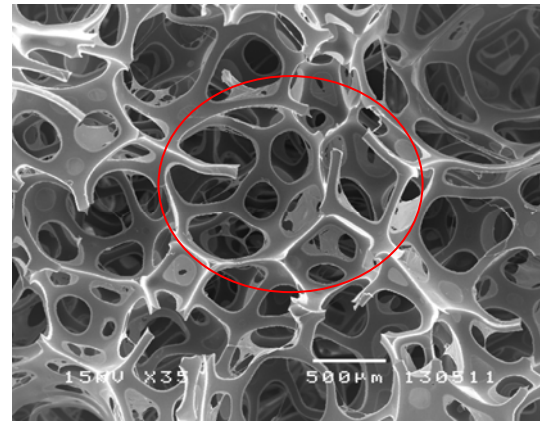
(e) Index 100, CaCO₃ 10%

Figure 5.12 SEM micrographs of cell structure of flexible polyurethane foam

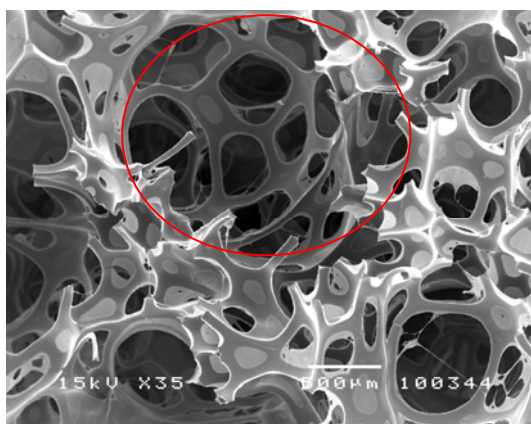
Index 100 with CaCO₃ 0, 3, 5, 7 and 10wt%



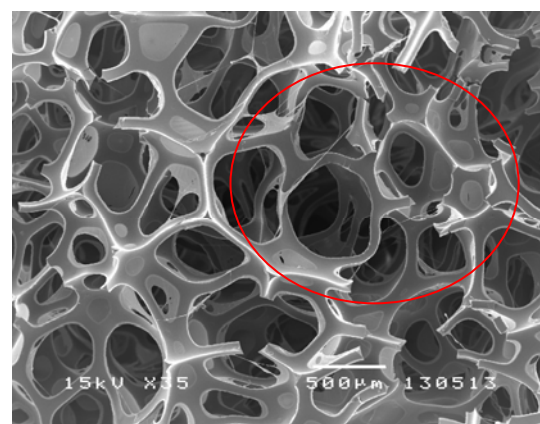
(a) Index 110, CaCO₃ 0%



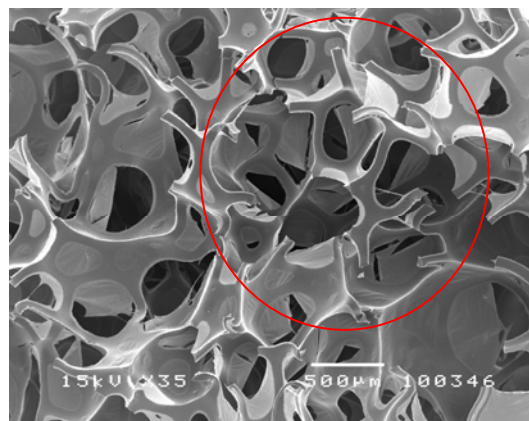
(b) Index 110, CaCO₃ 3%



(a) Index 110, CaCO₃ 5%



(d) Index 110, CaCO₃ 7%



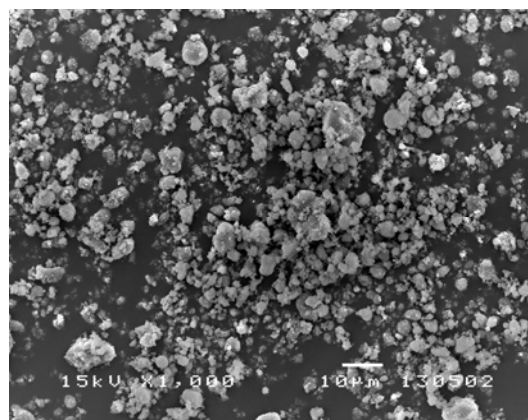
(e) Index 110, CaCO₃ 10%

Figure 5.13 SEM micrographs of cell structure of flexible polyurethane foam

Index 110 with CaCO₃ 0, 3, 5, 7 and 10wt%

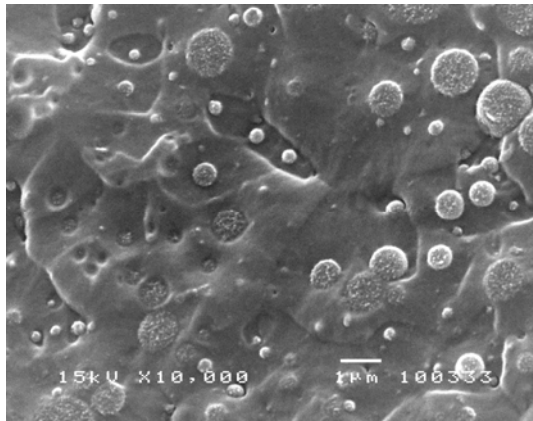
Although, the calcium carbonate fillers were added into polyurethane system, the agglomerate of particles was observed due to their high surface energy. Since calcium carbonate have shown the length in the order of micron, it was possible to observe individual calcium carbonates as shown in Figure 5.13. The diameter of calcium carbonate was measured to be about 1 micron (μm). As the size of particles was small, specific surface area was large, and so as surface energy. Thus the adhesive force between the particles was strong and the particles easily agglomerate. Relatively large agglomerating bodies with a number of weak joining interfaced were thus formed as shown in Figure 5.14. The calcium carbonate fillers were used extender or inert fillers with addition to polymer in order to reduce cost of raw material. However, effect of this filler was also to increase the properties of polymer [22].

The degree of calcium carbonate fillers dispersion in polyurethane foams were characterized by SEM and shown in Figure 5.15-5.17. It could be observed that at the same isocyanate index, calcium carbonate filler were increased, there were poor disperse in polyurethane foam structure.

