การใช้โพรพิลีนออกไซด์พอลิออลเป็นสารเปิดเซลล์ในโฟมพอลิยูรีเทนชนิดยืดหยุ่น

นายนิธิพงษ์ โชติวิทยพร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตร์มหาบัณฑิต
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USE OF PROPYLENE OXIDE POLYOL AS CELL OPENING AGENT IN FLEXIBLE POLYURETHANE FOAM

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	USE OF PROPYLENE OXIDE POLYOL AS CELL OPENING AGENT IN FLEXIBLE POLYURETHANE FOAM
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นิธิพงษ์ โชติวิทยพร : การใช้โพรพิลีนออกไซด์พอลิออลเป็นสารเปิดเซลล์ในโฟมพอลิยูรีเทนชนิดยืดหยุ่น (USE OF PROPYLENE OXIDE POLYOL AS CELL OPENING AGENT IN FLEXIBLE POLYURETHANE FOAM) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. นวลพรรณ จันทรศิริ, 122 หน้า.

งานวิจัยนี้เป็นการศึกษาการปรับเปลี่ยนสารเปิดเซลล์ในสูตรโฟมพอลิยูรีเทนชนิดยืดหยุ่นที่ใช้ผลิตเบาะรถยนต์และเฟอร์นิเจอร์ หน้าที่ของสารเปิดเซลล์ คือ เพิ่มโครงสร้างเซลล์เปิดในโฟมพอลิยูรีเทนชนิดยืดหยุ่น เพื่อป้องกันการหดตัวและการเสียรูปของโฟมภายหลังการเกิดปฏิกิริยาเสร็จสมบูรณ์ ปัจจุบันสารเคมีที่นิยมใช้เป็นสารเปิดเซลล์เชิงอุตสาหกรรม คือ พอลิอีเทอร์พอลิออลที่ประกอบด้วยเอทิลีนออกไซด์ในปริมาณสูง ซึ่งมีข้อด้อย คือ ราคาสูงและการแยกชั้น เนื่องจากความมีขั้วและความเข้ากันได้ดีระหว่างเอทิลีนออกไซด์และน้ำ ซึ่งสามารถเกิดพันธะไฮโดรเจนกับโมเลกุลของน้ำ ส่งผลให้เกิดการแยกชั้นออกจากพอลิออลที่ใช้ในสูตรพอลิยูรีเทนชนิดยืดหยุ่นในระหว่างการจัดเก็บก่อนนำไปใช้งาน ในงานวิจัยนี้ ใช้พอลิโพรพิลีนออกไซด์พอลิออลเป็นสารเปิดเซลล์ชนิดใหม่ในสูตรโฟมพอลิยูรีเทนชนิดยืดหยุ่น ซึ่งจุดเด่นของพอลิโพรพิลีนออกไซด์พอลิออล คือ ราคาถูกและมีความมีขั้วต่ำ ศึกษาสมบัติเชิงกลของพอลิยูรีเทนโฟมชนิดยืดหยุ่นที่เตรียมได้จากการใช้พอลิโพรพิลีนออกไซด์พอลิออล คือ ความแข็ง ความสามารถในการดึงยืด ความทนทานต่อการดึงยืด และความทนทานต่อการฉีกขาดเปรียบเทียบกับพอลิยูรีเทนโฟมชนิดยืดหยุ่นที่เตรียมได้จากการใช้สารเปิดเซลล์เชิงอุตสาหกรรม จากผลการวิจัยพบว่า พอลิยูรีเทนโฟมชนิดยืดหยุ่นทั้ง 2 สูตรที่ใช้สำหรับเบาะรถยนต์และเฟอร์นิเจอร์ที่เตรียมได้จากการใช้พอลิโพรพิลีนออกไซด์พอลิออลให้สมบัติเชิงกลที่ดี ในส่วนของปริมาณโครงสร้างเซลล์เปิด พบว่าในโฟมพอลิยูรีเทนชนิดยืดหยุ่นในสูตรสำหรับเบาะรถยนต์ที่เตรียมได้จากการใช้พอลิโพรพิลีนออกไซด์พอลิออลมีปริมาณของเซลล์เปิดที่เทียบเท่ากับการใช้สารเปิดเซลล์เชิงอุตสาหกรรม ในขณะที่โฟมพอลิยูรีเทนชนิดยืดหยุ่นในสูตรสำหรับเฟอร์นิเจอร์ที่เตรียมได้จากการใช้พอลิโพรพิลีนออกไซด์พอลิออล มีปริมาณเซลล์เปิดที่น้อยกว่าการใช้สารเปิดเซลล์เชิงอุตสาหกรรม

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ____________________________

ปีการศึกษา ________2555______________ ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก__________

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NITIPONG CHOTIWITTAYAPON: USE OF PROPYLENE OXIDE POLYOL AS CELL OPENING AGENT IN FLEXIBLE POLYURETHANE FOAM. THESIS ADVISER: ASSOC. PROF. NUANPHUN CHANTARASIRI, Ph. D., 122 pp.

In this work, modification of cell opening agent in automotive seating and furniture flexible polyurethane (FPUR) foam formulations was studied. The role of cell opening agent is to increase the open cell content and prevents the foam shrinkage after completely cured. Nowadays, conventional cell opening agents employed is polyether polyol which has high ethylene oxide content. The disadvantages of conventional cell opening agent are high cost and phase separation due to its high polarity and hydrophilic property of ethylene oxide unit which is able to form hydrogen bond with water molecules and causes layer separation from polyol in the foam formulation upon storage. In this work, pure propylene oxide (PO) polyol was used as a new cell opening agent in FPUR foam formulations. The advantages of PO polyol are low cost and PO polyol has low polarity. Mechanical properties of FPUR foams prepared from PO polyol, namely hardness, elongation, tensile and tear strength, were studied and compared with FPUR foams prepared from conventional cell opening agent. It was found that FPUR foams of both automotive seating and furniture formulations which were prepared from PO polyol gave good mechanical properties. For the amount of open cell content in comparison to FPUR foams prepared from conventional cell opening agent, automotive seating FPUR foam formulation prepared from PO polyol gave the same amount of open cell content while furniture FPUR foam formulation prepared using PO polyol had less open cell content.

Field of Study: Petrochemistry and Polymer Science Student's Signature ___________

Academic Year: 2012 Advisor's Signature ___________

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LIST OF ABBREVIATIONS

%	Percentage
%wt.	Percentage by weight
^{O}C	degree Celsius
cm	centimeter
CO_2	Carbon dioxide
EO	Ethylene oxide
FPUR	Flexible polyurethane
FRD	free rise density
FTC	force to crush
g	gram
h	hour
HR	High resilience
IFD	Indentation force deflection
ILD	Indentation load deflection
IR	Infrared
kg	kilogram
kgf	kilogram-force
KOH	Potassium Hydroxide
kPa	kilopascal
kV	kilovolt
L	liter

m	meter
m^3	cubic meter
MDI	Diphenylmethane diisocyanate
mg	milligram
ml	milliliter
mm	millimeter
Mw	Molecular weight
N	newton
nm	nanometer
pbw	parts by weight
PESE	Poly(ester-ether)
PET	Polyether polyol
PO	Propylene oxide
PPEO	Poly(propylene oxide-ethylene oxide)
PUR	Polyurethane
rpm	round per minute
RPUR	Rigid polyurethane
s	second
SAN	Styrene acrylonitrile
SEM	Scanning Electron Microscope
TDI	Toluene diisocyanate
UV	Ultraviolet

CHAPTER I
INTRODUCTION

Polyurethane (PUR) foams are one of the most versatile materials which are widely used in many applications. The PUR reaction consists of 2 main starting materials, polyol which contain hydroxyl group (-OH) and isocyanate which contain isocyanate group (-NCO). PUR foams can be used in many applications in many forms. Typical PUR foams are separated in two main categories, rigid polyurethane (RPUR) foams and flexible polyurethane (FPUR) foams, based on their physical forms. RPUR foams are used for insulation in appliances or in electronics, in construction application for buildings, in automotive such as bumper, spoiler or headlining in cars. FPUR foams are used in mattress, furniture, automotive seating and motorcycle saddle.

Flexible polyurethane foams (FPUR foams) are either produced using the continuous process or the batch process [1]. The continuous process produces FPUR foams in the long rectangular shape, which is called "slab-stock foam", while the batch process produces the FPUR foams in specific shape depending on mold or cavity used, which is called "molded foam".

Slab-stock foams are widely used in furniture and mattress applications or slice to thin sheet and use as laminating support materials. Molded foam are used in automotive seating and motorcycle saddle, however, some formulations can be used for furniture such as sofa or mattress.

In continuous process [1], polyol and isocyanate are mixed together at the mixing chamber using stirrer so called “low pressure mixing”, and then pour into the conveyor line. The conveyer is moving forward using the speed which synchronizes to the reaction speed. Foam will gradually rise up along with conveyor line which moving forward. After that slab-stock foams move to curing area to cool down the temperature inside foam bun before submit to further process. With this method, foam is allowed to rise up freely under ambient temperature and atmospheric pressure, most of the gases which generated upon reaction will easily release from foam bun right after it reach to foam skin.

In batch process [1], polyol and isocyanate are sprayed and mixed together at mixing head so called “high pressure mixing”, then injected into the mold. With this method, the mixture will flow inside the mold, fill all area during reaction, foam is not allowed to rise up freely unlike continuous process but force to pack inside the mold which result in higher density than its free rise form. After 3-5 min in hot mold, foam is taken out from the mold. The mechanical crushing process is required in batch process in order to eliminate all the hot gases which generated upon reaction and cannot easily release from foam skin inside the mold. This process includes compressive crushing by roller, vacuum rupture or time pressure release [2]. If hot gases are allowed to cool down within cell structure, the volume change between hot and cold gas will results in cell shrinkage and lead to foam shrinkage problem [3]. Thus, cell opening agent is the importance additive in order to prevent foam shrinkage during production.

Nowadays, conventional cell opening agent is polyethylene polyol (PET) which has high ethylene oxide (EO) contents [4]. The higher EO contents in polyol decreases the foaming reactivity by forming hydrogen bond with water and causes the cell struts to have not enough gel strength to resist the pressure from gas expansion results in open cell structure [4]. There are the disadvantages of high EO polyol in both technical term and commercial term. In technical term, high EO polyol causes phase separation in the formulated polyol due to its high polarity and can easily react with other ingredients to result in short shelf life of formulated polyol. While in commercial term, the cost per unit of high EO polyol is much higher than normal based polyol.

Objectives and scope of the research.

In this study, the pure propylene oxide (PO) polyol was used as cell opening agent. This is because PO polyol contains only less reactive secondary -OH that causes the delayed reaction in FPUR foams, which is the same effect as conventional cell opening agent. This research is focused on molded foam formulations for automotive seating application and furniture application. The automotive seating formulation used a mixture of toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) as isocyanate part in the reaction, while furniture formulation uses only MDI as isocyanate part. Both applications used formulated polyol system which contains 60 parts by weight (pbw) of long chain based polyol, and 40 pbw of styrene acrylonitrile polyol (SAN polyol) which contains 43% solid content. The formulations of both automotive seating and furniture are shown in Table 1.1.

Table 1.1 Reference formulations of automotive seating and furniture

Ingredients	**Automotive seating formulation (pbw)**	**Furniture formulation (pbw)**
Long chain base polyol	60.0	90.0
SAN Polyol	40.0	10.0
Conventional cell opening agent	2.0	5.0
PO Polyol	15.0	15.0
Cross-linker	0.5	0.5
Surfactants	0.6	1.0
Catalyst	0.6	0.6
Water content (%)	3.0, 3.5, 4.0	2.5, 3.0, 3.5
Isocyanate Index	90, 100, 110	70, 80, 90

From Table 1.1, the amount of some ingredients was varied in order to study the effect of PO polyol as cell opening agent. The variables that would be studied were water contents (%), amount of PO polyol and isocyanate index. The study was based on lab reactivity test by cup test method. The open cell contents were measured by two parameters. The first one was %settling, which was percent different between maximum height and the final height after gas release from FPUR foam). If there was more open cell contents, more gas could come out and therefore the FPUR foams have more %settling than less open cell contents foam. The second factor is the shrinkage of the FPUR foams which resulted from too much close cell in FPUR structure. All formulations were tested at three NCO indexes, 90, 100 and 110 for automotive seating formulation and 70, 80 and 90 for furniture formulation. One formulation in each application that was prepared using PO polyol as cell opening agent would be selected and tested by over-packing in molded method for force to crush measurement, mechanical properties analysis and SEM analysis. The data obtained from PO polyol formulation would be compared with reference formulation prepared using conventional cell opening agent.

CHAPTER II

THEORY AND LITERATURE REVIEWS

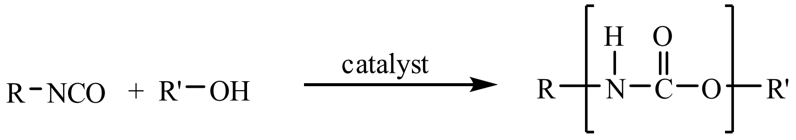
The reaction between alcohol and isocyanate to give an urethane has been known since 1849 by Wurtz and co-workers [1,5] but the extensive work to discovered polyurethane (PUR) was done by Prof. Dr. Otto Bayer and co-workers in 1937. PUR products include highly elastic foams use for mattress, car seat and furniture; highly rigid foams use for insulation materials, construction parts for building; flexible moldings with compact skins use for window frames, steering wheels and shoe soles [5]. A board range of PUR can be achieved by varying the components in PUR formulation such as type of isocyanate, polyol, surfactant or blowing agent or by adding specific additives.

2.1 Chemistry [1,3]

Polyurethane chemistry is based on the reactions between isocyanates and active hydrogen containing compounds. The basic principle of polyurethane chemistry using monofunctional reactants is described as follows:

2.1.1 The polymerization reaction (gel reaction)

The polymerization reaction is the reaction between active hydrogen containing compound so called “polyol” with isocyanate as follows:



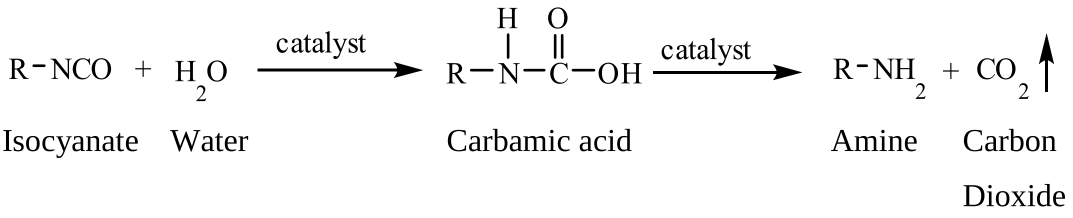
$$R{-}NCO + R'{-}OH \xrightarrow{\text{catalyst}} R{-}\left[\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O\right]{-}R'$$

Isocyanate Alcohol Urethane

When extending the monofunctional reactants to polyfunctional reactants, this reaction provide a direct route to crosslinked polymer to increase the molecular weight in polyurethane structure.

2.1.2 The gas-producing reaction (blowing reaction)

In order to become a foam-like structure, the PUR polymer must be expanded or blown by the introduction of bubbles and a gas. This reaction provides carbon dioxide gas from the reaction between isocyanate groups and water molecules results in carbamic acid intermediate which spontaneous decompose to an amine and carbon dioxide as follows:



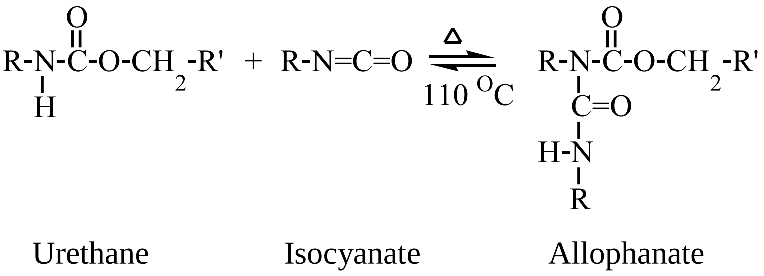
$$R{-}NCO + H_2O \xrightarrow{\text{catalyst}} R{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow{\text{catalyst}} R{-}NH_2 + CO_2\uparrow$$

2.1.3 Side reactions

There are many side reactions between isocyanate group and active groups yield from gel reaction and blowing reaction as follows:

2.1.3.1 Allophanate reaction

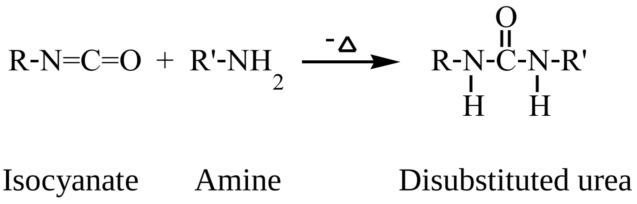
Urethane group from gel reaction further reacts with isocyanate to yield the allophanate group.



$$R{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}R' + R{-}N{=}C{=}O \underset{110\,^{O}C}{\overset{\Delta}{\rightleftharpoons}} R{-}\underset{\underset{\underset{\underset{R}{|}}{H{-}N}}{|}}{\underset{|}{C{=}O}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}R'$$

2.1.3.2 Disubstituted urea reaction

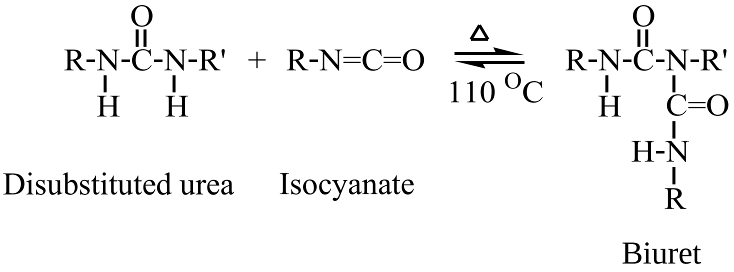
Amine group from blowing reaction further reacts with isocyanate to yield disubstituted urea group.



$$R{-}N{=}C{=}O + R'{-}NH_2 \xrightarrow{-\Delta} R{-}\underset{\underset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R'$$

2.1.3.3 Biuret reaction

The isocyanate group can further react with disubstituted urea to yield biuret group.



If the reactants are polyfunctional, all side reactions cause the higher crosslink density in PUR foam structure.

2.2 PUR foam components

Basically, PUR generated from the reaction between polyol and isocyanate. However, additives and other components are required in PUR formulation in order to achieve wide range of physical and mechanical properties. In this section, the basic components of PUR formulation are discussed based on flexible polyurethane foam (FPUR foam) formulation.

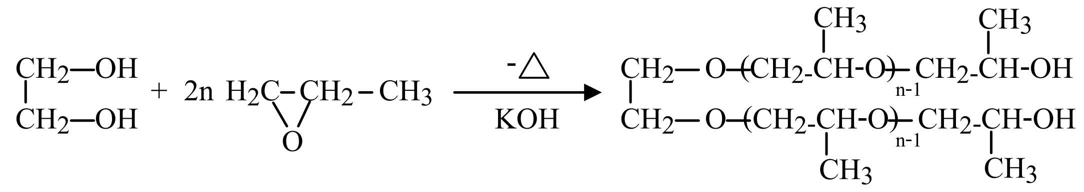
2.2.1 Polyols [3,5]

Polyols are source of reactive hydroxyl or other isocyanate reactive groups. Polyols are the largest groups of staring materials which influenced the processing and properties of FPUR foams determined by the chemical composition and molecular mass. In FPUR foams, more than ninety percent of polyols used are polyether polyols [3] while polyester polyols were used in small portions in specific applications.

2.2.1.1. Polyether polyols

Polyether polyols were widely used due to their low cost and low viscosity as compared to polyester polyol. Moreover, the polyether-based FPUR foams have good low-temperature behavior and high hydrolytic stability. However, the disadvantage of polyether polyols is the thermooxidative degradation on exposure to heat and atmospheric oxygen. The UV radiation is mainly responsible for light-induced degradation change.

Polyether polyols are produced by addition of cyclic ethers to polyfunctional starter as illustrated below, the cyclic ethers especially propylene oxide (PO) and ethylene oxide (EO). The functionality of polyols is depending on the functionality of the starter. Table 2.1 shows the common starters for FPUR foams polyols.



Usually, the structure of EO and PO units can be designed as homo blocks of either EO or PO, or as mixed blocked by feeding EO and PO mixture to the starter. The EO and PO ratio in mixed block polyether polyols determines the reactivity of polyol. The polyols with terminal EO units containing primary hydroxyl groups have higher reactivity than polyols containing terminal PO units [5]. Beside of one phase polyether polyols, polyether dispersions (two phase systems with a solid polymer as the disperse phase) are a further group of polyether polyols. This polyols contain solid dispersions such as styrene acrylonitrile polymers (SAN polyols), which are used as fillers to increase the hardness and strength of FPUR foams. The dispersion are milky white, high viscosity than the corresponding base polyols and completely stable to sedimentation.

Table 2.1 Common starters for FPUR polyols

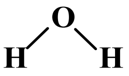
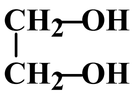
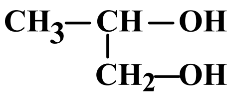
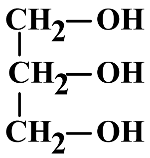
Desired functionality	Name	Structure
2	Water	
2	Ethylene Glycol	 $\begin{array}{l}CH_2{-}OH\\ \mid\\ CH_2{-}OH\end{array}$

Table 2.1 (cont.) Common starters for FPUR polyols

Desired functionality	Name	Structure
2	1,2-Propylene glycol	 $CH_3-\underset{\underset{CH_2-OH}{\vert}}{CH}-OH$
3	Glycerine	 $\begin{array}{l}CH_2-OH\\ \vert\\ CH_2-OH\\ \vert\\ CH_2-OH\end{array}$
4	Ethylene diamine	$H_2N-CH_2-CH_2-NH_2$

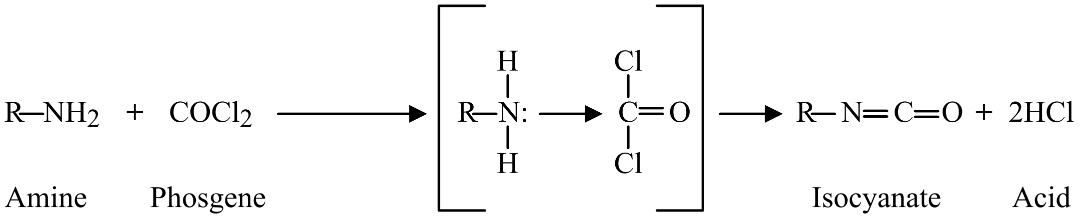
2.2.1.2. Polyester polyols

Polyester polyols give superior FPUR foams mechanical properties and resistance to light and thermal aging but have less hydrolytic stability as compared to polyether polyols. Moreover, they are expensive and more viscous which cause the difficulty to process. Polyester polyols are used in specific application such as footwear and shoe soles which require outstanding mechanical properties.

Polyester polyols are produced by polycondensation of di- and trifunctional hydroxyl groups with dicarboxylic acids or their anhydrides. Common dicarboxylic acids or anhydrides are succinic acid, glutaric acid, adipic acid, phthalic anhydrides, etc.

2.2.2 Isocyanate [1,3,5]

Isocyanate is the source of NCO groups which react with hydroxyl group (–OH group) and other functional groups from polyols, water and crosslinker in the formulation. Nowadays, more than 90% of FPUR foams are produced from aromatic isocyanate containing at least two NCO groups per molecule. The most commercially viable methods of producing isocyanates involved amine phosgenation, as shown below:



$$\underset{\text{Amine}}{R-NH_2} + \underset{\text{Phosgene}}{COCl_2} \longrightarrow \left[R-\overset{H}{\underset{H}{N}}: \longrightarrow \overset{Cl}{\underset{Cl}{C}}=O \right] \longrightarrow \underset{\text{Isocyanate}}{R-N=C=O} + \underset{\text{Acid}}{2HCl}$$

Normally, the reaction is carried out in a chlorinated aromatic solvent in order to removing excess phosgene in later purification steps.

The most commonly aromatic isocyanates used for FPUR foams are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

2.2.2.1 Toluene diisocyanate (TDI)

TDI used in industry has two isomers which are 2,4 isomer and 2,6 isomer as shown in Figure 2.1.

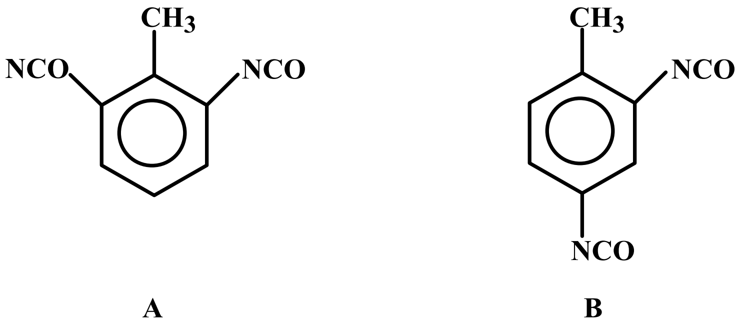


Figure 2.1 Isomers of toluene diisocyanate (TDI); (a) 2,6 TDI, (b) 2,4 TDI

Usually the pure 2,4 isomer or mixtures of 2,4 TDI with 2,6 TDI are used for industrial application. TDI 80 is blended between 2,4 TDI and 2,6 TDI in the ratio of 80:20, respectively. TDI 65 is blended between 2,4 TDI and 2,6 TDI in the ratio of 65:35, respectively. The 2,4 isomer is more reactive than 2,6 isomer, according to Figure 2.1, the steric hindrances affect the reaction of the various isomer position. At room temperature, the relative reaction rates are illustrated below in Figure 2.2.

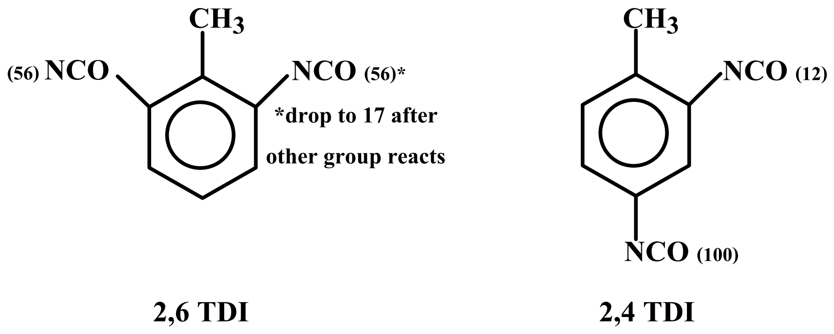


Figure 2.2 Relative reaction rates of 2,6 TDI and 2,4 TDI

Varying the isomer ratios has dramatic effects on polymer properties. Higher load bearing foams obtains from TDI 65. In some system, the addition of a modified TDI or polymeric MDI to TDI was used in order to achieve desired FPUR foams properties.

2.2.2.2 Diphenylmethane diisocyanate (MDI)

Various forms of MDI are used in high resilience and high density FPUR foams. The most commonly used MDI in industry has 2 isomers, 4,4 MDI and 2,4 MDI as shown in Figure 2.3.

Pure two-ring isomers are solids at room temperatures, but it can be liquefied by inclusion of carbodiimide structures. In some cases, not only monomeric MDI but polymeric MDI (Figure 2.4) is used in order to alter the reactivity, physical and mechanical properties of final FPUR foams.

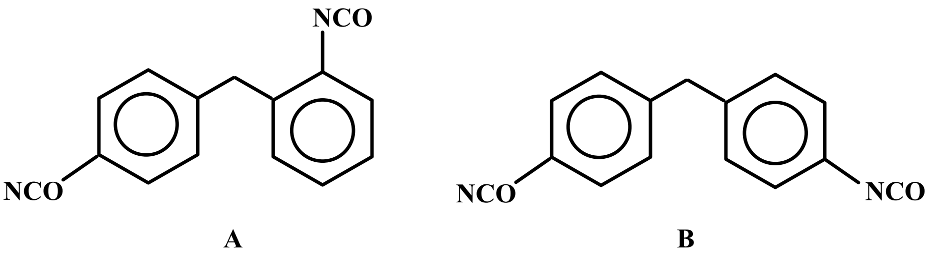


Figure 2.3 Isomers of diphenylmethane diisocyanate (MDI); (a) 2,4 MDI, (b) 4,4 MDI

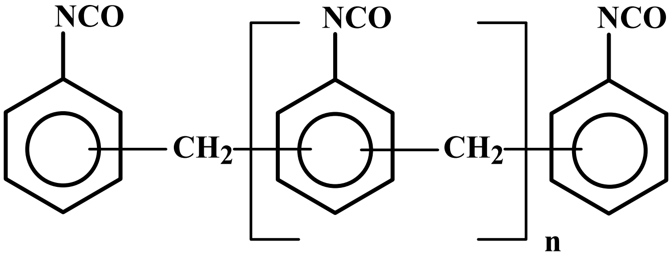


Figure 2.4 Structure of polymeric MDI

2.2.2.3 Isocyanate index

Isocyanate index represents the amount of isocyanate (NCO group) required to react with hydroxyl group (-OH) in polyol or other functional groups from water or other additives in term of stoichiometric equivalents. This theoretically stoichiometric amount of isocyanate may be adjusted higher or lower, depending on the required reactivity or final properties. The isocyanate index equation is shown in later sections.

Variation of isocyanate index has a significantly effect on the hardness of final FPUR foams. This is because of the increasing in covalent cross-linking results from more complete consumption of isocyanate reactive sites caused by the presence of excess isocyanate groups.

2.2.3 Water [1,3]

Water is considered as chemical blowing agent since water is a source of active hydrogens which react with isocyanate group in the system to give carbon dioxide gas. The gas diffused into nucleated bubbles and causes the foam expansion. Beside of carbon dioxide gas, the reaction between water and isocyanate yield the polyurea molecules which enter into and contribute to the properties of final FPUR foams. Only demineralized water should be used for FPUR foams production.

The water amounts in FPUR foams formulation can also effect to final properties and density. When larger amounts of water were used while keeping other compositions constant, the final FPUR foams normally have higher modulus due to increasing volume fraction of the polyurea-rich hard phase and FPUR foams density is lower due to the generation of larger amount of the carbon dioxide gas.

2.2.4 Surfactants [3]

In FPUR foams production, nonionic silicone-based surfactants are used. These surfactants perform several functions such as lower surface tension, emulsify incompatible formulation ingredients, promote nucleation of bubbles during mixing. The most important surfactant function is to stabilize the rising foam by reducing stress concentration in thinning cell-walls, counter react the defoaming effect of any solids added to or form during the foam reaction, for example, precipitated polyurea structures formed during foam reaction. The surfactants prevent the coalescence of rapidly growing cells until those cells have attained sufficient strength through polymerization to become self-supporting. Without silicone, continuing cell coalescence would lead to foam collapse. Figure 2.5 shows surfactants structures in FPUR foams production.

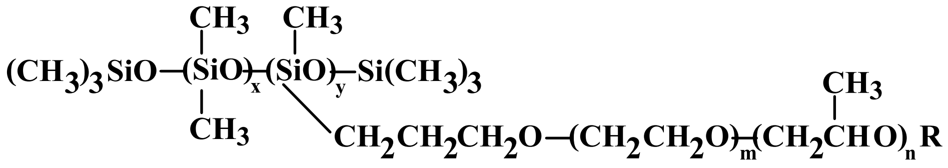


Figure 2.5 Chemical structure of surfactant (nonhydrolyzable type)

The amounts of surfactants in formulation affect the final FPUR foams. If the high amount of surfactant is used, FPUR foams have tendency to shrinkage due to over stabilize by surfactants. On the other hand, if too low amount of surfactant is used, FPUR foams have tendency to collapse.

2.2.5 Catalysts [3]

Nowadays, all commercially manufactured of FPUR foams are made in the presence of at least one catalyst. Usually, various combinations of catalysts are used in order to establish an optimum balance of gel reaction (isocyanate with polyols) and blowing reaction (isocyanate with water). The polymer formation rate and the expansion rate must be balanced so that the cell-walls develop sufficient strength to maintain their structure without collapse or shrinkage from the gas generation rate and gas diffusion rate from cell structure. Catalysts are also importance for assuring completeness of reaction or “cure” in finished FPUR foams.

2.2.5.1 Amine catalysts

The most commonly catalyst used for FPUR foam productions is tertiary amine catalyst. Most amines catalysts offer some contribution to the gel reaction. The catalytic activity of amines is due to the presence of a free electron pair on the nitrogen atom. Steric hindrance about the nitrogen atom and the electric effect of substituent groups are the main factors influencing the relative catalytic activity.

The type and concentration of amine catalyst can be selected in order to achieve the optimum reactivity such as cream time, gel time, rise time or the cure ability of outer FPUR foams skin. In general, the requirements for good catalytic activity including the characteristic described below:

- Strong nucleophile capable of attacking the carbon of isocyanate groups.
- Capable of readily forming an active hydrogen amine complex.
- Soluble in water and forms stable hydrogen bonds with water.

2.2.5.2 Delayed action catalysts

The demand for better in-mold flow ability and faster curing along with a need of balancing of FPUR foams reactivity has led to the development of delayed action catalyst consists of compounds that are not reactive at room temperature but become effective when the initial reaction exotherm warm up the mixture temperatures. The most common approach is to use a tertiary amine salt in a suitable solvent such as a low molecular weight glycol or water.

2.2.6 Additives [3]

2.2.6.1 Colorants

Many FPUR foam products use colorants during manufacturing to identify product grade, to conceal yellowing or to make an appealing consumer product.

2.2.6.2 UV stabilizers

All FPUR foams based on aromatic isocyanates will turn yellowish upon storage or aging with exposure to light. Therefore, light protection agents, such as hydroxybenzotriazoles, zinc dibutyl thiocarbamate, 2,6-ditertiary butylcatechol have been used to improve the light stability of FPUR foams.

2.2.6.3 Flame retardants

Low density, open cell FPUR foams have a large surface area and high permeability to air and thus will burn easily when have a sufficient of ignition source and oxygen. Flame retardants are often added to reduce this flammability. The most widely used flame retardants are the chlorinated phosphate ester, chlorinated paraffins. The melamine powders have also been used.

2.2.6.4 Auxiliary blowing agents

Auxiliary blowing agents are considered as physical blowing agents since they are nonreactive and contribute nothing to polymer structure; such blowing agents give softer foams than those blown to the same density with only water. The functions of auxiliary blowing agents are to absorb heat from the exothermic reaction, vaporizing and providing additional gas useful in expanding to the lower density FPUR foams. The auxiliary blowing agents most often used in extra-low-density are fluorocarbon such as methylene chloride or acetone.

2.2.6.5 Cell opening agents

In some FPUR foams, especially in molded FPUR foams, it is necessary to add cell opening agents in order to obtain the foams that do not shrink upon cooling. More discussion of cell opening agents is provided in later section.

2.3 FPUR Foam calculations. [3]

2.3.1 Functionality

The functionality is the number of isocyanate reactive sites on a molecule. For polyols, an average functionality is generally used.

$$\text{Average Functionality} = \frac{\text{total moles OH}}{\text{total moles polyol}}$$

2.3.2 Hydroxyl number (OH number)

OH number is the number calculated from a wet analytical method for the hydroxyl content in polyol. It is the milligrams of potassium hydroxide (KOH) equivalent to the hydroxyl to the hydroxyl content in one gram of polyol or other hydroxyl compound.

$$\text{OH Number} = \frac{56.1 \text{ x } 1000}{\text{Equivalent Weight}}$$

Where 56.1 is the atomic weight of KOH and 1000 is the number of milligram in one gram of sample. OH number reported in the units of mg/KOH

2.3.3 Acid number

Acid Number represents the amount of residual acidic material in a polyol. This number arises from the wet analytical method and reported in the same unit as OH number (mg/KOH)

2.3.4 Equivalent weight of a polyol

Equivalent Weight is the weight of a compound per reactive site.

$$\text{Equivalent Weight} = \frac{\text{Molecular Weight (Mw)}}{\text{Functionality}}$$

Since polyols have a Mw distribution, an average equivalent weight is used. These calculations are done using the product analyzed hydroxyl content and acid number.

$$\text{Equivalent Weight} = \frac{56.1 \text{ x } 1000}{\text{OH Number + Acid Number}}$$

For most polyol in use today, the acid number is very low and can be ignored. If the acid number is larger than 1.0, it should be factored into the above equation.

2.3.5 Equivalent weight of a polyol blend

Some systems have more than one polyols in formulation. The net equivalent of a polyol blend is given by:

$$\text{Equivalent Weight}_{BLEND} = \frac{100}{\frac{\text{Wt. \% Polyol A}}{\text{Eq. Wt. Polyol A}} + \frac{\text{Wt. \% Polyol B}}{\text{Eq. Wt. Polyol B}} + \ldots\ldots}$$

2.3.6 Equivalent weight of an isocyanate

The equivalent weight of an isocyanate is the weight of isocyanate compound per isocyanate site. This is calculated from the analyzed isocyanate (NCO) content.

$$\text{Equivalent Weight} = \frac{42 \text{ x } 100}{\%\text{NCO}}$$

where 42 is the atomic weight of the NCO group.