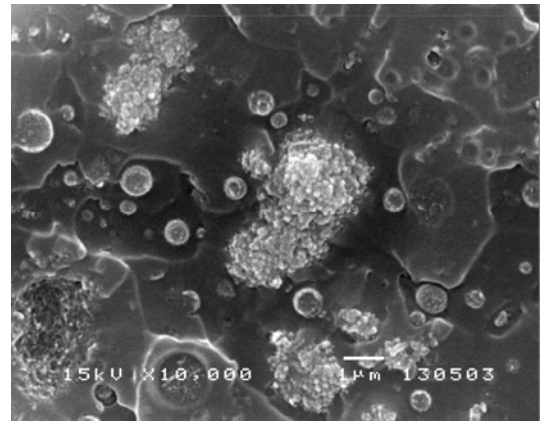


CaCO₃ (x 1000)

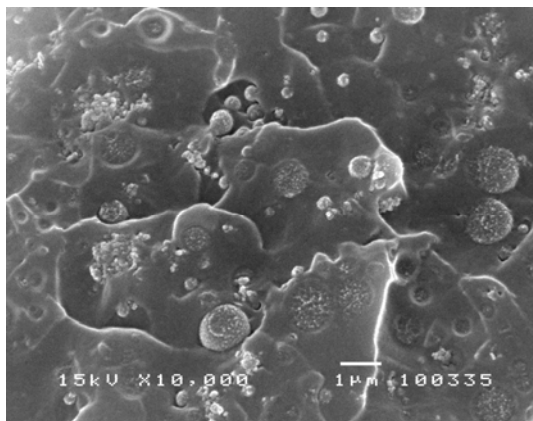
Figure 5.14 SEM micrographs of CaCO₃ (x 1000)



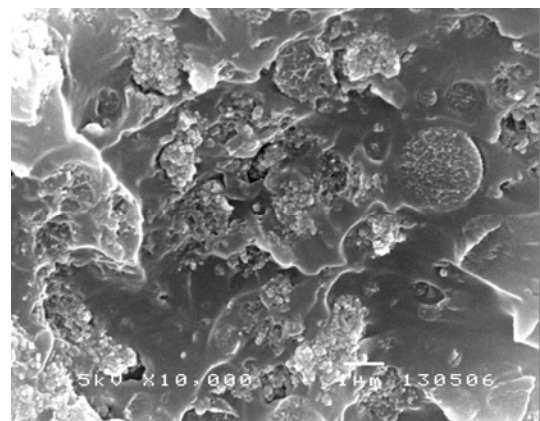
(a) Index 90, CaCO₃ 0%



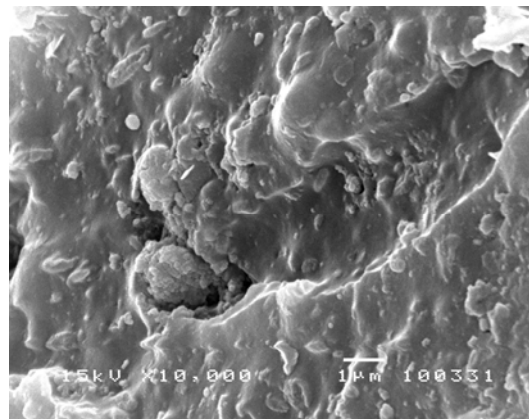
(b) Index 90, CaCO₃ 3%



(c) Index 90, CaCO₃ 5%

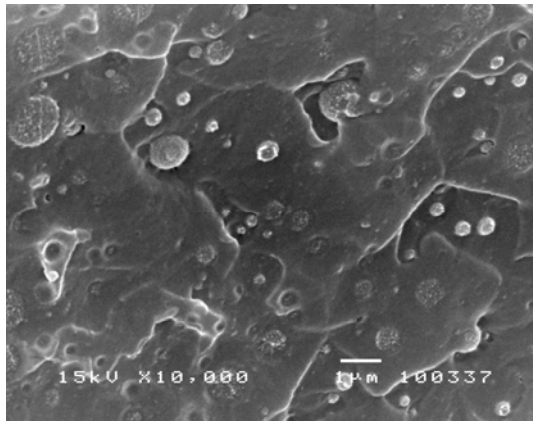


(d) Index 90, CaCO₃ 7%

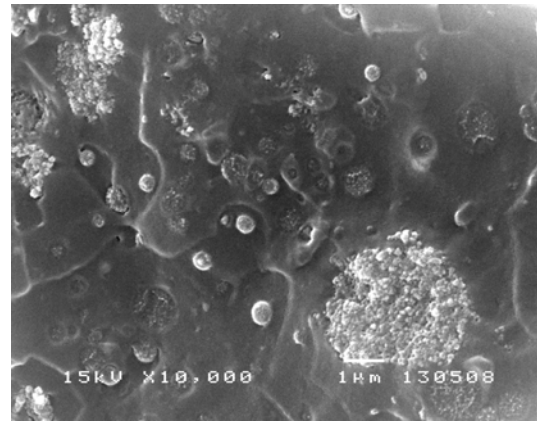


(e) Index 90, CaCO₃ 10%

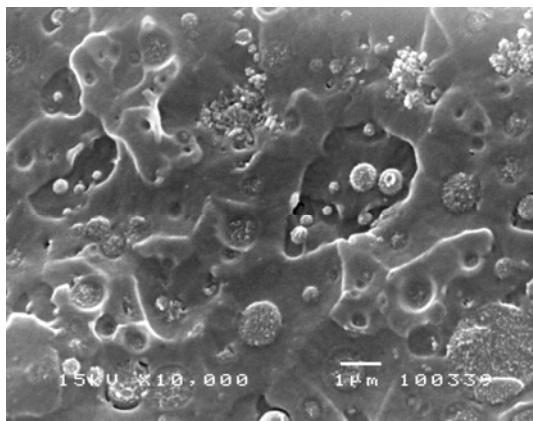
Figure 5.15 SEM micrographs morphology of flexible polyurethane foam Index 90 with CaCO₃ 0, 3, 5, 7 and 10 wt%