2.3.7 Equivalent weight of an isocyanate blend

Some systems using a blend of different isocyanates, the net equivalent of a isocyanate blend is given by:

$$\text{Equivalent Weight}_{BLEND} = \frac{100}{\frac{\text{Wt. \% Iso A}}{\text{Eq. Wt. Iso A}} + \frac{\text{Wt. \% Iso B}}{\text{Eq. Wt. Iso B}} + \ldots\ldots}$$

2.3.8 Equivalent weight of water

Water reacts with two isocyanate groups and thus the equivalent weight is given by:

$$\text{Eq. Wt. of Water} = \frac{\text{Molecular Weight (Mw)}}{\text{Functionality}} = \frac{18}{2} = 9$$

2.3.9 Isocyanate index

Isocyanate index is the ratio of equivalent weight of isocyanate used to the theoretical equivalent weight times 100. Theoretical equivalent weight is equal to one equivalent isocyanate per one equivalent polyol side compounds; this is an index of 100.

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

2.4 FPUR foams manufacturing process. [3,5]

FPUR foams manufacturing process can be broadly grouped into two main processes, the flexible slabstock foam process and flexible molded foam process.

2.4.1 Flexible slabstock foam

Based on different chemistry of the polyols used for flexible slabstock foam, three fundamentally different types of slabstock have to be considered: (1) conventional polyether foam from polyether polyols with mainly secondary OH groups, (2) high resilience (HR) foam from polyether polyols with mainly primary OH groups and (3) polyester foam from polyester polyols.

The isocyanate used for polyether and HR foam is TDI 80 while the typical isocyanate for polyester foam is TDI 65 or blends of TDI 65 and TDI 80.

Most of the production of slabstock foams using continuous process with low pressure machine mixing. In low pressure machine mixing technology, the streams are metered into a large mixing chamber under low pressure (< 20 bar). The components are effectively mixed with a large, high-shear stirrer operating at 2,000 – 6,000 round per minutes (rpm).

2.4.1.1 Flexible slabstock foam production

The raw materials are processed in fully continuous conveyor line give flexible foams slab up to 220 cm wide, 120 cm high and of any length from 10 m (short slabs) to 120 m (long slabs). The internal temperatures in slab stock foam during production are up to 165 ^{O}C, which resulted from the exothermic polymerization reaction. This temperature must not be exceeded; otherwise, severe scorching (internal yellowing color) and even self-ignition of FPUR foams may occur. The foaming process is complete after ca. 3.0 minutes and final curing takes around 10 hours up to 72 hours depending on the foam types. The slabs are therefore stored in curing storage facilities until they have cooled to room temperatures before transferred to further processing such as fabricating or trimming etc. to minimize the trimming losses of foam buns from dome shaped under free-rise condition, various technologies are applied in order to produce rectangular slabs such as Hennecke Planibloc process (Figure 2.6).

In Hennecke Planibloc process, immediately after cream line, paper or a nonporous film is fed on top of the foam. The paper or film is pressed on the foam surface by means of weight or spring-loaded pressure-regulating members (A). These pressure elements are positioned on top of the foam bun from the cream line to a few feet past the full-rise point. In order to allow the gasses generated during the foaming process to escape, a spike roller perforates the paper at point (B). After the last pressure element, the paper is peeled off and rewound. Although this method produces the good rectangular block shape but the disadvantage is that the top of foam bun cannot be observed during the reaction. This can lead to more waste or scrap foam in the case of mechanical or human error.

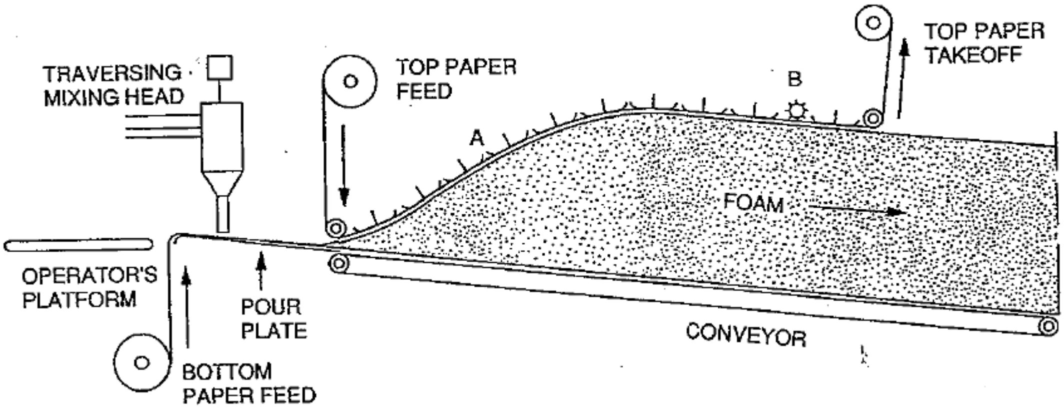


Figure 2.6 Hennecke Planibloc manufacturing process [3]

2.4.1.2 Flexible slabstock foam applications

The variety of properties and continuous development of new flexible slabstock foam formulation and processing techniques have made its indispensable for many applications.

- **Furniture**: Polyether type slabstock foam (conventional type) is used as a simple seat cushion to very comfortable seat cushion in furniture application by varying the different types of properties; e.g., density, hardness or elasticity.
- **Mattress:** The advantages of slabstock foams for full foam mattress are the relative low weight (e.g., versus latex foam) and freedom of design by combining various foam type such as conventional type, high-resilience type

or viscoelastic type and various foam grades (density, hardness). Not only in full foams mattress, in steel-spring mattresses, a layer of slabstock foam is used as cushioning and lining material.

- **Fabrics Lamination:** The polyester foam types are preferred for lamination application due to their melting properties and their specific cell structure. The foam can be bonded one or two sides with textile width by adhesive or flame lamination and are widely used for automotive interior trim application such as seat or headliner cover.
- **Automotive industry:** Other applications in automotive industry beside of the laminating material are sun visor filling or sound absorption materials for passenger, engine and trunk compartments. Slabstock foams also used as sealing and filter materials in the ventilation system.
- **Other application:** In household application, slabstock foams can be used as under-carpet padding, doormats and cleaning brushes. The ability of slabstock foams to absorb airborne noise efficiently is exploited for noise abatement. For use as filter materials; e.g., in ventilation and air conditioning systems or a dust filter in breathing mask.

2.4.2 Flexible molded foam

The molding process is developed due to the demand of complex shapes of FPUR foams which normal trimming process of slabstock foams cannot be used. The molding process is also used when the products are needed to incorporate with metal frames, metal inserts or even steel springs (e.g., for furniture, automotive seating application).

Normally the molding process uses the high-pressure mixing method. On a high-pressure mixing, the streams are metered under high pressure (100-200 bar) into a small mixing chamber. There is no stirrer in this method but the mixing is achieved by the impingement of the components under high velocity through nozzle in the small-volume mixing chamber.

2.4.2.1 Molded foam production and molding process

Generally, the molded foams are produced from trifunctional polyether polyols with enhanced reactivity (high proportion of primary –OH groups) in the molecular weight range of 5,000 – 6,000 g/mol. A variety of isocyanates are used, usually with a functionality exceeding two such as modified TDI types, blends of TDI and higher functional MDI or even special MDI types. On de-molding, the cured foam is closed-celled (the closed-celled level is depending on the open cell content in FPUR foams). This results from the over-packing of rising foam in close mold. The de-molding foams must be mechanically crushed to avoid shrinkage and to achieve consistent physical properties.

In general, molded foams process divided into 2 categories, the hot-cure process and cold-cure process. Both processes share the same processing concept. The only thing which is different is the temperature using for curing the FPUR foams in mold. In hot-cure process the production line using the huge oven to heat up and cure foams in mold, the temperature normally use around 120 – 150 ^{O}C. In cold-cure, there is no heating oven, but the molds contain the hot water circulation system which supplies hot water to heat up the mold and cure the FPUR foams in mold.

Nowadays, most of the manufacturing processes use the cold-cure process. The mold temperature was controlled in the range of 40 – 65 ^{O}C; in some cases the mold temperature can go lower even equal to room temperature. The mold temperature and the curing time required before de-molding are depending on the combination of polyols, the isocyanate, the catalyst package and the shape of the cavity. Usually, the foam can be de-molded after 2-6 minutes. Figure 2.7 shows the example of molding process for FPUR foams in industry.

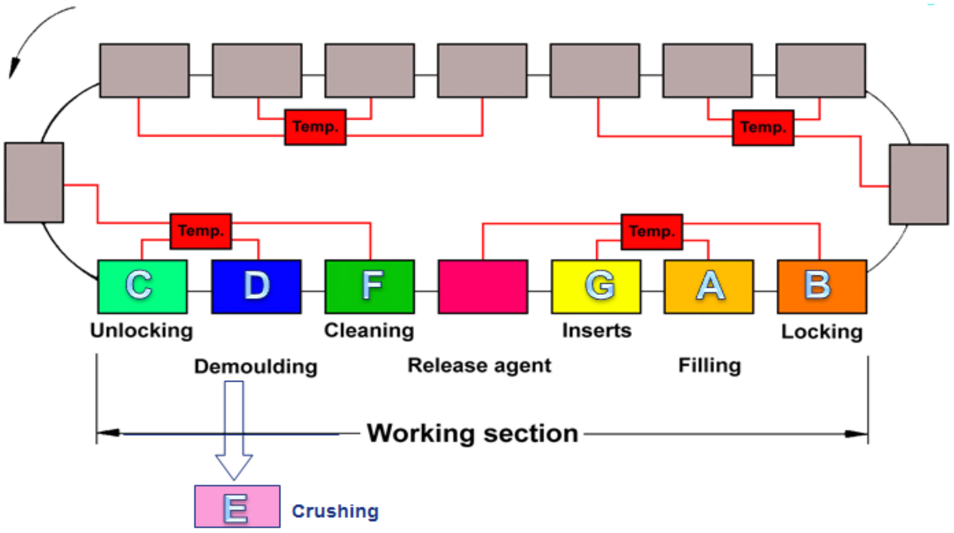


Figure 2.7 FPUR foam molding process [5]

From Figure 2.7, the molding cycle started at point (A) where the FPUR foams was injected into the mold by mixing machine, and then the mold closed at point (B). Foams were allowed to cure in the mold while the mold moving forward. At point (C) and (D), mold was unlocked and then foam was de-molded. The close-celled foams after de-molded as described above must be mechanically opened at point (E). This can be achieved by roller crushers with counter rotation rollers, compressing the foams to a fraction of their original height, or by fast alteration of the ambient pressure in a pressure chamber (vacuum crushing). After foams were removed from the molds, the mold continue moving to cleaning station [at point (F)] to take off the foam scrap which remain in the ventilation area, and then moved to point (A) to inject the foam into the mold again. Some parts may need to produce incorporated with metal frames or metal inserts which can be done at point (G).

One hour after de-molding, molded foams have reached only 50-80% of their final hardness. Therefore, foam parts need to be handled with care in the first few hours after production. Depending on the chemistry and the climatic conditions, final properties are achieved after 5-12 hours after production.

2.4.2.2 Flexible molded foam application

- **Furniture:** Flexible molded foams are used for office chairs, armrests, and in specific combinations with steel springs, which are incorporated into the molded foam.
- **Automotive and transportation seat pads:** Flexible molded foams produce either from TDI or MDI are used in all kind of seat pads, seat cushions, backrests, headrests, etc. in passenger cars, motorcycles and commercial vehicles, aircraft and railways. Not only seat pads, flexible molded foams also. Table 2.2 gives general overviews of the properties of seat pad foams in comparison between produced from TDI and MDI.

Table 2.2 Average properties for seat grades of flexible molded foams [5]

Property	Unit	TDI based molded foam	MDI based molded foam
Apparent density (core)	Kg/m^3	35-50	45-65
Elongation	%	100-150	90-120
Tensile Strength	kPa	130-200	100-160
Tear strength	N/m	200-450	160-250
Hysteresis (Energy dissipation)	-	Low	medium
Humid aging	-	Good	good-very good
Dry compression set 50%, 70 ^{O}C, 22 h	%	4-8	4-8

2.5 Literature reviews

The molded FPUR foams was developed due to the demand of very complex shape products and the products which produce incorporated with spring, metal frames or metal inserts [5]. With these requirements the conventional FPUR slabstock foams cannot be used. It is estimated that 20 percent of total FPUR foams production worldwide involves one of the molding technique. Molded foam can be used in all form of transportation seating and trim parts, as well as in some upholstered furniture, bedding, packaging and novelty items [3].

“HR Foams” is an abbreviation for the words “high resiliency foams” which is one of the FPUR molded foams using in most applications either automotive seating, household furniture or mattress. The word HR refers to the foams having ball rebound properties higher than those obtained with conventional slabstock foams. Today, the term HR is referred to as cold-cure foams. HR molded foams also offer the superior support factor (ratio of 65% hardness IFD to 25% hardness IFD) than those of conventional slabstock foams. An improvement in support factor means that a foam can offer higher load bearing at the use deflection and still maintain its soft initial feel.

The first HR molded foam appeared during the 1960s. These foams were based on ethylene-oxide-capped polyether triols. Copolymer or grafted polyols were introduced for this application in the late sixties [3].

In automotive seating application, during the first age of automotive industry since 1920s, the materials such as spring with wood plate cover, hair and its substitutes, cloth, rubberized latex and latex foam have been used as seat cushion. In 1954, the first FPUR foams introduced to automotive seating application. The first FPUR foams used is polyester slabstock foam. However, due poor hydrolytic property, it was replaced by polyether molded foams in 1957 [6]. Until today, there are many researches study in the development of FPUR molded foams reactivity and mechanical properties [7,8]. Regarding to automotive seating application, the development were done from both MDI-based FPUR foams [9] and TDI-based FPUR foams [10,11] in order to improve the mechanical properties and also comfort ability.

Nowadays, in the production of HR mold foams, crushing process is the must-have process required at all production lines. Since the final parts after de-molding process contain a lot of close-cells structure. Just after production, such cells are filled with hot, pressurized carbon dioxide gas. As the foam cools, two things happen: the internal gas pressure diminished and the carbon dioxide diffused out from the cells roughly fifteen times faster than air diffused into the cells. The net result is a partial vacuum in the cell which, when taken over a population of closed-cells, cause the foam to shrink and lose physical dimensions [3]. The crushing process causes the carbon dioxide to diffuse out from the clos-cells structure before it cools down. Thus, this can prevent foam shrinkage during production. The amount of closed-cell in FPUR foams is depending on the FPUR foam formulation. Sometimes, although the final products passed through the crushing process but foam shrinkage still observed due to too much closed-cell content in FPUR foams structure. The selection of FPUR foams formulation using the suitable type and amount of cell opening agent and the understanding of cell opening mechanism are a crucial part in novel HR molded foams production.

The first cell opening mechanism for FPUR foams was first introduced in 1996 by Yasunaga and coworkers [12] by using the parallel plate rheometer. The result from parallel plate rheometer showed that the normal force of FPUR foam rapidly increased as the foam modulus increased due to phase separation of urea domain (Figure 2.8), then the force suddenly decreased when the gas from reaction was released from the plate. The point that normal force suddenly dropped, which was the onset of cell opening, occurred before the visual blow-off was observed. At the onset of cell opening, the estimate open cell content was approximately 9%.

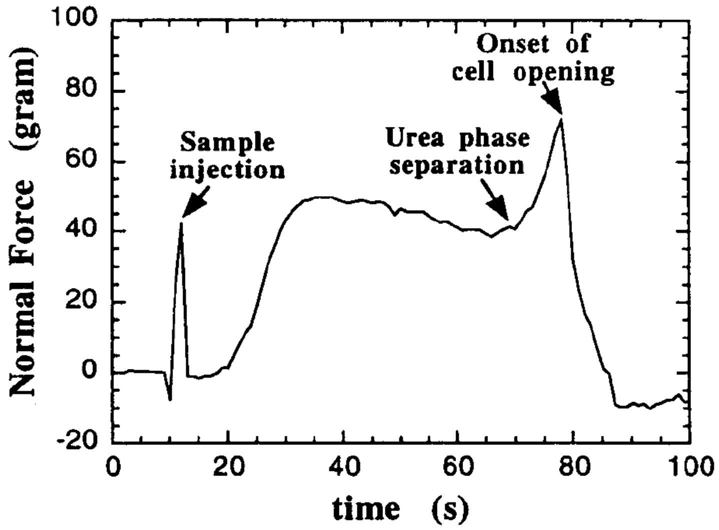


Figure 2.8 Typical normal force profile from parallel plate rheometer [12]

In the FPUR foams prepared from formulation using glycerol, urea phase separation was not observed, and therefore there was no onset of cell opening. This implied that cell opening occurred primarily due to urea precipitation.

The cell opening mechanism by Yasunaga and coworkers was reviewed and discussed in 1999 by Zhang and coworkers [13]. Besides of urea phase separation many cell opening mechanisms were purposed such as:

- Solid particle defoaming; the presence of "solventphobic" solid particles can destabilize a liquid foam system (Figure 2.9). This will cause liquid drainage away from the particles and start the de-wetting process which cause thinning and rupture of the film results in open cell structure.

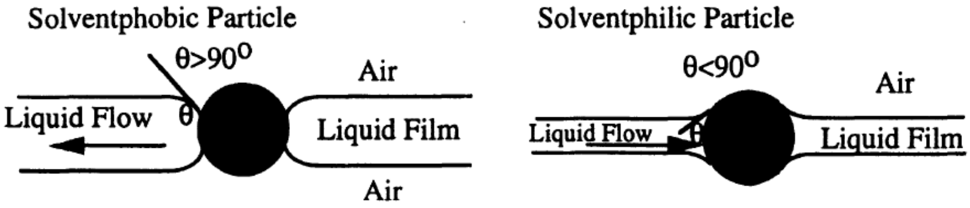


Figure 2.9 The liquid film rupture process by "solventphobic" particles [13]

- Surfactant phase separation (Insoluble liquid droplets defoaming); this mechanism assumes a decrease in solubility of surfactant in polyol with increasing temperature. As the temperature rises until above a critical value, the surfactant will phase separate (become a liquid droplets) and act like a defoamer. This insoluble liquid droplets can de-wet and cause the film rupture in the same way as solid particle.
- Spontaneous film rupture mechanism; this mechanism assumes that in liquid film with no heterogeneous structures such as particles and droplets, the film will rupture by the growth of surface waves on the film surfaces. The wave originated from thermal motion will grow rapidly when the film reaches the critical thickness. The critical thickness of polyurethane foam was calculated to be 15 nm.