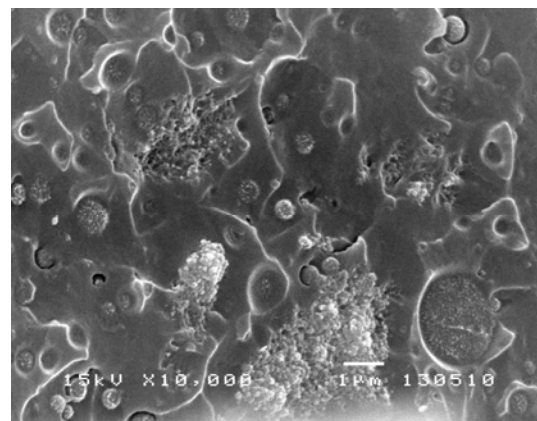
(a) Index 100, CaCO₃ 0%



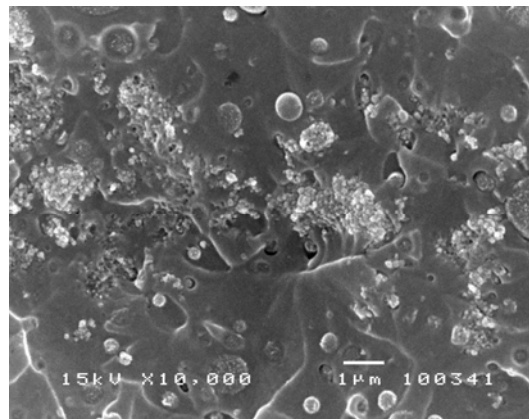
(b) Index 100, CaCO₃ 3%



(c) Index 100, CaCO₃ 5%



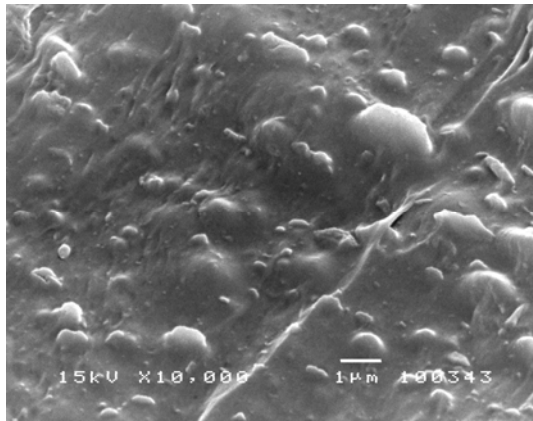
(d) Index 100, CaCO₃ 7%



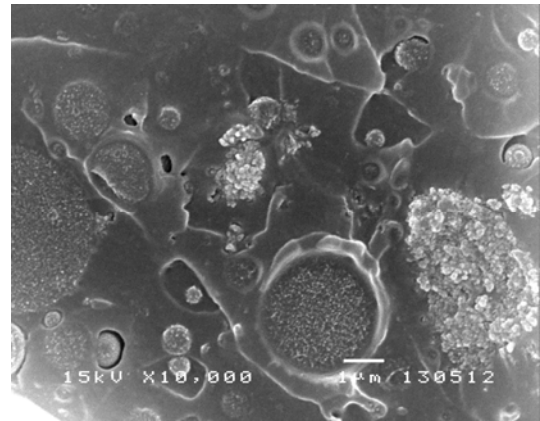
(e) Index 100, CaCO₃ 10%

Figure 5.16 SEM micrographs morphology of flexible polyurethane foam

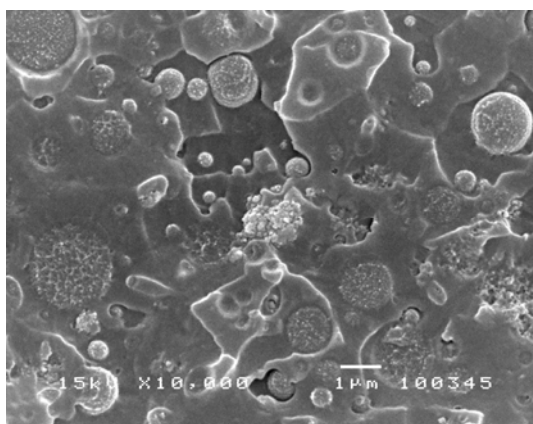
Index 100 with CaCO₃ 0, 3, 5, 7 and 10 wt%



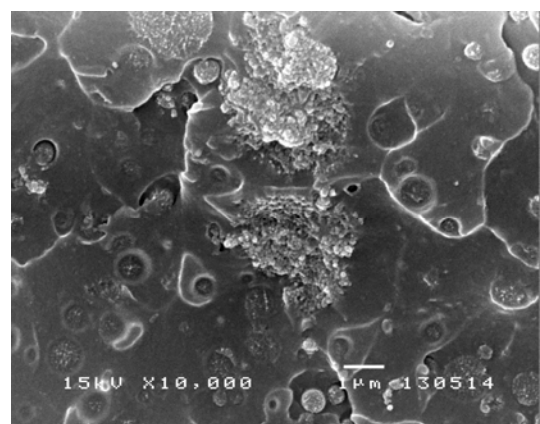
(a) Index 110, CaCO₃ 0%



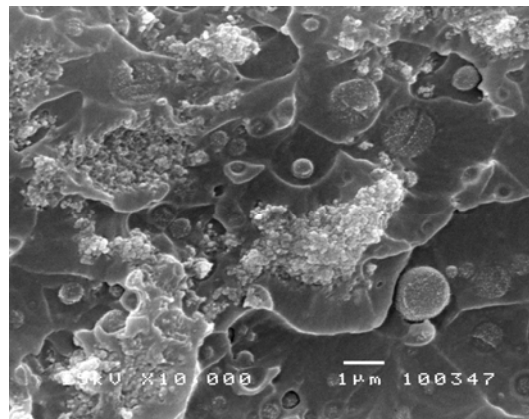
(b) Index 110, CaCO₃ 3%



(c) Index 110, CaCO₃ 5%



(d) Index 110, CaCO₃ 7%



(e) Index 110, CaCO₃ 10%

Figure 5.17 SEM micrographs morphology of flexible polyurethane foam

Index 110 with CaCO₃ 0, 3, 5, 7 and 10 wt%

5.6 Mechanical properties of polyurethane composite foams

In this study, the isocyanate index of polyurethane foams were varied in the range of 90-110 and calcium carbonate filler were varied in the range of 0-10% by weight of polyol. After that polyol was mixed with isocyanate and was poured into an open mold to produce the free rise foam. The tensile strength, elongation at break, hardness, resilience were tested for all flexible polyurethane foams and composite foams.

5.6.1 Tensile strength and elongation

Tensile property was tested according to the standard JIS K6301. The tensile strength of polyurethane composite foams was shown in Figure 5.18. It could be observed that the tensile strength increased dramatically with an increase of calcium carbonate filler at all isocyanate index. In addition, the tensile strength of the polyurethane foam increased 6.7% for isocyanate index 90, 8% for isocyanate index 100 and 37% for isocyanate index 110. Furthermore, isocyanate index was increased, the reaction of polyurethanes foams will be NCO terminated [23]. These free NCO groups will be reacted further groups. The increased chemical crosslinking leads to a change in morphology and affects the mechanical properties. The increased in isocyanate index or NCO/OH ratio would increase the intermolecular attraction which in true increase the tensile strength and decrease the elongation.

The calcium carbonate fillers were dispersed in polyurethane foam structure which could be seen in SEM micrographs as shown in Figure 5.15-5.17. In addition, the calcium carbonate fillers of this study have average particle size about 1 micron (μm) which the tiny particle would act as a reinforcing filler to increase strength

properties [22]. Therefore, tensile strength was depended on both filler content and particle size.

Furthermore, Figure 5.19 has shown the relationship between elongation at break and the content of calcium carbonate filler. As a result, the elongation at break of the composites decreased with an increase of calcium carbonate filler, but the slightly decrease occurred when calcium carbonate content was higher than 3 wt%. This response was related to the interaction between the polyurethane and the calcium carbonate filler [24] and the dispersion of calcium carbonate in the PU matrix [25]. Tensile strength and elongation could be qualitatively correlated with the polymer structure.

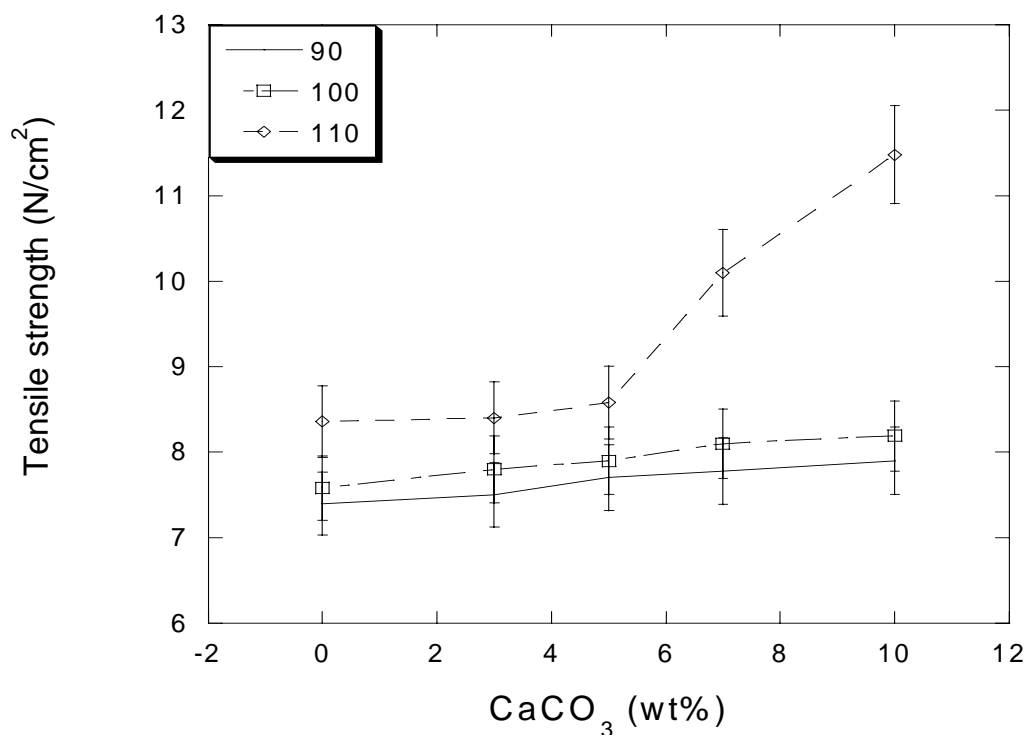


Figure 5.18 Effect of the CaCO₃ filler content on tensile strength of flexible polyurethane foam at 90-110 isocyanate index

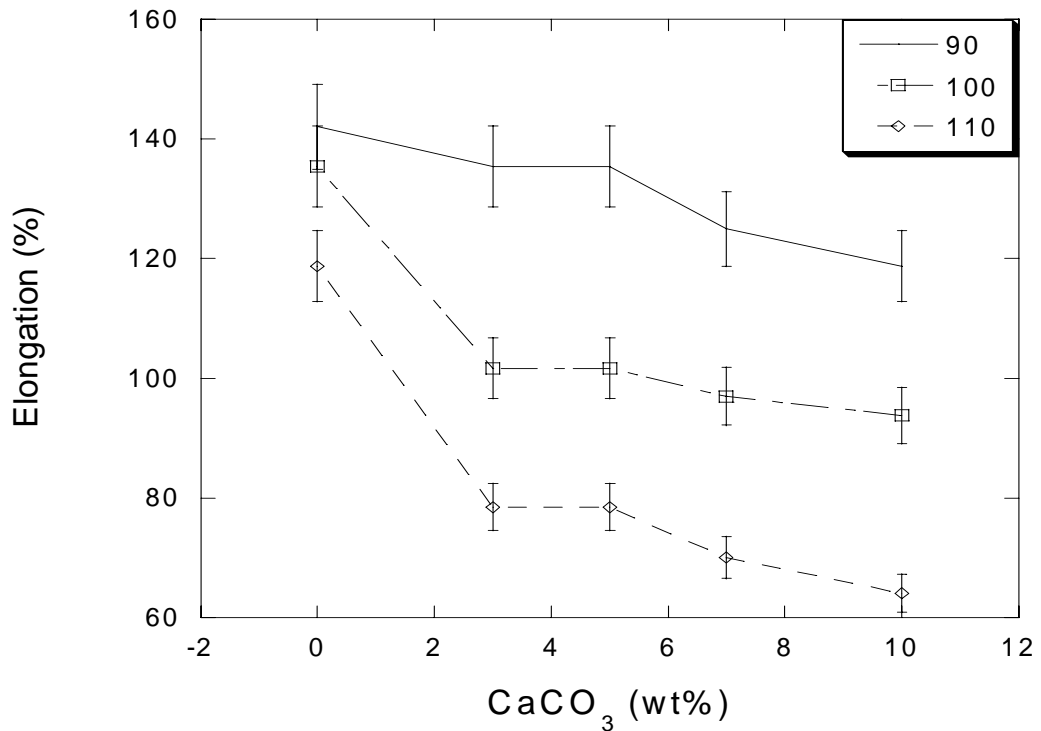


Figure 5.19 Effect of the CaCO₃ filler content on elongation of flexible polyurethane foam at 90-110 isocyanate index

5.6.2 Hardness

Hardness property was performed according to the JIS K6301. The polyurethane foam which increased an isocyanate index would affect to increase hardness properties. As mentioned above, the soft segment was increased with an increase of isocyanate index, thus increasing hardness properties [11]. In addition, increasing the isocyanate index was increased the intermolecular interaction of polyurethane matrix [12-14]. Furthermore, there were in accordance with the soft segment increased, the tensile strength and hardness increased and the elongation at break decreased [15]. In addition, the NCO/OH ratio was affected the mechanical properties of polyurethane foam which have been studied by several approaches. When the NCO/OH ratio was greater than one, the formation of polyurethanes will be NCO terminated. These free NCO group will react further to form three-dimensional

allophanate or biuret crosslinks. The increased in chemical crosslinking leads to a change in morphology and increases hardness properties [13].