However, the mechanisms described above were examined with various experiments. Foam column tests were performed to test the stability of liquid foam with and without the addition of urea particles. The similar liquid foam stability regardless to the addition of urea particles shows that the solid de-wetting mechanism should not be correct. In the case of insoluble liquid defoaming mechanism, element mapping of surfactant was obtained for final cured foams. The results show that surfactant is very homogeneously distributed in foam samples and no surfactant phase separation is observed. Hence, the surfactant phase separation is not valid. Using light interference microscopy which examines the thickness profile and the window thickness distribution, the thinnest film found in polyurethane is thicker than 150 nm which is and order of magnitude higher than the critical thickness of polyurethane foam (15 nm). This result also denied the spontaneous rupture mechanism.

Zhang and coworkers [13] proposed that urea particles cannot de-wetting and cause the film to rupture but the precipitated urea will trigger the cell opening by affecting the rheological properties of the foam matrix. The rheological of a model compound made to simulate the polyurethane phase separation was measured using the lubricated squeeze flow apparatus. A strong extensional thinning behavior can cause cell window rupture as shows in Figure 2.10.

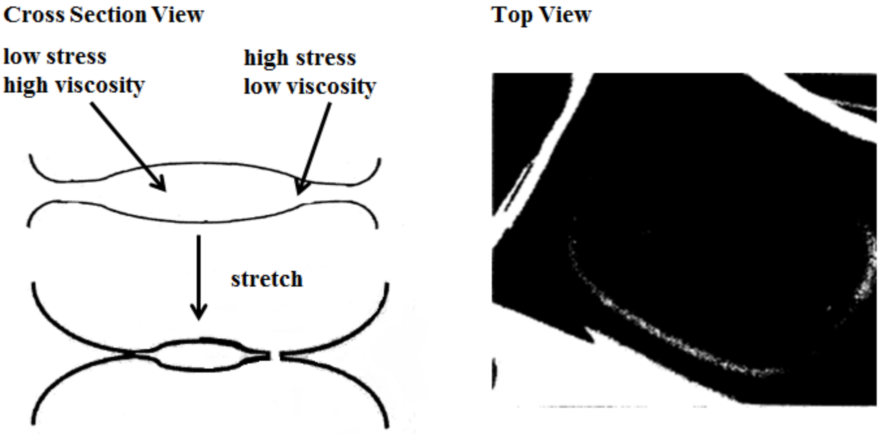


Figure 2.10 Schematic of localized film thinning due to the extensional thinning behavior of the foam matrix [13]

From Figure 2.10, when the urea phase separation occurs, the cell window (usually have a dimple shape) will exhibit the extensional thinning behavior. The edge of cell window (thinner part) will have higher stress and lower viscosity than the center (thicker part), results in film thinning localization to the edge of the cell window and causes the cell windows to thin rapidly and form pin holes. These pin holes can further develop into partially open or fully open cell windows depending on the matrix viscosity and time available for cell opening. This is the reason that the cell opening always happens a few seconds after urea phase separation regardless what surfactant used in the formulation.

The thickness distribution of cell window influences the final open cell morphology of FPUR foams. Figure 2.11 shows how open cell windows with different morphologies are obtained. The thinner windows will rupture first when the foam matrix viscosity is low and has high flowability. Thus, the rupture window flows back to the struts and smooth edge will be obtained and form the fully open cell windows with smooth edge [Figure 2.11 (a)]. The medium thickness windows form pin holes later when the viscosity is higher, so the rupture windows have limited flowability. The limited growth of pin holes results in partially open cell windows and open cell window with rough edge [Figure 2.11 (b), (c)]. The closed-cell windows [Figure 2.11 (d)] occur when the windows are too thick and cannot form pin holes due to the time for window thinning is less than the time for gel reaction.

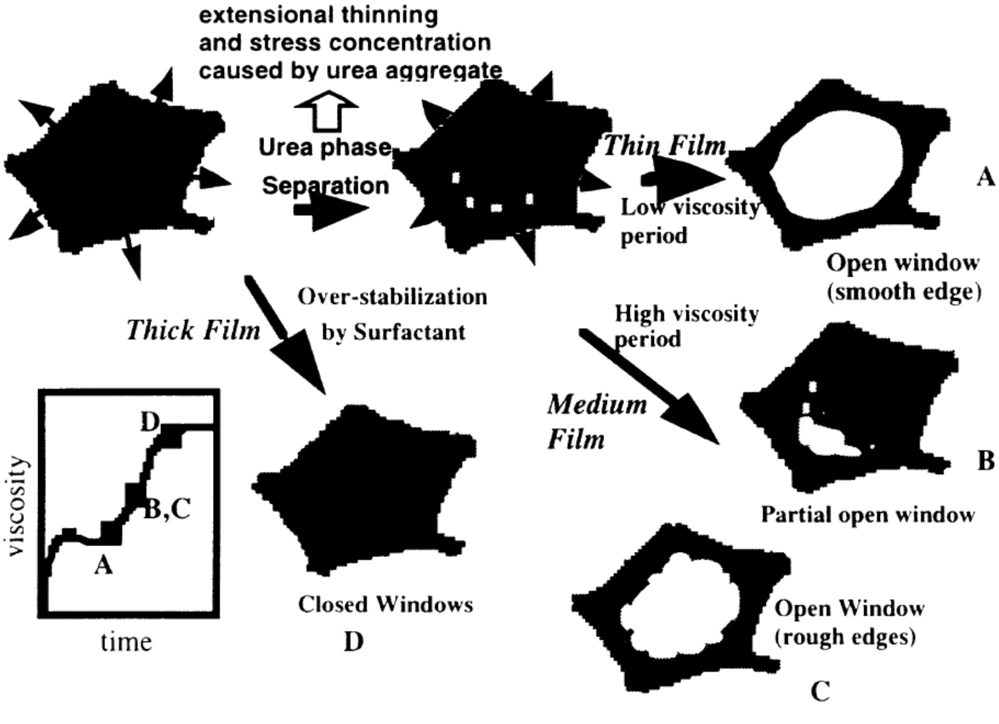


Figure 2.11 Open cell development with the different window thickness [13]

In the case of cell opening agent, many ingredients were tested and used as cell opening agent in both rigid and flexible PUR foams [14,15]. In 1990, Jerram and coworkers [16] claimed the use of high functionality polyether polyol as cell opening agent. This polyol is based on an initiator or initiator mixture having an average at least about 4.0 active hydrogens per molecule. The polyol has a molecular weight of at least 5,000 and contains at least 50 %wt. oxyethylene units and sufficient oxypropylene units to render its compatible with other components. It is shown that the use of high functionality polyether polyol at 0.2 to 3.0 pbw yields the greater proportions of open cell FPUR foams, less shrinkage and distortion of the foam is experienced.

Later in 1999, INOLEX Investment Corporation claimed the use of a monoester or polyester of a polyether polyol as cell opening agent [17]. This polyether polyol has a molecular weight (Mw) about 100 to 2000 and comprises a monofunctional or polyfunctional initiator having at least one esterification site. The formula of this cell opening agent is illustrated below:

$$\mathbf{P\text{-}((CH_2CHR^1\text{-}O)_nX)_m}$$

wherein P is a monofunctional or polyfunctional initiator having at least one esterification site

X is independently selected from the group consisting of hydrogen and $–C(O)R^2$, wherein at least one X is $–C(O)R^2$

R^1 is independently selected from the group consisting of hydrogen and aliphatic hydrocarbons of form 1 to about 4 carbon atoms.

R^2 is independently selected from the group consisting of saturated and unsaturated, linear and branched hydrocarbons of from about 3 to about 25 carbon atoms.

In 2002, Song and coworkers [4] studied the influence of different type of cell opening agents. They studied the effect of conventional cell opening agent type, poly(propylene oxide-ethylene oxide) (PPEO) and compared with the poly(ester-ether) type (PESE). The presence of PPEO and PESE, which are highly hydrophilic, delayed the FPUR foam reactivity due to the strong hydrogen bond between PPEO/PESE and water molecules. Thus, the molecular weight build up from the isocyanate-water reaction is less and causes the lower gelation in FPUR foam matrix. The resulting membranes are easy to rupture by the pressure increase from CO_2 gas generated and results in open cell network. In the presence of PESE, the delayed in reactivity is greater than PPEO since the PESE has both ether and ester linkages in the molecule which exhibits a higher level of hydrogen bond. They found that the use of PESE as cell opening agent yielded the open cell FPUR foams with better stability and mechanical properties than PPEO because PESE has higher solubilizing ability for associated urea than PPEO.

The cell opening agent can be used in the form of solid particles as well. Dai and coworker claimed the use of polysilsesquioxane particles as cell opening agent in 2011 [18]. This cell opening agent generally takes the form of particles having diameters 2 micrometers or smaller.

Besides of the use of cell opening agent, other components in FPUR foam formulation also influence and may use to control the open cell content in FPUR foams. Surfactant is one of those components. In 1999, Zhang and coworkers [19] studied the role of silicone surfactant in FPUR foams. They found that the key to control the open cell structure are the silicone/polyether ratio and the backbone length. Since the surfactants with high polyether content provide higher surface tension gradient along the film to retard drainage which results in lower percentage of open cell windows. High silicone content provides lower surface tension and this leads to a decrease in bubble size and increase in bubble generation rate. However, due to low film elasticity, these foams are unstable and potentially lead to foam collapse. The silicone surfactant with longer backbone improves the film elasticity. However, because of the higher surface tension, these foams have cell with larger cell size and as a consequence of larger cell size, these foams are unstable. To balance the surface tension and film elasticity, surfactants with siloxane backbone to polyether ratio from 0.32 to 0.50 were suggested.

The useful information of open cell mechanism and the study of cell opening agents lead to the development in FPUR molded foam production. In 2003, Park and coworkers [20] studied the noncrushing FPUR molded foam for automotive seating application by reducing the crosslink density and increasing the content of urea segment using the modified MDI as isocyanate in FPUR foam formulation.

CHAPTER III
EXPERIMENTAL

3.1 Materials

All materials used in this study were obtained from commercial sources. The long chain based polyether polyol, styrene acryonitrile (SAN) polyol, catalyst, crosslinker, surfactant, conventional cell opening agent, blowing agent, toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) were supported from Bayer Thai Co., Ltd. (BayerMaterialscience, Samutprakarn, Thailand). The materials used in this study and their properties are shown in Table 3.1. All chemicals were used as received.

Table 3.1 Raw materials for FPUR foams preparation and their properties

Materials	**Properties**
Arcol® polyol 1362	- Long chain based polyol OH value = 28 mgKOH/g
Hyperlite® E-850	- Hardener polyol OH value = 20 mg KOH/g, contained 43% solid content.
Arcol® PO polyol	- PO polyol as cell opening agent OH value = 56 mg KOH/g
High EO content polyether polyol	- Conventional cell opening agent OH value = 37 mg KOH/g
Glycerine	- Crosslinker OH value = 1830 mg KOH/g
Organo-modified polysiloxanes	- Surfactant.
Triethylene diamine in dipropylene glycol	- Tertiary amine catalyst

Table 3.1 (cont.) Raw materials for FPUR foams preparation and their properties

Materials	**Role**
Distilled water	- Chemical blowing agent
Toluene diisocyanate blended with methylene diphenyl diisocyanate (80:20)	- Isocyanate (automotive seating) NCO content = 44.8%
Methylene diphenyl diisocyanate	- Isocyanate (furniture) NCO content = 32.5%

3.2 FPUR foam preparation

In this work, FPUR foams preparation was separated into 2 mixing steps. In the first step, formulated polyol was prepared by mixing polyether polyol (either based polyol or hardener polyol) and other additives such as cell opening agent, crosslinker, catalyst, surfactant and blowing agent together. After that, all materials were homogenized by mechanical stirrer at 2,000 rpm for 2 minutes. In the second step, formulated polyol was mixed together with isocyanate by use of mechanical stirrer. The mixing procedure was depending on testing method. Figure 3.1 shows the FPUR foam preparation using cup test and molded test method.

3.2.1 FPUR foam preparation by cup test method

In cup test method, the formulated polyol was mixed together with isocyanate in the 700 ml cup by mechanical stirrer at 4,000 rpm for 5 seconds. The FPUR mixture was poured into 2.0 L cup to measure the foam reactivity. FPUR foam reactivity measured was cream time (the time that FPUR mixture started to rise up), gel time (the time that FPUR foam developed enough gel strength to resist light impressions and is dimensionally stable), rise time (the time that FPUR rised to maximum height before gas blow off from foam bun) and settling (the observable loss in height of FPUR foam between maximum height and the height at 5.0 minutes after reaction). After curing for 24 hours at room temperature, FPUR foams were cut to cubic shape having the size of 5.0 x 5.0 x 5.0 cm for density measurement.

3.2.2 FPUR foam preparation by molded test method.

In molded test method, FPUR foams were prepared using 2 mixing steps as described in 3.2.1. But in second step, formulated polyol and isocyanate were mixed together by mechanical stirrer at 5,500 rpm for 7 seconds, and then the FPUR mixture was poured into aluminum molded having the size of 400 mm. widths, length and 100 mm. thicknesses (400 mm x 400 mm x 100 mm). The mold's temperature was controlled at 60 – 65 ^{O}C. FPUR foams were left in the mold for curing for 5 minutes, after that foams were removed from the mold (de-mold) and waited for 1 minute before performing force to crush measurement to measure the open cell content. After 24 hours FPUR foams were submitted to physical and mechanical analysis.

3.3 Measurements

The FPUR foam reaction in cup test method was investigated using FOAMAT machine which used the ultrasonic wave to measure the rise profiles and rising speed, The reactivity, cream time, gel time was investigated by stopwatch while rise time and %settling were investigated using FOAMAT machine. The free rise density (FRD) was measured according to JIS 6400-1 by cutting the foam into cubic shape having a size of 5.0 cm x 5.0 cm x 5.0 cm. The average values of three specimens were reported.

The force to crush measurement and mechanical property analysis were performed using Zwick/Roell universal testing machine. Hardness (25% ILD) test was performed according to ASTM D 3574-95. Tensile strength, tear strength, elongation and ball rebound were performed according JIS 6400-1 using the specimens' thickness of 10 mm. The wet and dry compression set were performed according to JIS 6400-1. The strengths and elongation of five specimens per sample were measured and averaged. For wet and dry compression set, three specimens per sample were measured and averaged. The FPUR foams preparation and measurement process were shown in Figure 3.1

Morphology of FPUR foams was studied with a Phillips XL-30 scanning electron microscope. The samples were cut and gold sputtered before scanning in perpendicular to the foam rising direction. The accelerating voltage was 20 kV.

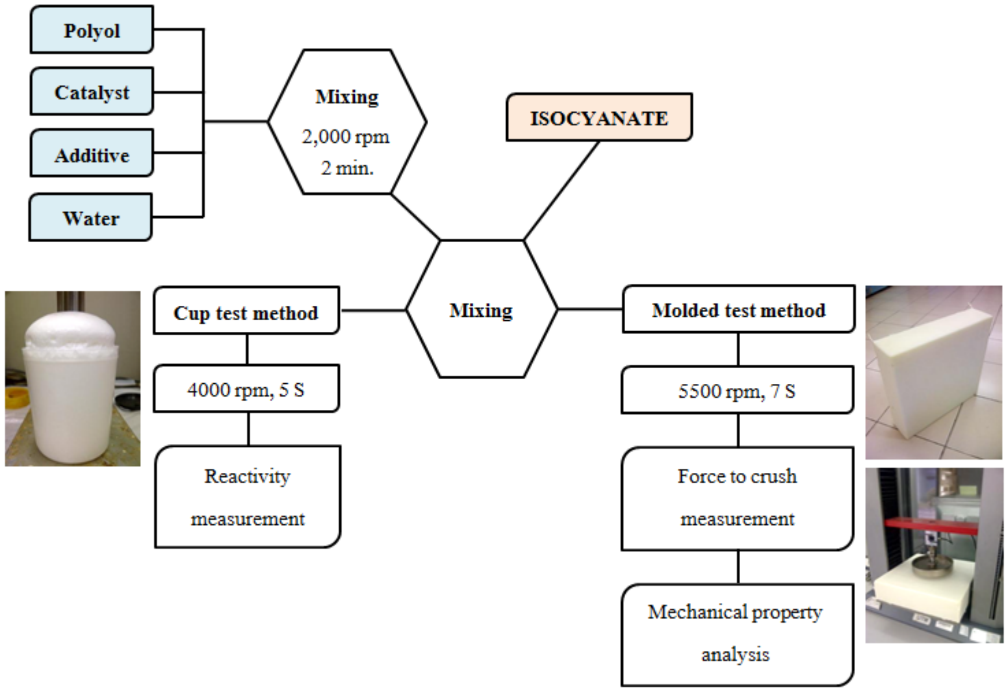


Figure 3.1 FPUR foam preparation and measurement process

Phase separation measurement between cell opening agent and other ingredients in formulated polyol was investigated by varying the amount of cell opening agent in formulated polyol at 1.0, 2.0, 3.0, 4.0 and 5.0 pbw. The formulated polyol were put into glass test tubes. The test tubes were put into the oven for aging test in comparison with formulated polyol prepared using PO polyol as cell opening agent. The aging test was performed at 70 °C. The test tubes were taken out for phase separation measurement by visual observation every day until the phase separation observed.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of flexible polyurethane (FPUR) foams for automotive seating application

4.1.1. Cup test experiments using reference FPUR foam formulations

The flexible polyurethane foams were prepared in 2 steps. In first step, polyol and other additives such as catalyst, surfactant, crosslinker, cell opening agent and blowing agent were mixed together in 700 mL cup for 2 minutes by the mechanical stirrer at 2,000 rpm to homogenize the polyol mixture, the polyol mixture from first step so called "formulated polyol". In second step, the isocyanate was added into the formulated polyol then the reaction mixture were mixed by mechanical stirrer at 4,000 rpm for 5.0 second to obtained homogeneous mixture then pour into plastic cup to measure the reactivity. The reactivity which was measured during foaming reaction including cream time, gel time, rise time and %settling. After that, the foams were kept in room temperature for 24 hours before cut and measure the foam density.

In this work, the amount of total base polyol, crosslinker, conventional cell opening agent, catalyst and surfactants were fixed. The amounts of blowing agent were varied at 3.0%, 3.5% and 4.0%. The isocyanate (TDI: MDI blended) was varied according to the NCO indexes of 90, 100 and 110. The foam formulations using conventional cell opening agent (reference formulation) are shown in Table 4.1.

4.1.1.1 FPUR foam reactivity and rise profiles

The reactivity of FPUR using conventional cell opening agent is shown in Table 4.2, the foam appearances are shown in Figure 4.1. FPUR foam reactivity measured was cream time, gel time, rise time and %settling. After that FPUR foams were left for curing at room temperature. After 24 hours, FPUR foams were cut to cubic shape having the size of 5.0 x 5.0 x 5.0 cm for density measurement.

Table 4.1 FPUR foam formulations prepared by using conventional cell opening agent (reference formulation) for automotive seating application

Formulations (pbw)	**Reference formulation**		
	#1	**#2**	**#3**
Arcol Polyol® 1362	60.0	60.0	60.0
Hyperlite® E-850	40.0	40.0	40.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	2.0	2.0	2.0
Surfactant	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6
Blowing agent (water, %)	3.0	3.5	4.0
Isocyanate (TDI:MDI blended) : 100 pbw formulated polyol			
NCO index 90	33.6	38.1	42.8
NCO index 100	37.3	42.4	47.5
NCO index 110	41.0	46.6	52.3

Table 4.2 Reactivity of FPUR foam prepared by using reference formulation at different blowing agent contents (%) and NCO indexes

Water content (%)	**3.0**			**3.5**			**4.0**		
NCO indexes	**90**	**100**	**110**	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10	10	10	10
Gel time (s)	58	62	65	62	64	66	62	66	68
Rise time (s)	86	89	89	89	89	90	84	86	68
Settling (%)	8.1	13.2	20.3	8.0	15.3	24.0	9.8	16.2	80.0
Foams density (kg/m^3)	35.5	38.0	42.0	30.2	32.5	42.7	28.2	32.2	-

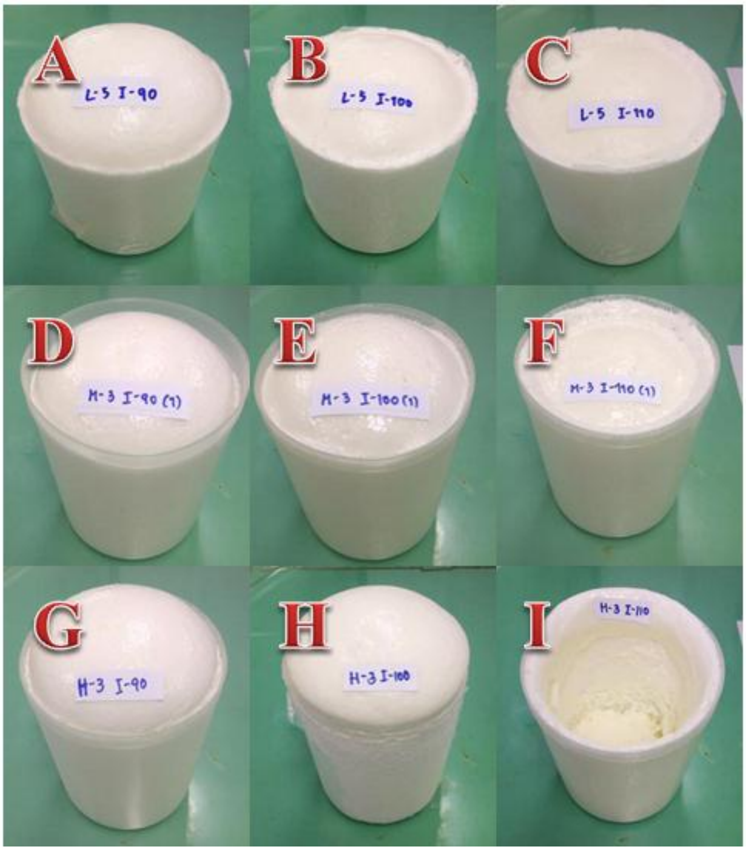


Figure 4.1 FPUR Foam appearances (a), (b) and (c) 3.0% water content at NCO indexes of 90, 100 and 110, respectively; (d), (e) and (f) 3.5% water content at NCO indexes of 90, 100 and 110, respectively; (g), (f) and (I) 4.0% water content at NCO indexes of 90, 100 and 110, respectively

4.1.1.2 Effect of blowing agent (water) content to foam reactivity and rise profiles

Figure 4.2 shows the foam reactivity in comparison between formulations which contained 3.0%, 3.5% and 4.0% water content at the NCO index of 100. Lower water content formulation (3.0% water content) gave faster gel time and slower rise time than higher water content formulation (3.5% or 4.0% water content). This is because of at low water content, the blowing reaction between water and isocyanate group to give carbon dioxide is not enough to dominate the overall reaction. The gel catalyst promotes gel reaction to be faster than blowing reaction. If foam formulation has too much water content (4.0% water content), the blowing reaction will dominate the overall reaction which results in faster rise time due to higher amount of carbon dioxide generated. The gas will blow off from FPUR cell structure at the time when gel strength is not strong enough. Thus, the cell structures rupture to give open cell structure in FPUR foam.

High water content in foam formulation also generated high amount of amine by-product from blowing reaction. These amines further react with isocyanate to form urea in FPUR foam. The urea precipitation from cell window causes pin holes in polyurethane film. The pin holes occur at cell window then develop to open cell structure. This made foams using higher water content formulation have higher settling due to higher open cell content. The change in settling was more observable at the NCO index of 110 when higher isocyanate was presented in FPUR formulation as shown in Figure 4.3. High water content formulation together with high NCO index led to foam collapse as shown in Figure 4.1(i) and also very fast rise time, which was abnormal, as shown in Figure 4.3. For the foam density the more water content in foam formulation, the higher gas was generated from blowing reaction which gave foams having lower density.

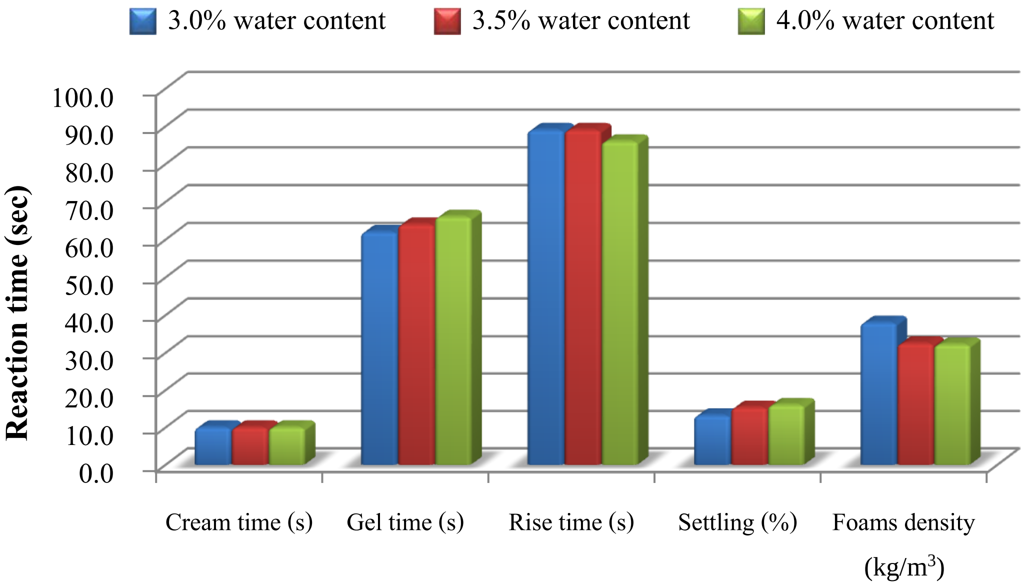


Figure 4.2 Reactivity of FPUR foams prepared by using reference formulation at the NCO index of 100

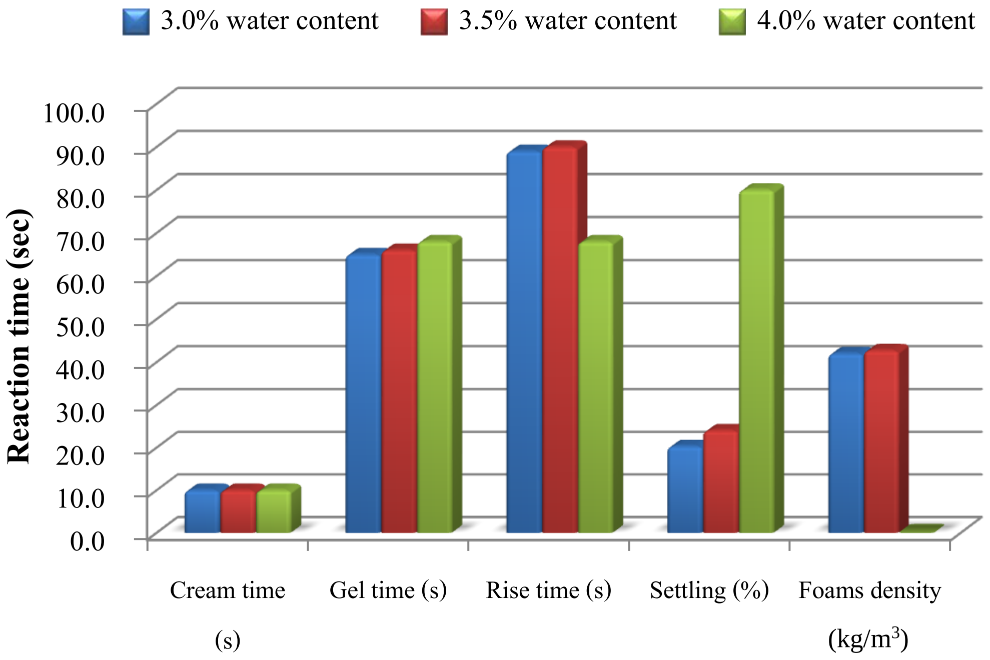


Figure 4.3 Reactivity of FPUR foams prepared by using reference formulation at the NCO index of 110

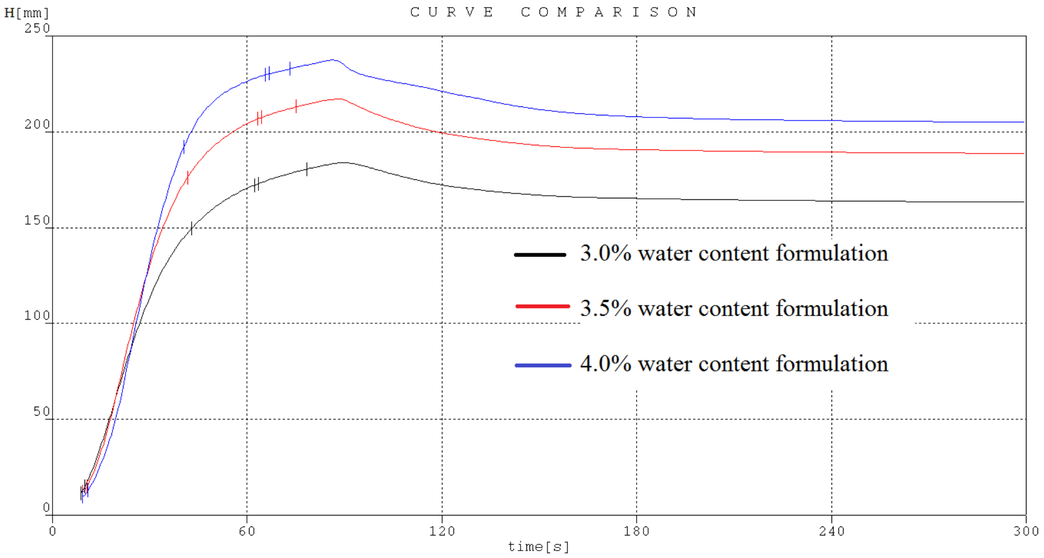


Figure 4.4 Rise profiles of FPUR foam prepared by using reference formulation at the NCO index of 100

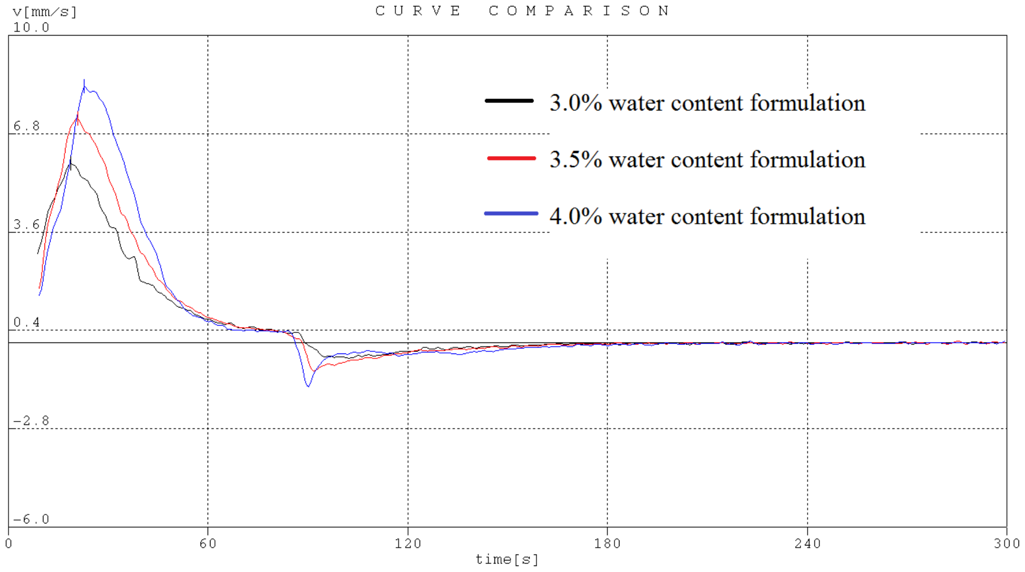


Figure 4.5 Rising speed of FPUR foam prepared by using reference formulation at the NCO index of 100

Figures 4.4 and 4.5 show FPUR foam rise profiles (foam height in mm vs. reaction time) and rising speed (foam rising speed in mm/sec vs. time) of reference formulation having 3.0%, 3.5% and 4.0% water content, respectively. The rising speed of higher water content formulation in Figure 4.5 is faster and the maximum foam height in Figure 4.4 is higher due to higher gas generated from blowing reaction, Figures 4.4 and 4.5 demonstrate that higher water content formulation gives faster foam reactivity and lower foam density.

4.1.1.3 Effect of the NCO indexes to foam reactivity and rise profiles

NCO index is directly related to the amount of isocyanate group which will react with other functional group in the FPUR foam formulation. Increased NCO index promotes blowing reaction more than gel reaction, which is the same effect as increasing water content. Higher NCO index resulted in slower gel time, faster rise time, higher settling and higher foam density. Figure 4.6 shows reactivity of foam formulation contained 3.5% water content in comparison between the NCO indexes of 90, 100 and 110.

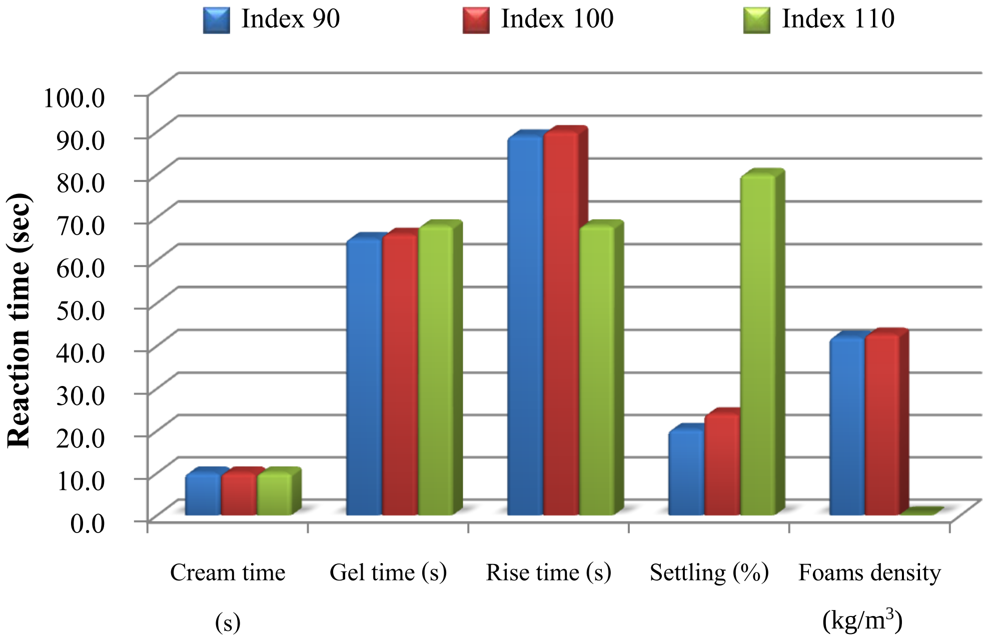


Figure 4.6 Reactivity of FPUR foams prepared by using reference formulation contained 3.5% water content at the NCO indexes of 90, 100 and 110

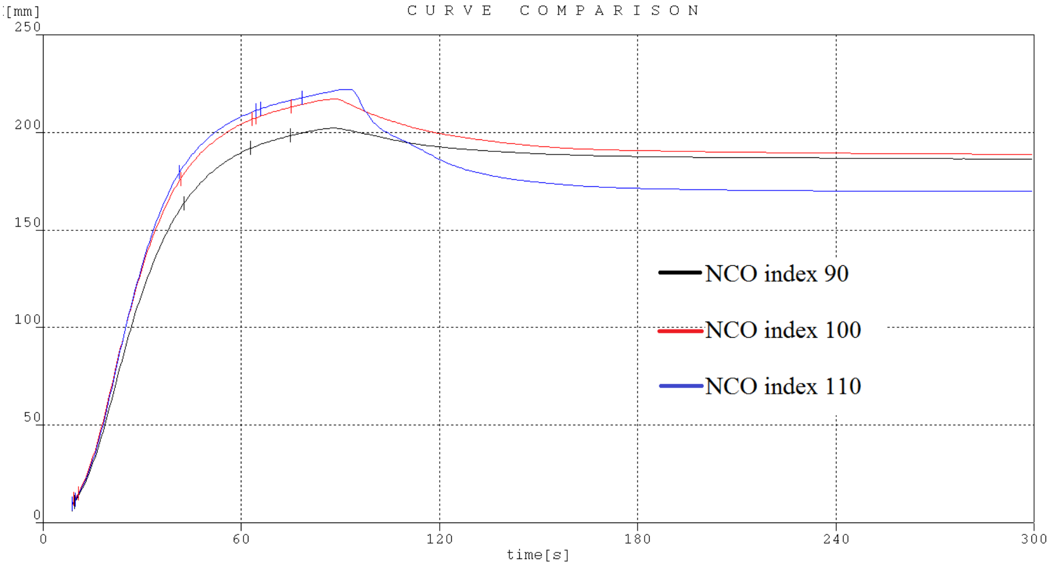


Figure 4.7 Rise profiles of FPUR prepared by using reference formulation with 3.5% water content

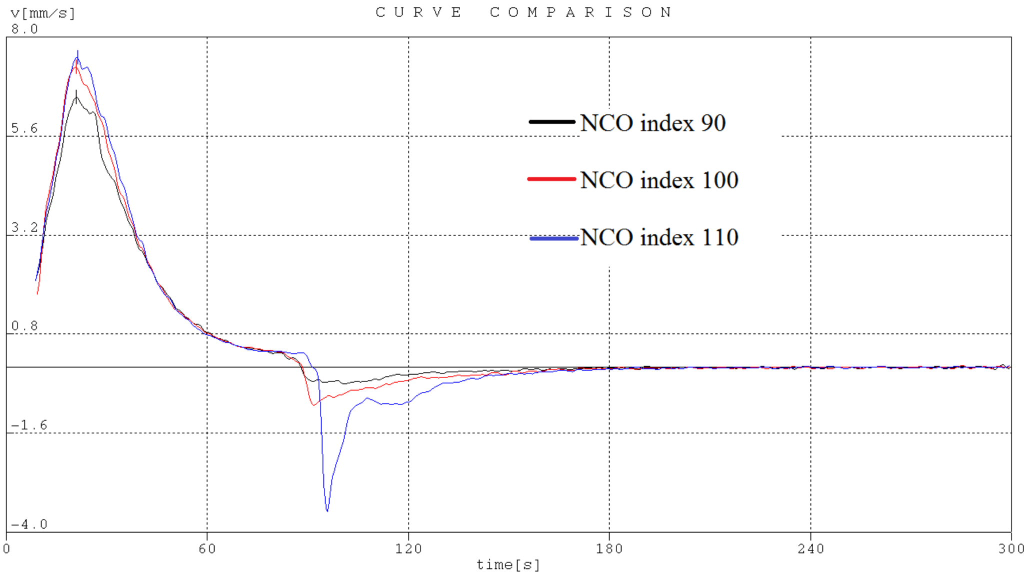


Figure 4.8 Rising speed of FPUR prepared by using reference formulation with 3.5% water content

Figures 4.7 and 4.8 show rise profiles and rising speed of the reference formulation when compared at the NCO indexes of 90, 100 and 110, respectively. It is clearly shown that the effect of NCO indexes to reactivity and rise profiles is the same as the effect of water content in FPUR foam formulation. Higher NCO indexes resulted in faster reactivity, higher settling and higher foam height.