Effect of the calcium carbonate filler loading on the hardness of flexible polyurethane were shown in Figure 5.20. It could be observed that the hardness increased with an increase of calcium carbonate content 0-10% at isocyanate index 90-100. Because calcium carbonate fillers were tiny particle and it has higher surface area which densely dispersed in the structure of the polyurethane foam which result in the increase of hardness properties of the polyurethane foam.

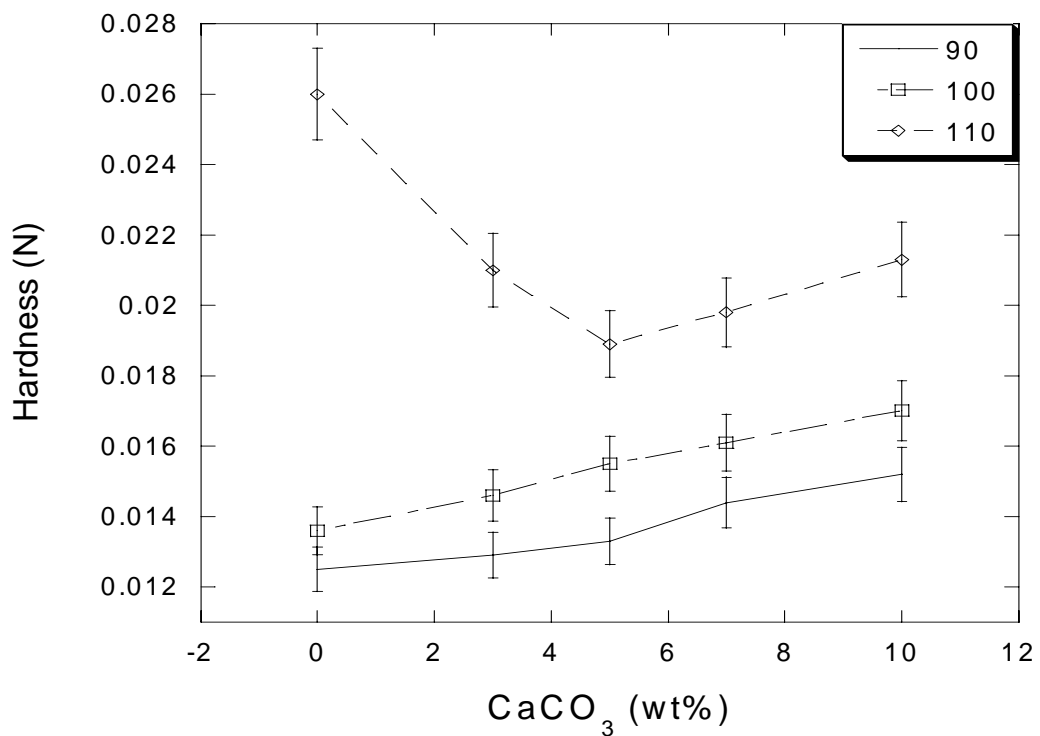


Figure 5.20 Effect of the calcium carbonate filler content on hardness of flexible polyurethane foam at 90-110 isocyanate index

However, the hardness property decreased with an increase of the calcium carbonate content at 0-5wt% of isocyanate index 110 which could be due to the presence of calcium carbonate fillers which obstructed the chemical crosslinking of polyurethane matrix. The hardness of PU composite foam was increased when the

filler content was higher than 5 wt% at isocyanate index 110 which could be due to the cell collapse which was observed after rise time of the foam formation.

5.6.3 Resilience (ball rebound) test

Resilience property was performed according to the ASTM D3574. In general, resilience properties of the polyurethane foam was decreased when an increase of isocyanate index. The polyurethane foam with higher isocyanate index would increase the intermolecular interaction and increase the chemical cross-linking thus increased hardness properties and decreased resilience properties.

The effect of the calcium carbonate filler on the resilience test of flexible polyurethane were shown in Figure 5.21. It could be observed that the resilience test decreased with an increase of calcium carbonate content. The resilience of polyurethane foam decreased 4.16, 2.48, 4.61 % as the filler increased from 0 to 10 wt%. However, the resilience properties of polyurethane foam with isocyanate index 110 increased with an increase of calcium carbonate and attain a maximum value at 5 wt% of fillers.

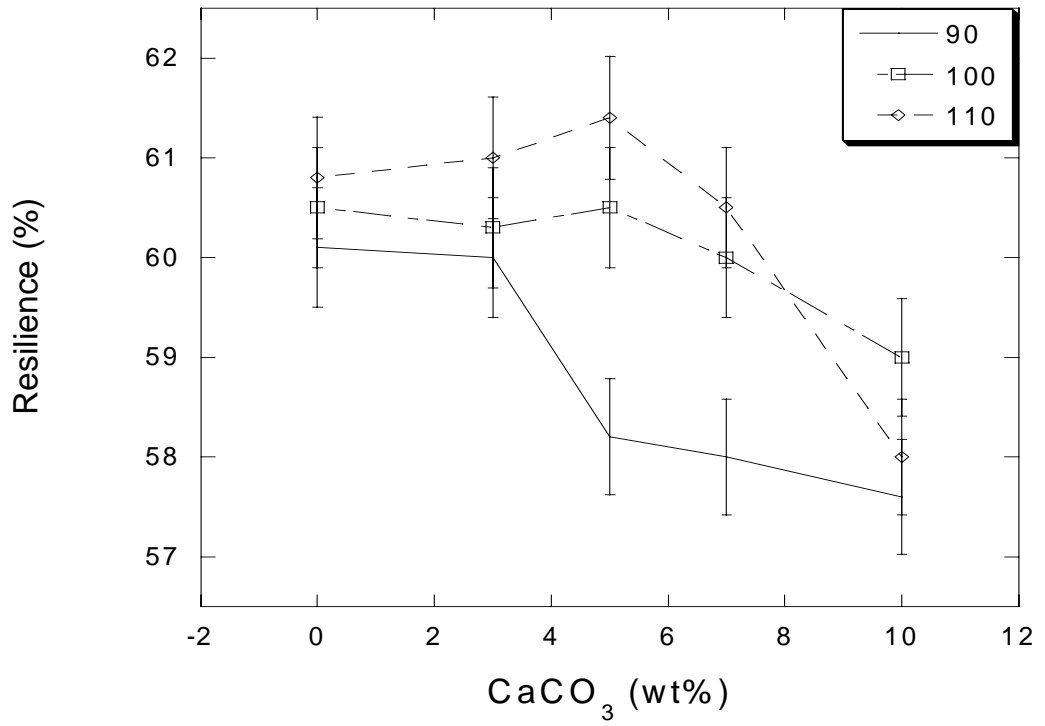


Figure 5.21 Effect of the calcium carbonate filler content on resilience of flexible polyurethane foam at 90-110 isocyanate index

CHAPTER VI

CONCLUSIONS

Flexible polyurethane foam composites were prepared by mixing the polyol, isocyanate and calcium carbonate filler. These fillers were varied 0, 3, 5, 7 and 10% by weight of polyol, and the isocyanate index were varied 90, 100 and 110. First, polyol was mixed with calcium carbonate filler by mechanical stirrer. Second, isocyanate was poured into this mixture and stirred until it was homogeneously mixed. Third, the mixture were poured into the mold to produce the free rise foam then cream time, gel time and rise time were measured. As the result, the viscosity of polyol blend with calcium carbonate fillers were increased with increased calcium carbonate filler content at the same temperature.