From Figures 4.3 and 4.6, the settling and foam density of formulation contained 4.0% water content at the NCO index of 110 were too high, and this caused foam collapse (%settling = 80.0% in Table 4.2). Therefore, the formulation cannot be used as the reference formulation. The cell opening agent content in formulation with 4.0% water content was decreased from 2.0 pbw to 1.5 pbw (Table 4.3) in order to obtain good foam appearance. The foam reactivity and appearance obtained before and after decrease of cell opening agent amount are shown in Table 4.4 and Figure 4.9, respectively. Figure 4.9 (c) shows the foam collapse resulting from too much open cell structure at the NCO index of 110. After decreasing the cell opening agent from 2.0 pbw to 1.5 pbw, foam appearance was good at the NCO index of 110 and no foam collapse was observed (Figure 4.9 (f)).

Table 4.3 FPUR foam formulation with 4.0% water content obtained at different cell opening agent amount

formulations	**Cell opening agent amount**	
(pbw)	**2.0 pbw**	**1.5 pbw**
Arcol Polyol® 1362	60.0	60.0
Hyperlite® E-850	40.0	40.0
Crosslinker	0.5	0.5
Surfactant	0.6	0.6
Catalyst	0.6	0.6
Blowing agent (water)	4.00%	4.00%
Isocyanate (TDI:MDI blended) / 100 pbw formulated polyol		
NCO index 90	46.0	46.0
NCO index 100	51.1	51.1
NCO index 110	56.2	56.2

Table 4.4 Reactivity comparison of reference formulation with 4.0% water content obtained from different cell opening agent amount

Cell opening agent amount	**2.0 pbw**			**1.5 pbw**		
NCO indexes	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10.0	10.0	10.0	10.0	10.0	10.0
Gel time (s)	62.0	66.0	68.0	60.0	64.0	68.0
Rise time (s)	84.0	86.0	68.0	94.0	96.0	95.0
Settling (%)	9.8	16.0	80.0	5.8	10.4	17.2
Foams density (kg/m^3)	28.2	32.2	-	26.4	28.3	35.8

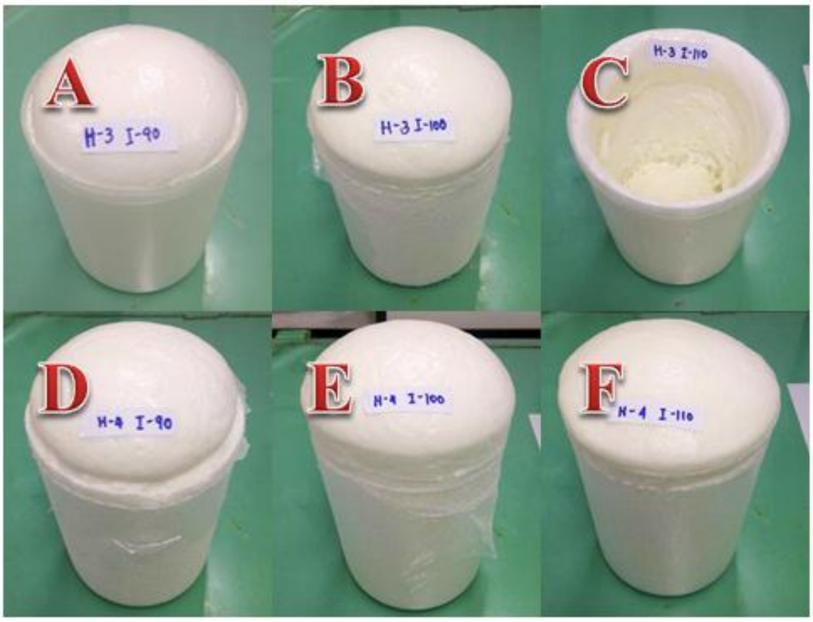


Figure 4.9 FPUR foam appearances prepared from the formulation contained 4.0% water content; (a), (b) and (c) 2.0 pbw cell opening amount at the NCO indexes of 90, 100 and 110, respectively; (d), (e) and (f) 1.5 pbw cell opening amount at the NCO indexes of 90, 100 and 110, respectively

The results of foams reactivity in Table 4.4 showed that the decrease in cell opening agent did not only reduce the open cell content which resulted in lower settling, but also made the rise time slower. This is because there is less gas amount that blows off through cell structure less in FPUR foam due to less open cell structure. After reducing the amount of cell opening agent in FPUR foam formulation, the foam appearances were good and no foam collapse was observed. Therefore, the FPUR reference formulations at different water contents were changed according to Table 4.5

Table 4.5 FPUR reference formulations prepared at different blowing agent (water) contents

Formulations (pbw)	**Reference formulation**		
	#1	**#2**	**#3**
Arcol Polyol® 1362	60.0	60.0	60.0
Hyperlite® E-850	40.0	40.0	40.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	2.0	2.0	1.5
Surfactant	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6
Blowing agent (water)	3.00%	3.50%	4.00%
Isocyanate (TDI:MDI blended) / 100 pbw formulated polyol			
NCO index 90	33.6	38.1	42.8
NCO index 100	37.3	42.4	47.5
NCO index 110	41.0	46.6	52.3

4.1.2. Cup test experiments using additional PO polyol as cell opening agent in FPUR foam formulation

From the reference formulation, the PO polyol was used as cell opening agent instead of the conventional cell opening agent in reference formulation. The amounts of PO polyol were varied at 2, 4, 6, 8 and 10 pbw while the water content was fixed at 3.5%. The FPUR foam preparation step is the same as described in 4.1.1. All formulations were prepared at the NCO indexes of 90, 100 and 110 (Table 4.6).

Table 4.6 FPUR foam formulations prepared using PO polyol as cell opening agent at different PO polyol amounts and isocyanate indexes of 90, 100 and 110

Formulations (pbw)	**#1**	**#2**	**#3**	**#4**	**#5**
Arcol Polyol® 1362	60.0	60.0	60.0	60.0	60.0
Hyperlite® E-850	40.0	40.0	40.0	40.0	40.0
PO polyol	2.0	4.0	6.0	8.0	10.0
Crosslinker	0.5	0.5	0.5	0.5	0.5
Surfactant	0.6	0.6	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6	0.6	0.6
Blowing agent (water)	3.50%	3.50%	3.50%	3.50%	3.50%
Isocyanate (TDI:MDI blended) / 100 pbw formulated polyol					
NCO index 90	41.0	41.0	41.0	41.0	41.0
NCO index 100	45.5	45.5	45.5	45.5	45.5
NCO index 110	50.0	50.0	50.0	50.0	50.0

FPUR foams reactivity is shown in Tables 4.7 and 4.8. Foam appearances are shown in Figure 4.10. The criteria for this reactivity testing are settling which represent to open cell content in foam and foam appearances which have to be good, no foam collapse and shrinkage presented. %Settling is normally control at 5.0% - 25.0%. If settling is too large, the foams have tendency to collapse.

Table 4.7 FPUR foams reactivity prepared using PO polyol as cell opening agent at the amount of 2.0, 4.0 and 6.0 pbw and NCO indexes of 90, 100 and 110

PO polyol (pbw)		**2.0**			**4.0**			**6.0**	
NCO indexes	**90**	**100**	**110**	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10	10	10	10
Gel time (s)	59	62	65	59	65	66	59	65	65
Rise time (s)	100	104	111	101	106	111	103	106	113
Settling (%)	3.6	5.2	8.6	3.7	5.5	9.3	4.0	5.4	9.8
Foams density (kg/m^3)	27.5	28.2	31.5	27.8	28.3	30.7	27.9	28.4	31.6

Table 4.8 FPUR foams reactivity prepared using PO polyol as cell opening agent at the amount of 8.0 and 10.0 pbw and NCO indexes of 90, 100 and 110

PO polyol (pbw)		**8.0**			**10.0**	
NCO indexes	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10
Gel time (s)	63	66	68	64	67	70
Rise time (s)	108	112	120	109	114	122
Settling (%)	4.5	6.0	9.8	4.7	7.5	10.2
Foams density (kg/m^3)	28.2	29.5	33.2	29.0	30.4	34.1

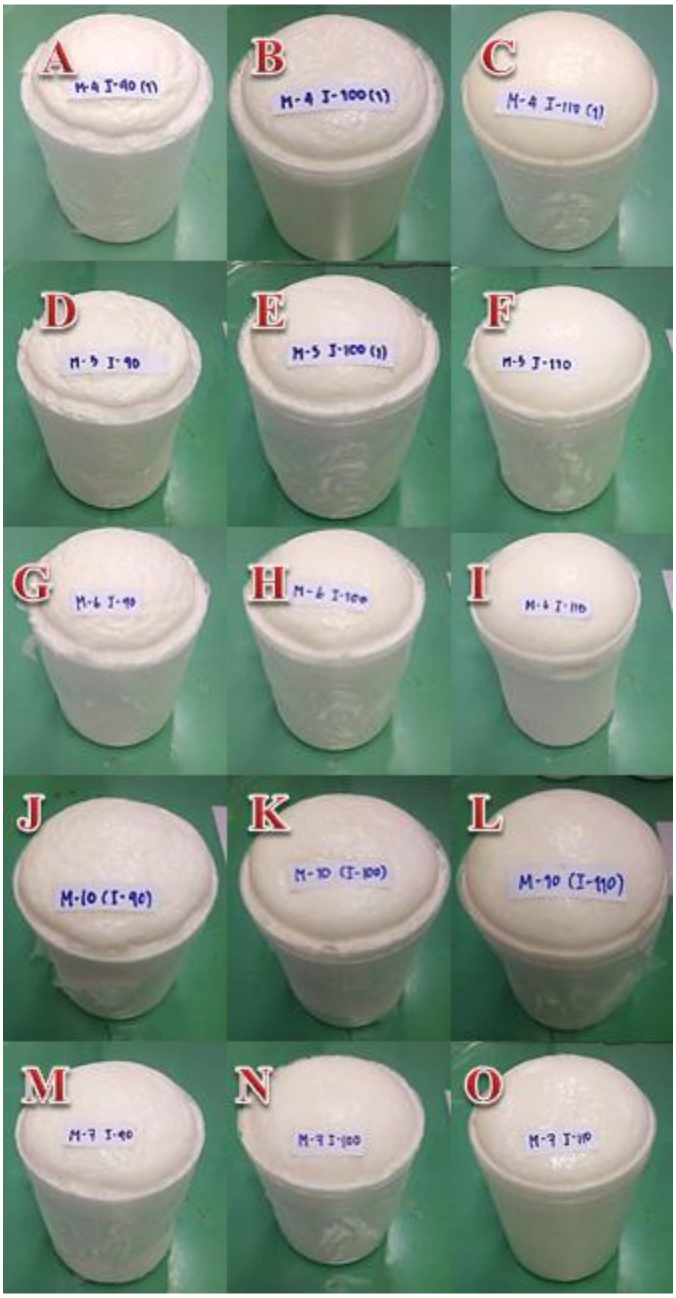


Figure 4.10 FPUR Foam appearances prepared using PO polyol as cell opening agents; (a), (b), (c) 2.0 pbw PO polyol at the NCO indexes of 90, 100 and 110 respectively; (d), (e), (f) 4.0 pbw PO polyol at the NCO indexes of 90, 100 and 110 respectively; (g), (h), (i) 6.0 pbw PO polyol at the NCO indexes of 90, 100 and 110 respectively; (j), (k), (l) 8.0 pbw PO polyol at the NCO indexes of 90, 100 and 110 respectively; (m), (n), (o) 10.0 pbw PO polyol at the NCO indexes of 90, 100 and 110 respectively

4.1.2.1 The effect of PO polyol to foam reactivity and rise profiles

When the PO polyol amount in foam formulation was increased (Figures 4.11 – 4.13) slower gel time, slower rise time and higher %settling were obtained. This is because of PO polyol is considered as one of the based polyol in FPUR foam formulations, the additional PO polyol dilute the catalyst concentration in foams formulations. Thus, the higher PO polyol content in foam formulations causes the slower foams reactivity. The other explanation is PO polyol contained only secondary –OH group which is less reactive when compare to primary –OH group from ethylene-oxide capped polyol which is used as the based polyol. The secondary –OH group from PO polyol potentially delayed the gel reaction in FPUR reaction and results in slower gel time. If the gel reaction is less the strength of FPUR structure is not strong enough to resist the pressure from gas CO_2 generated from blowing reaction. The result is cell rupture and makes FPUR foams have higher open cell content and higher settling as same as using conventional cell opening agent. The higher settling results in higher foams density as PO polyol content increased. Anyhow, the small amounts of PO polyol are not as effective as using conventional cell opening agent. The settling and foams appearance of formulation contained 2.0, 4.0, 6.0 and 8.0 pbw PO polyol are not as good as the foams using conventional cell opening agent, foam shrinkage at skin surface were observed especially at low NCO index (index 90) as shown in Figure 4.6 (a), (d), (g) and (j). The PO polyol content required in order to get open cell content enough to resist foam shrinkage is 10.0 pbw as shown in Figure 4.6 (m), (n) and (o)

Besides using additional amount of PO polyol in FPUR foams formulations, partially substitution of based polyol with PO polyol should be the better way to obtain enough open cell in FPUR foam without too much effect on the foams reactivity and density.

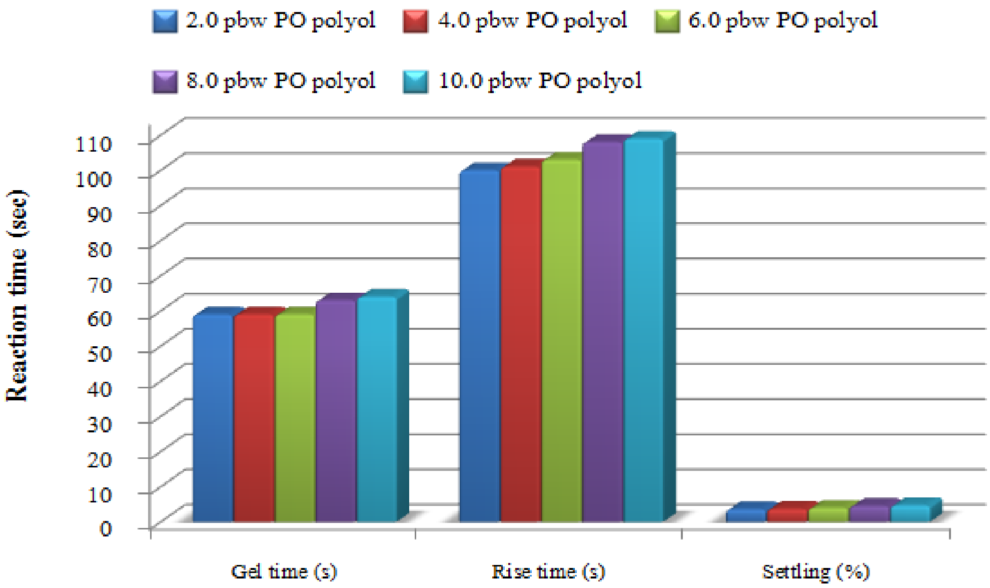


Figure 4.11 Reactivity of FPUR foams prepared by using PO polyol as cell opening agent at the NCO index of 90

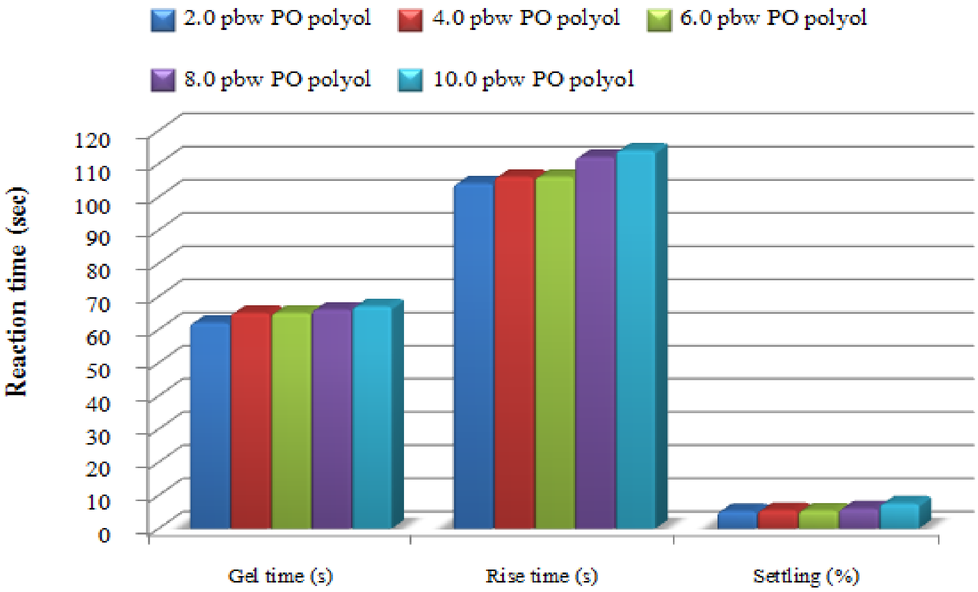


Figure 4.12 Reactivity of FPUR foams prepared by using different amounts of PO polyol as cell opening agent at the NCO index of 100