In addition, the cream time, gel time and rise time of the flexible polyurethane tended to decrease when increase calcium carbonate filler content. However, cell foam was collapse when addition calcium carbonate content with 7-10 wt% at isocyanate index 110. Therefore, the rise time at this condition was dramatically increased. As the result, the density of the composite foam were increased with increased calcium carbonate filler and increased isocyanate index, especially at filler content 7-10 wt%, isocyanate index 110. In addition, the FTIR spectrum of polyurethane composite foams showed the similar peak at the same frequency. However, the peak representing the urethane linkage and ether linkage was decreased and increased respectively when increase calcium carbonate content in which it was affected the mechanical properties of composite foams.

Furthermore, the tensile strength and hardness properties were increased with increased calcium carbonate content. In contrast, the elongation at break and resilience properties were decreased as the filler content increased.

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APPENDICES

APPENDIX A

CALCULATION ISOCYANATE INDEX

The reactive component

The amount of isocyanate required to react with the polyol and any other reactive additives, is calculated in the usual way to obtain the chemically stoichiometric equivalents. This theoretically stoichiometric amount of isocyanate may then be adjusted upwards or downwards, depending on the polyurethane system, the properties required of the polymeric product and known effects such as the scale of manufacture and the ambient condition.

Isocyanate index (Index number)

The amount of isocyanate used relative to the theoretical equivalent amount, is known as the Isocyanate index or sometimes the Index number.

$$\text{Isocyanate index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} \times 100$$

Calculating the ratio of the components required.

The conventional way of calculating the ratio of the components required for polyurethane manufacture is to calculate the number of parts by weight of the isocyanate that are required to react with 100 parts by weight (pbw) of the polyol and proportionate amounts of additives. The analytical data required for the calculation are the isocyanate value of the isocyanate and the hydroxyl value, residual acid value. This information is given by the supplier with each batch of urethane chemicals. To avoid mistakes it is usual to print this information on each drum of material.

Isocyanate value. The isocyanate value is the weight percentage of reactive – NCO group :

$$\text{Isocyanate value} = \% \text{ - NCO groups} = \frac{42 \times \text{functionality}}{\text{Molecular weight}} \times 100$$

$$\text{or } \frac{4200}{\text{Equivalent weight}}$$

Hydroxyl value (Hydroxyl number) The hydroxyl value (OHV) sometime calls the hydroxyl number of the polyol, is expressed in mg KOH/g of polyol. This convention arised from the method of determining hydroxyl values by acetylation with pyridine and acetic anhydride in which the result is obtained as the difference between two weight of KOH in milligrams that will neutralize the acetic capable of combining by acetylation with 1 g of the polyol. Polyols are sometimes characterized quoting the weight percentage hydroxyl groups. This is related to OHV :

$$\begin{aligned} \% \text{Hydroxyl groups} &= \text{OHV} \times \frac{1.7}{56.1} = \frac{\text{OHV}}{33} \\ \text{or Equivalent weight} &= \frac{56.1 \times 1000}{\text{OHV}} \end{aligned}$$

Acid value The acid value is also expressed as mg KPH/g of polyol and is numerically equal to OHV in isocyanate usage. (see below).

Water content Water reacts with two –NCO groups and the equivalent weight of water is thus :

$$\frac{\text{molecular weight}}{\text{functionality}} = \frac{18}{2} = 9$$

Example 1

How much TDI (48% NCO value), at an isocyanate index Of 105, is required to make a foam blown with 3 parts of water per 100 parts of a polyester polyol having an OHV of 51 mg KOH/g and an acid value of 2.0 mg KOH/g?

$$\text{Equivalent weight of TDI} = \frac{42}{48} \times 100 = 87.5$$

$$\text{Equivalent weight of the polyester polyol} = \frac{56100}{(51+2)} = 1058$$

Therefore :

The amount of TDI required to react with 100 parts by weight of polyester polyol is :

$$\frac{100}{1058} \times 87.5 = 8.27 \text{ pbw of TDI}$$

The amount of TDI required to react with 3 pbw of water (the water content of the polyester polyol + the water added for the blowing reaction) is :

$$\frac{3}{9} \times 87.5 = 29.16 \text{ pbw of TDI}$$

The total TDI required to react with 100 pbw of polyol + 3 pbw of water is :

at 100 Index, $29.16 + 8.27 = 37.4$ pbw of TDI

at 105 Index, $37.4 \times \frac{105}{100} = 39.2$ pbw of TDI

APPENDIX B

**DATA OF CREAM TIME, GEL TIME AND RISE TIME OF FLEXIBLE
POLYURETHANE COMPOSITE**

Cream time of flexible polyurethane foam (Second)

% Filler	Isocyanate index		
	90	100	110
0	24.60	21.20	21.20
3	22.10	19.20	18.60
5	20.40	19.00	18.50
7	20.00	18.50	18.20
10	19.80	18.40	18.10

Gel time of flexible polyurethane foam (Second)

% Filler	Isocyanate index		
	90	100	110
0	86.80	84.20	82.00
3	80.80	80.20	80.00
5	80.20	78.40	77.40
7	78.00	76.00	75.00
10	75.40	74.20	74.00

Rise time of flexible polyurethane foam (Second)

% Filler	Isocyanate index		
	90	100	110
0	114.80	112.20	111.40
3	110.00	109.00	108.00
5	107.60	106.83	105.20
7	108.00	105.00	103.00
10	109.60	104.20	200.00