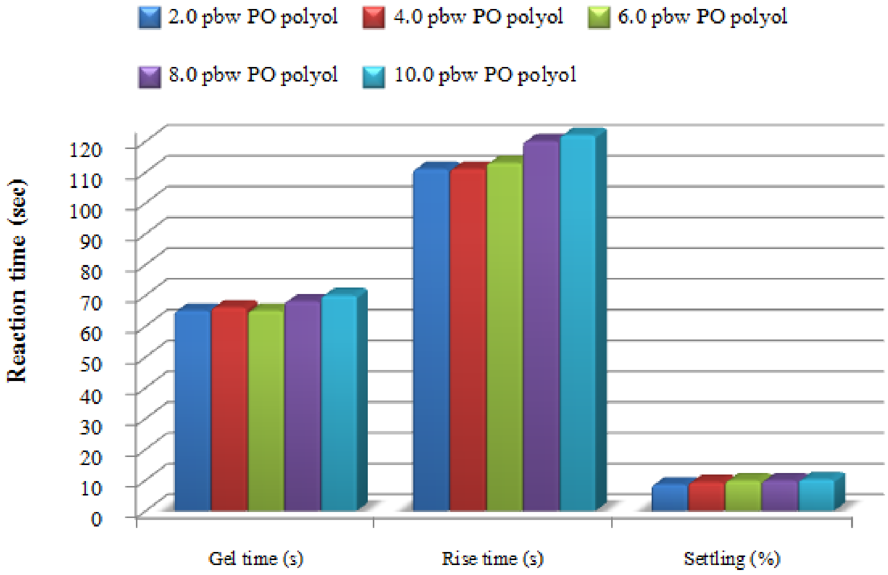


Figure 4.13 Reactivity of FPUR foams prepared by using different amounts of PO polyol as cell opening agent at the NCO index of 110

Figures 4.14 and 4.15 show rise profiles and rising speed in comparison between FPUR formulations prepared by using PO polyol as cell opening agent at 2.0 – 10.0 pbw at the NCO index of 100, respectively. It could be clearly observed that increased of PO polyol delayed in both FPUR foam rise profiles and rising speed.

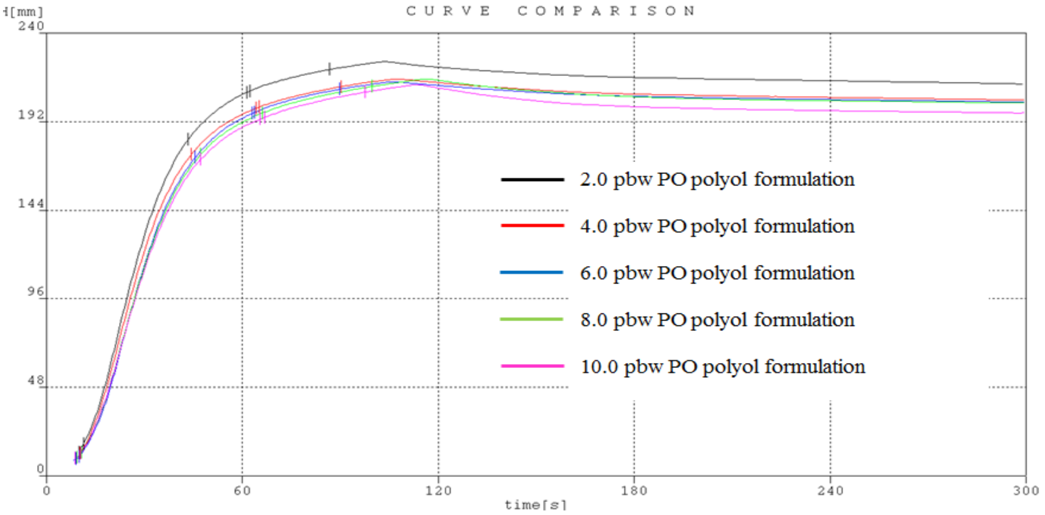


Figure 4.14 Rise profiles of FPUR foams prepared by using 2.0 – 10.0 pbw of PO polyol as cell opening agent

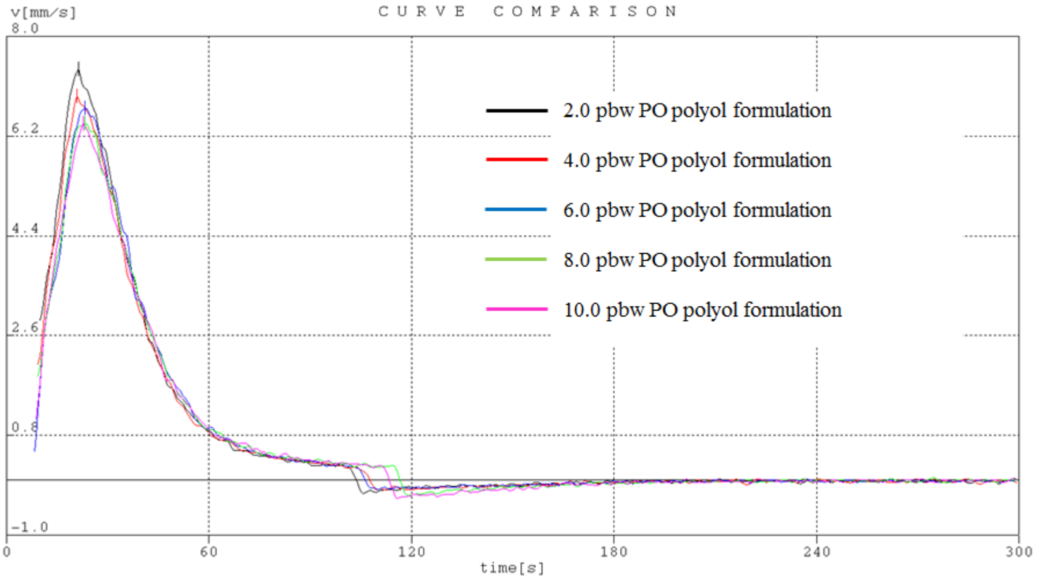


Figure 4.15 Rising speed of FPUR foams prepared by using 2.0 – 10.0 pbw of PO polyol as cell opening agent

The maximum height of FPUR foam prepared from the formulation contained 2.0 pbw PO polyol (Figure 4.14) was the highest due to a large amount of closed cell formation. Therefore, CO_2 gas cannot blow off from the foam matrix and the trapped gas continued to expand and the foam continued to rise until reaching the maximum height.

4.1.3. Cup test experiments using substituted PO polyol as cell opening agent in FPUR foam formulation

From 4.1.2, the suitable PO polyol amount to act as cell opening agent is 10.0 pbw. However, the additional PO polyol delayed the foam reactivity. Hence, the PO polyol was used as partially substituent of based polyol at 10.0 pbw 15.0 pbw in the reference formulation. The foam reactivity and appearances obtained from these two substituted PO polyol formulations were compared to those obtained from reference formulation prepared with 3.5% water content at the NCO indexes of 90, 100 and 110 (Table 4.9).

4.1.3.1 Effect of substituted PO polyol to foam reactivity and rise profiles

Foam reactivity after partially substitution of base polyol with 10.0 pbw of PO polyol in comparison with those prepared from additional 10.0 pbw of PO polyol at NCO index 90, 100 and 110 are shown in Table 4.10. FPUR foam reactivity of all substituted PO polyol formulations in comparison with reference formulation are shown in Table 4.11. Figure 4.16 compares the foam appearance prepared from substituted PO polyol and reference formulations.

Table 4.9 FPUR foam formulations prepared by partially substituted PO polyol in the reference formulation

Formulations (pbw)	**Reference formulation**	**Substituted PO polyol formulation**	
		10.0 pbw	**15.0 pbw**
Arcol Polyol® 1362	60.0	50.0	45.0
Hyperlite® E-850	40.0	40.0	40.0
PO polyol	-	10.0	15.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	2.0	-	-
Surfactant	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6
blowing agent (water)	3.50%	3.50%	3.50%
isocyanate (TDI:MDI blended) / 100 pbw formulated polyol			
NCO index 90	38.1	38.5	38.7
NCO index 100	42.4	42.7	43.0
NCO index 110	46.6	47.0	47.3

Table 4.10 FPUR foam reactivity prepared from additional and substituted 10.0 pbw of PO polyol at the NCO indexes of 90, 100 and 110

Foam reactivity	**Additional PO polyol 10.0 pbw**			**Substituted PO polyol 10.0 pbw**		
NCO indexes	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10
Gel time (s)	64	67	70	61	64	66
Rise time (s)	109	114	122	92	96	103
Settling (%)	4.7	7.5	10.2	5.3	8.1	11.6
Foam density (kg/m^3)	29.0	30.4	34.1	29.4	30.3	35.7

Table 4.11 FPUR foam reactivity prepared from substituted PO polyol and reference formulations at the NCO indexes of 90, 100 and 110

Substituted PO polyol formulation	**Reference formulation**			**10.0 pbw PO polyol**			**15.0 pbw PO polyol**		
NCO index	**90**	**100**	**110**	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10	10	10	10
Gel time (s)	62	64	66	61	64	66	60	64	66
Rise time (s)	89	89	90	92	96	103	80	87	94
Settling (%)	8.0	15.3	24.0	5.3	8.1	11.6	8.8	10.7	30.8
Foam density (kg/m^3)	30.2	32.5	42.7	29.4	30.3	35.7	31.8	32.6	40.1

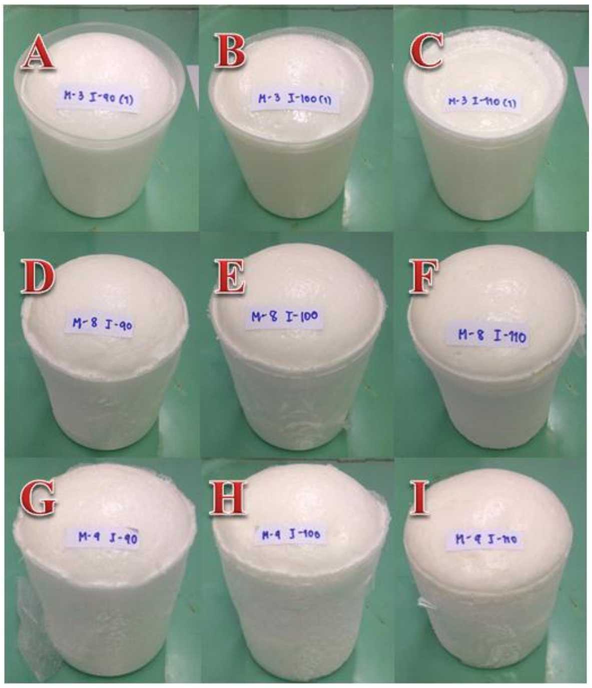


Figure 4.16 FPUR foam appearances prepared from reference and substituted PO polyol formulations; (a), (b), (c) reference formulation at the NCO indexes of 90, 100 and 110, respectively; (d), (e), (f) 10.0 pbw substituted PO polyol at the NCO indexes of 90, 100 and 110, respectively; (g), (h), (i) 15.0 pbw substituted PO polyol at the NCO indexes of 90, 100 and 110, respectively

Comparison of the reactivity between additional PO polyol and substituted PO polyol in foam formulations from Table 4.10 shows that substituted PO polyol formulations give faster foam reactivity since the catalyst was not diluted with additional amount of polyol. While the reactivity comparison between reference and substituted PO polyol formulation in Table 4.11 shows that 15.0 pbw substituted PO polyol formulation gives closer foam reactivity to reference formulation than 10.0 pbw substituted PO polyol formulation. However, the higher %settling of 15.0 pbw substituted PO polyol at NCO index of 110 indicated that 15.0 pbw substituted PO polyol has less stability than 10.0 pbw substituted PO polyol (Figure 4.14 (i)).

Both of 10.0 and 15.0 pbw substituted PO polyol formulations give slower foam reactivity when compared to the reference formulation. Figures 4.17 and 4.18 show the rise profiles and rising speed comparison between the reference, 10.0 pbw substituted PO polyol and 15.0 pbw substituted PO polyol formulations, respectively.

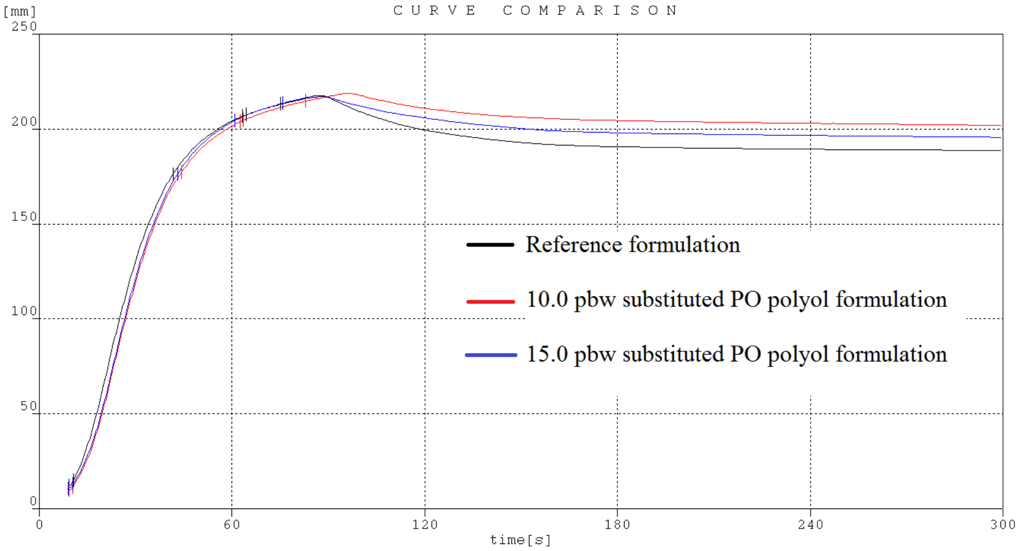


Figure 4.17 Comparison of FPUR rise profiles prepared by using reference, 10.0 pbw substituted PO polyol and 15.0 pbw substituted PO polyol formulations with 3.5% water content

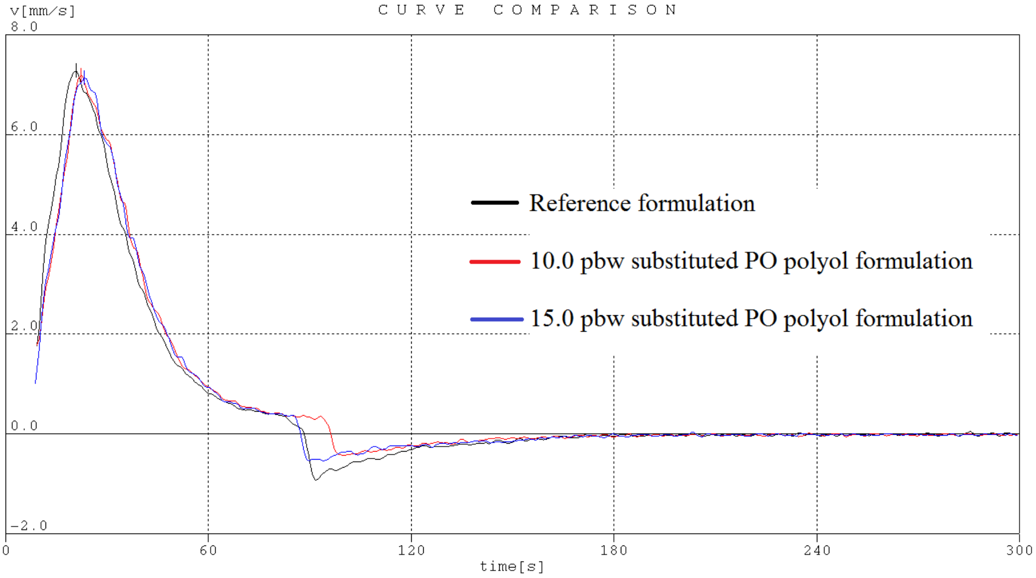


Figure 4.18 Comparison of FPUR foams rising speed prepared by using reference, 10.0 pbw substituted PO polyol and 15.0 pbw substituted PO polyol formulations with 3.5% water content

The rise profile of 15.0 pbw substituted PO polyol formulation (blue line) in Figure 4.17 is similar to that of reference formulation (black line) while 10.0 pbw substituted PO polyol formulation (red line) gives slightly slower rise time than that of reference and 15.0 pbw substituted PO polyol formulations.

The rising speed of 10.0 and 15.0 pbw substituted PO polyol formulations (Figure 4.18, red line and blue line, respectively) are similar and slower than that of reference formulation (Figure 4.18, black line). Although the rising speed of 10.0 and 15.0 pbw substituted PO polyol are the same, however, the rise profile of 15.0 pbw substituted PO polyol formulation is faster. This indicated that the faster rise time in 15.0 pbw substituted PO polyol formulation comes from the higher open cell content as compared to 10.0 pbw substituted PO polyol formulation.

4.1.3.2 Effect of water content variation to foam reactivity and rise profiles

From 4.1.3.1, the minimum amount of PO polyol that can be used as cell opening agent in FPUR foam formulation with 3.5% water content is 10.0 pbw. The amount of water in FPUR foam formulation has effect on open cell content in FPUR foam employing in automotive seating application. Wide range of water content is used to achieve several of FPUR foam core density. Normally, FPUR foam core density for backrest application is in the range of 35 – 40 kg/m^3, while FPUR foam core density in cushion application is in the range of 40 – 45 kg/m^3. Thus, the PO polyol will also be used as cell opening agent in automotive FPUR foam formulation with variable water contents. The study of open cell content is based on the method described in 4.1.3.1.