APPENDIX C

DATA OF PHYSICAL PROPERTIES OF FLEXIBLE POLYURETHANE

COMPOSITE

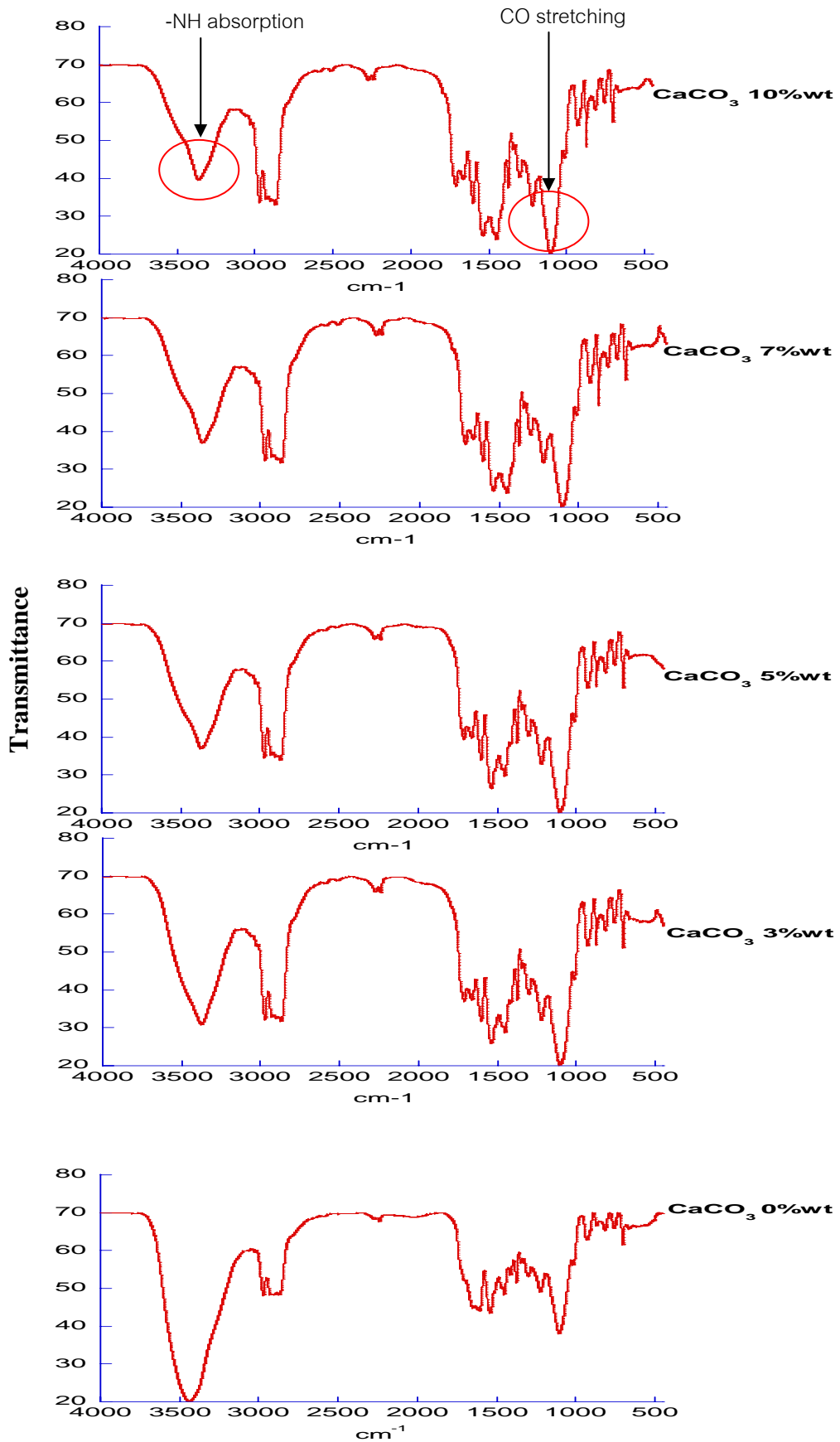
Density of the flexible polyurethane composite (g/cm³)

% Filler	Isocyanate index		
	90	100	110
0	0.0255	0.0268	0.0270
3	0.0257	0.0265	0.0273
5	0.0264	0.0266	0.0280
7	0.0273	0.0274	0.0360
10	0.0275	0.0279	0.0447

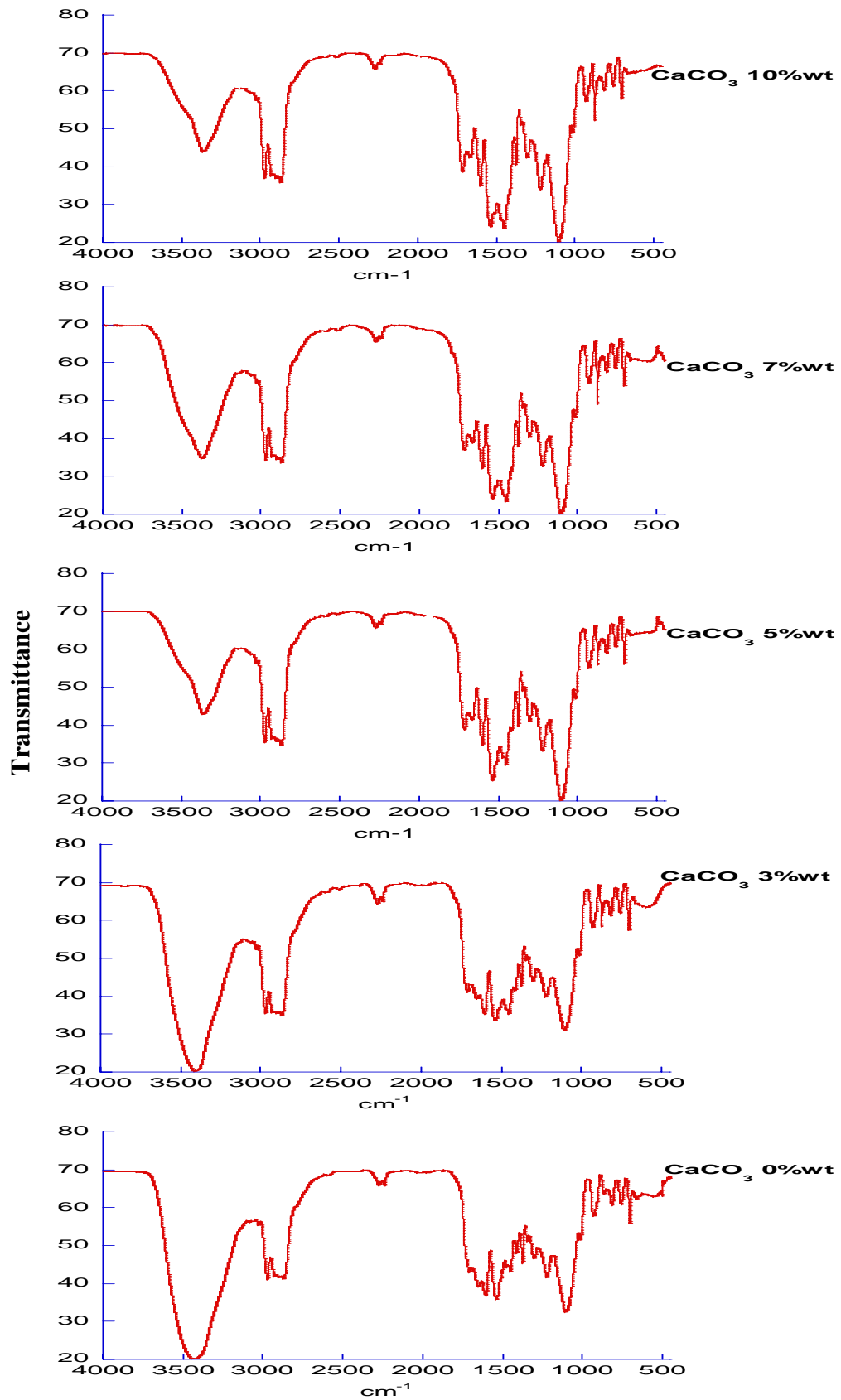
APPENDIX D

FTIR SPECTROSCOPY OF FLEXIBLE POLYURETHANE COMPOSITE

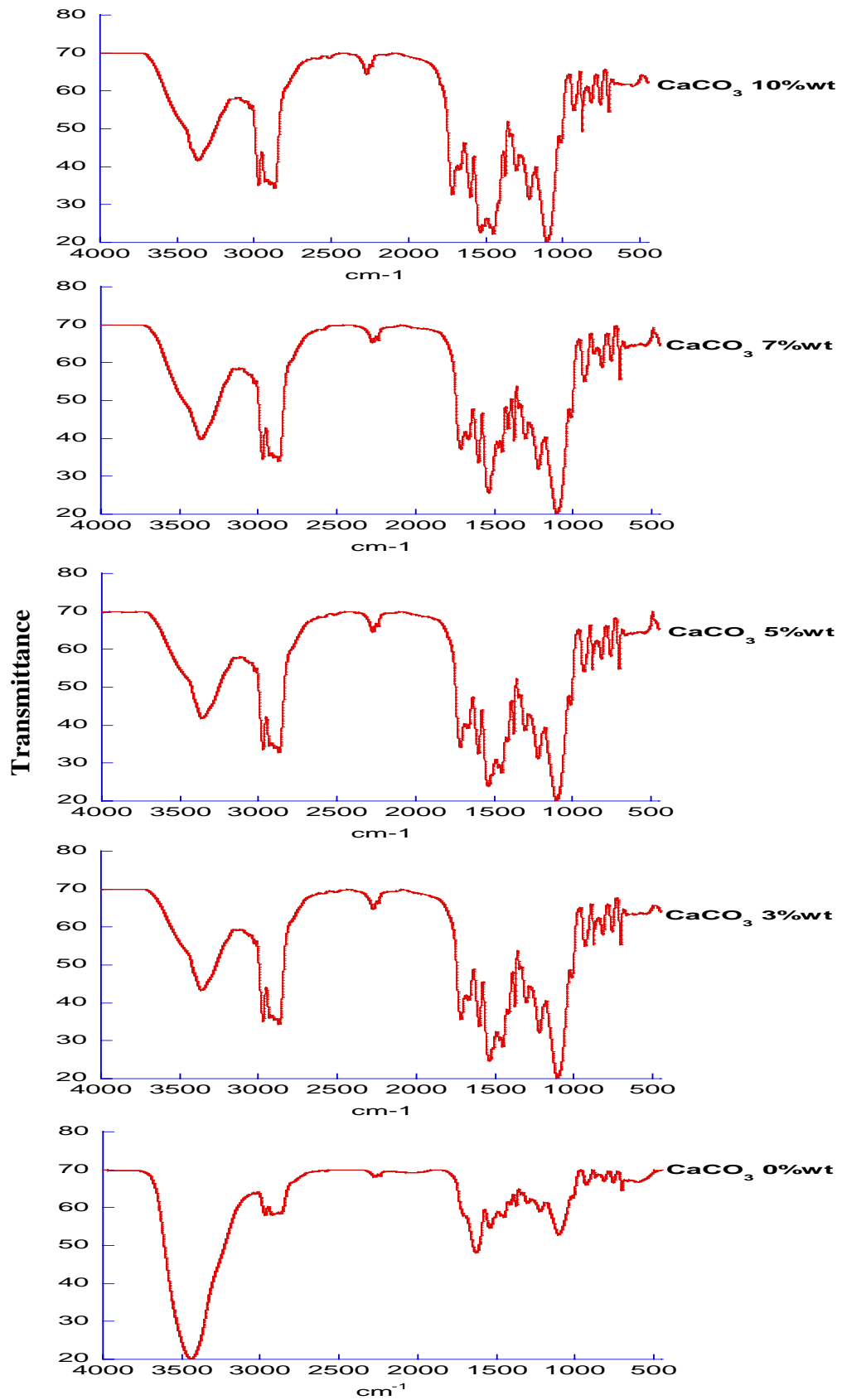
FTIR of polyurethane foam at isocyanate index 90



FTIR of polyurethane foam at isocyanate index 100



FTIR of polyurethane foam at isocyanate index 110



APPENDIX E
DATA OF MECHANICAL PROPERTIES OF FLEXIBLE POLYURETHANE
COMPOSITE

Tensile strength of the flexible polyurethane composite (N/cm²)

% Filler	Isocyanate index		
	90	100	110
0	7.40	7.58	8.36
3	7.50	7.80	8.40
5	7.70	7.90	8.58
7	7.78	8.10	10.1
10	7.90	8.19	11.48

Elongation of the flexible polyurethane composite (%)

% Filler	Isocyanate index		
	90	100	110
0	142.08	135.38	118.75
3	135.38	101.67	78.45
5	135.38	101.67	78.45
7	125.00	97.00	70.00
10	118.75	93.75	64.06

Hardness of the flexible polyurethane composite (N/cm²)

% Filler	Isocyanate index		
	90	100	110
0	0.0125	0.0136	0.026
3	0.0129	0.0146	0.021
5	0.0133	0.0155	0.0189
7	0.0144	0.0161	0.0198
10	0.0152	0.017	0.0213

Resilience of the flexible polyurethane composite (%)

% Filler	Isocyanate index		
	90	100	110
0	60.10	60.50	60.80
3	60.00	60.30	61.00
5	58.20	60.50	61.40
7	58.00	60.00	60.50
10	57.60	59.00	58.00

BIOGRAPHY

Miss Wirongrong Sri-ngo was born in Kalasin, Thailand on August 28, 1981. She graduated secondary school level from Kosumwittayasan School in 1997 and high school level from Kosumwittayasan School in 2000. In 2004, she received Bachelor's Degree in Chemical Engineering from King Mongkut's Institute of Technology Ladkrabang. After graduation, she works at the Summit Auto Seat Industry. In 2006, she studies for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

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