4.1.3.2.1 Effect of substituted PO polyol in FPUR foam formulation having 3.0% water content (low water content FPUR foam formulation)

The water content in reference FPUR foam formulation in 4.1.3.1 was decreased from 3.5% to 3.0%. The same formulation as employed in the previous experiments, 10.0 and 15.0 pbw substituted PO polyol formulations were used. The FPUR foam formulations are shown in Table 4.12. Table 4.13 shows FPUR foam reactivity of reference and substituted PO polyol formulations.

Table 4.12 FPUR foam formulations prepared by using substituted PO polyol in reference formulation having 3.0% water content

Formulations (pbw)	**Reference formulation**	**Substituted PO polyol formulation**	
		10.0 pbw	**15.0 pbw**
Arcol Polyol® 1362	60.0	50.0	45.0
Hyperlite® E-850	40.0	40.0	40.0
PO polyol	-	10.0	15.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	2.0	-	-
Surfactant	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6
Blowing agent (water)	3.00%	3.00%	3.00%
Isocyanate (TDI:MDI blended) / 100 pbw formulated polyol			
NCO index 90	33.6	33.8	34.0
NCO index 100	37.3	37.6	37.8
NCO index 110	41.0	41.3	41.6

Table 4.13 FPUR foam reactivity of reference and substituted PO polyol formulations having 3.0% water content at the NCO indexes of 90, 100 and 110

Substituted PO polyol (pbw)	**Reference formulation**			**10.0 pbw PO polyol**			**15.0 pbw PO polyol**		
NCO index	**90**	**100**	**110**	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10	10	10	10
Gel time (s)	58	62	64	59	60	64	59	62	65
Rise time (s)	86	88	89	96	105	106	86	93	102
Settling (%)	8.1	11.9	20.3	5.6	6.7	11.9	8.8	13.3	16.4
Foam density (kg/m^3)	35.5	38.0	41.9	35.5	34.7	39.8	39.0	39.4	41.1

From Table 4.13, the reactivity result is the same as the previous experiments, substituted PO polyol into FPUR foam formulation resulted in slower reactivity and lower %settling. The reactivity of 15.0 pbw substituted PO polyol formulation is faster than that of 10.0 pbw PO polyol formulation and closer to the reference formulation, however, less %settling at NCO index of 110 is obtained. FPUR foam appearances (Figure 4.19) show slightly foam shrinkage in 10.0 pbw substituted PO polyol formulation at the NCO indexes of 90, however, no foam shrinkage is observed in reference and 15.0 pbw substituted PO polyol formulations. The results indicate that 15.0 pbw substituted PO polyol formulation gives open cell FPUR foam which has better foam stability than reference formulation due to its lower %settling in low water content FPUR foam formulation.

Figures 4.20 and 4.21 show rise profile and rising speed of reference and substituted PO polyol formulations, respectively. From Figure 4.20, the rise profiles of substituted PO polyol formulation is higher than those of reference formulation but rising speed in Figure 4.21 shows no different between reference and substituted PO polyol formulation. This indicated that both reference and substituted PO polyol formulations have the same blowing speed from gas generated from blowing reaction, however, the foams have less gel strength from slower gel time which make substituted PO polyol formulation has open cell structure in FPUR foam.

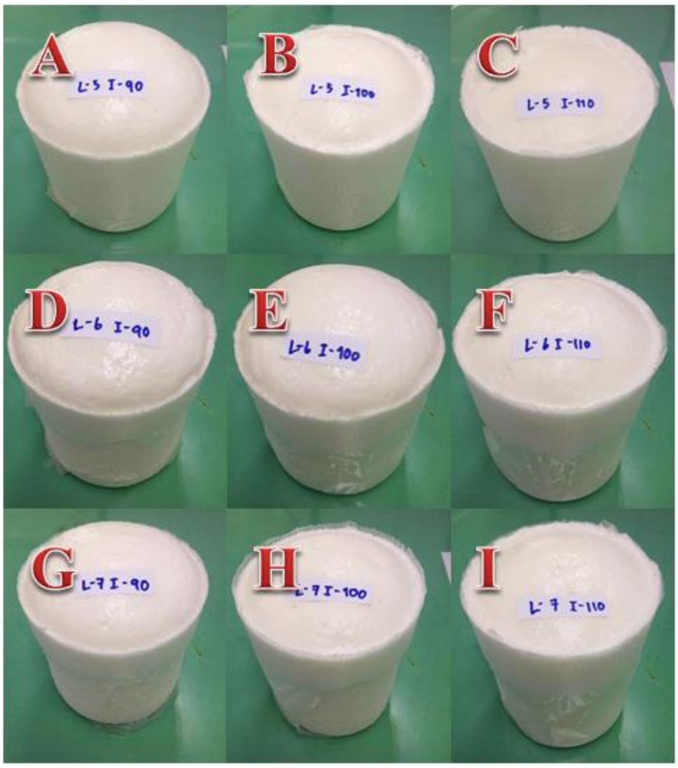


Figure 4.19 FPUR Foam appearances reference formulation and substituted PO polyol formulation contained 3.0% water content; (a), (b), (c) reference formulation at the NCO indexes of 90, 100 and 110 respectively; (d), (e), (f) 10.0 pbw substituted PO polyol at the NCO indexes of 90, 100 and 110 respectively; (g), (h), (i) 15.0 pbw substituted PO polyol at the NCO indexes of 90, 100 and 110 respectively

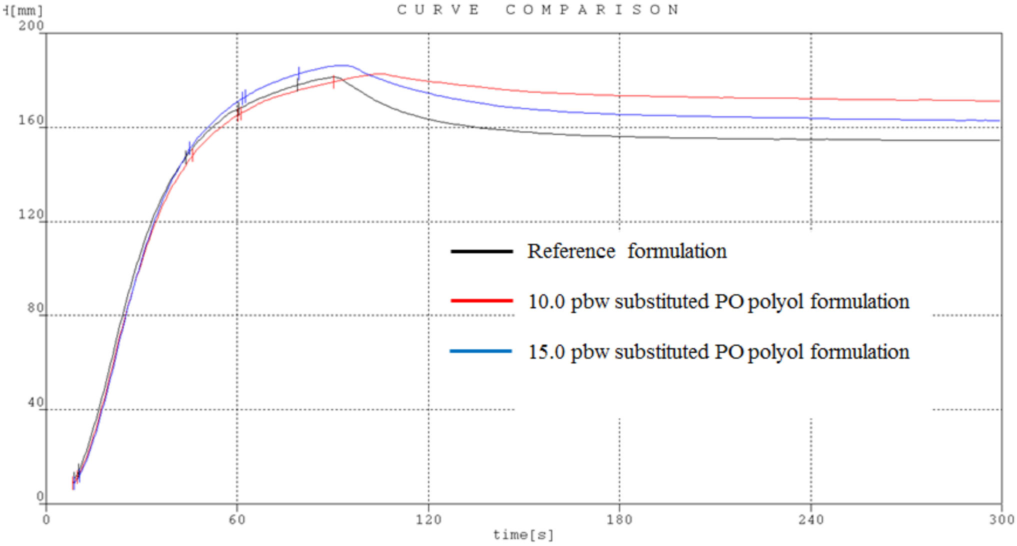


Figure 4.20 Rise profiles comparison of FPUR foams prepared by using reference, 10.0 and 15.0 pbw substituted PO polyol formulations with 3.0% water content

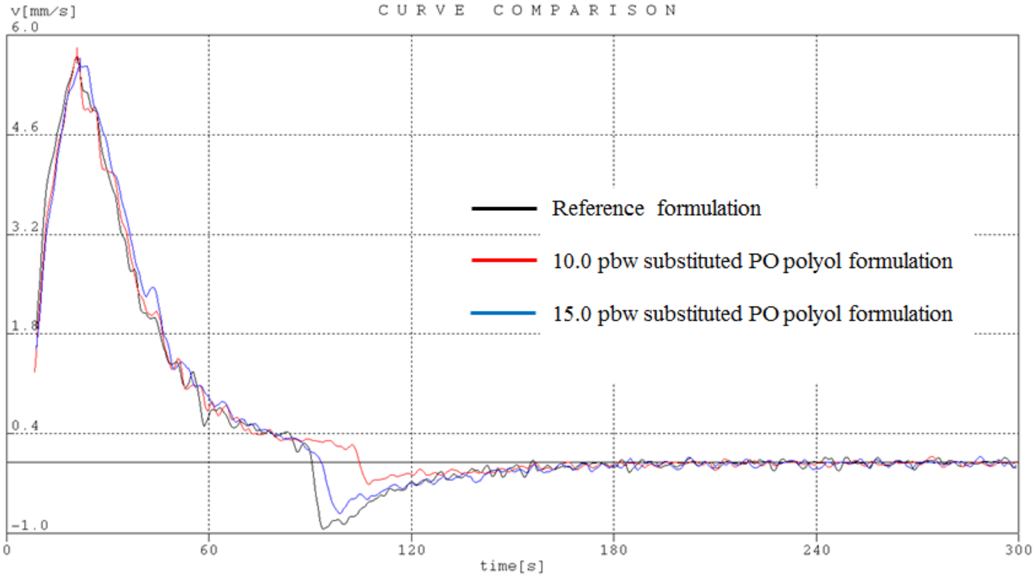


Figure 4.21 Rising speed comparison of FPUR foams prepared by using reference, 10.0 and 15.0 pbw substituted PO polyol formulations with 3.0% water content

4.1.3.2.2 Effect of substituted PO polyol in FPUR foam formulation having 4.0% water content (high water content FPUR foam formulation)

The water content in reference FPUR foam formulation in 4.1.3.1 was increased from 3.5% to 4.0%. The substituted PO polyol amount was still fixed at 10.0 and 15.0 pbw, which was the same as previous experiment. The FPUR foam formulations are shown in Table 4.14. Table 4.15 shows FPUR foam reactivity of reference and substituted PO polyol formulations.

Table 4.14 FPUR foam formulations prepared by using substituted PO polyol in reference formulation with 4.0% water content

Formulations (pbw)	**Reference formulation**	**Substituted PO polyol formulation**	
		10.0 pbw	**15.0 pbw**
Arcol Polyol® 1362	60.0	50.0	45.0
Hyperlite® E-850	40.0	40.0	40.0
PO polyol	-	10.0	15.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	1.5	-	-
Surfactant	0.6	0.6	0.6
Catalyst	0.6	0.6	0.6
Blowing agent (water)	4.00%	4.00%	4.00%
Isocyanate (TDI:MDI blended) / 100 pbw formulated polyol			
NCO index 90	42.8	43.2	43.4
NCO index 100	47.5	48.0	48.2
NCO index 110	52.3	52.8	53.1

Table 4.15 FPUR foam reactivity of reference and substituted PO polyol formulations with 4.0% water content at the NCO indexes of 90, 100 and 110

Substituted PO polyol (pbw)	**Reference formulation**			**10.0 pbw PO polyol**			**15.0 pbw PO polyol**		
NCO index	**90**	**100**	**110**	**90**	**100**	**110**	**90**	**100**	**110**
Cream time (s)	10	10	10	10	10	10	10	10	10
Gel time (s)	60	64	68	59	62	67	60	62	68
Rise time (s)	94	96	96	89	94	100	85	90	95
Settling (%)	5.8	10.4	17.2	5.8	12.3	12.8	9.1	13.9	35.0
Foams density (kg/m^3)	26.4	28.3	35.8	25.2	28.2	35.6	29.5	31.3	46.7

The reactivity results in Table 4.15 show the same trend as in 4.1.3.1. The formulation containing 4.0% water content has slower reactivity after substituted with PO polyol and 10.0 pbw substituted PO polyol gives closer reactivity result to the reference formulation than 15.0 pbw substituted PO polyol. Unlike low water content formulation, FPUR foam formulation in 4.3.1.2.1 with 3.0% water content, 15.0 pbw substituted PO polyol formulation with 4.0% water content has less foam stability than reference formulation due to its higher %settling. Figure 4.22 shows FPUR foam appearances which show that either 10.0 or 15.0 pbw substituted PO polyol formulation give open cell FPUR foam without any shrinkage. In the case of 15.0 pbw substituted PO polyol formulation at NCO index of 110, the foam almost collapse due to its high %settling.

Figures 4.23 and 4.24 show rise profiles and rising speed of reference and substituted PO polyol formulations, respectively. The results from rise profiles in Figure 4.23 show that substituted PO polyol has lower foam height and slower rising profile than reference formulation. The rising profile of 15.0 pbw substituted PO polyol is slower than reference formulation during first 60 seconds. After 60 seconds (or after gel time), the foam blow to the maximum height with the same rate as observed in reference formulation. This indicates that there is less molecular weight built up during first 60 seconds but strong blowing after that time causes 15.0 pbw substituted PO polyol formulation to have higher open cell content but less foam stability than reference formulation. The rising speed in Figure 4.24 shows that substituted PO polyol has slower rising speed which explains the slower rising profile in Figure 4.23.

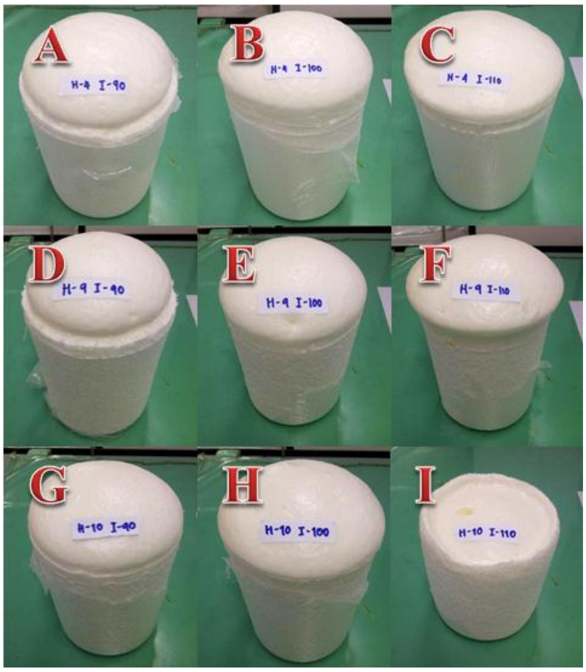


Figure 4.22 FPUR foam appearances of reference formulation and substituted PO polyol formulations with 4.0% water content; (a), (b), (c) reference formulation at the NCO indexes of 90, 100 and 110, respectively; (d), (e), (f) 10.0 pbw substituted PO polyol formulation at the NCO indexes of 90, 100 and 110, respectively; (g), (h), (i) 15.0 pbw substituted PO polyol formulation at the NCO indexes of 90, 100 and 110, respectively

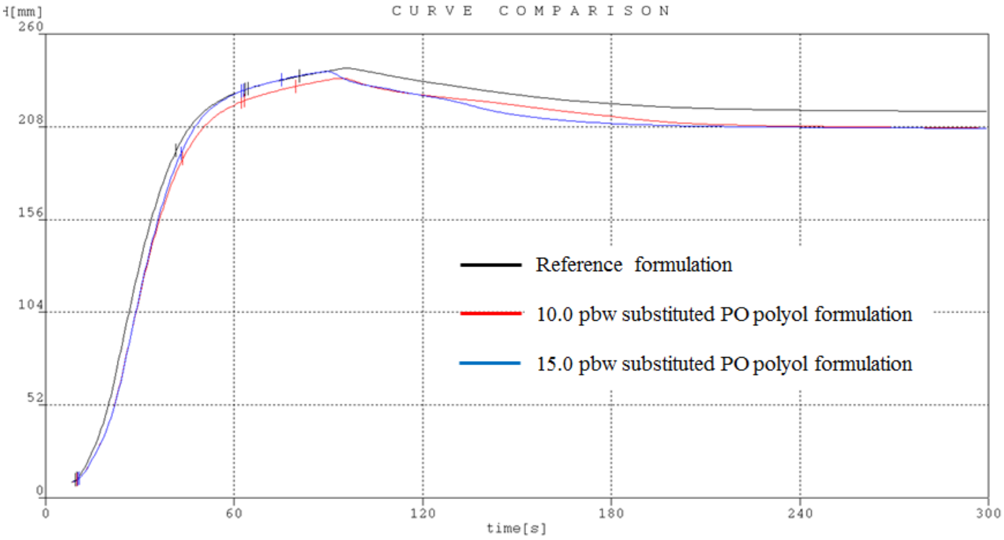


Figure 4.23 Rise profiles comparison of FPUR foams prepared by using reference, 10.0 and 15.0 pbw substituted PO polyol formulations with 4.0% water content

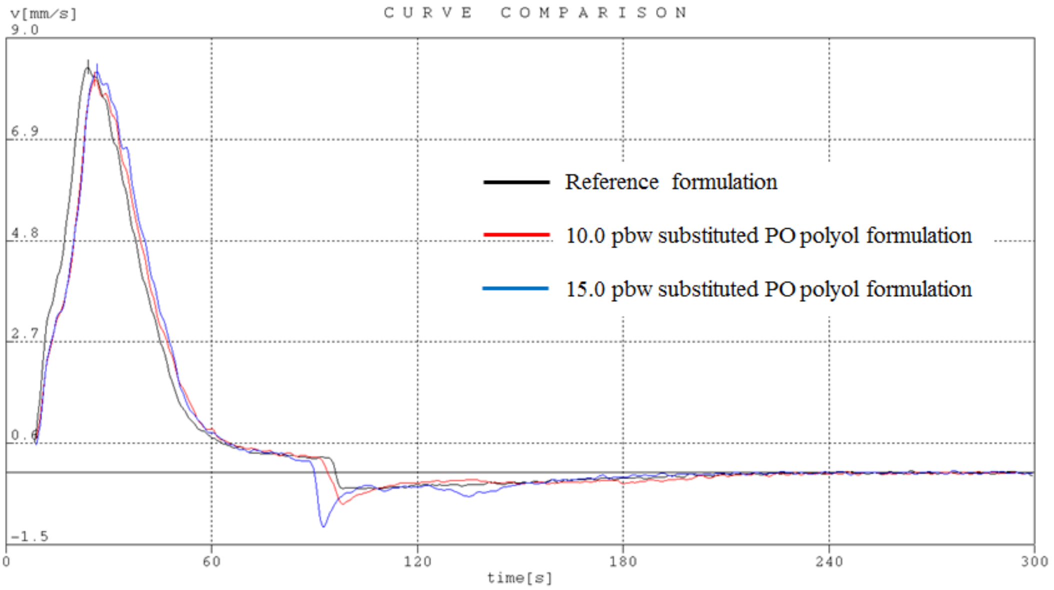


Figure 4.24 Rising speed comparison of FPUR foams prepared by using reference, 10.0 and 15.0 pbw substituted PO polyol formulations with 4.0% water content

4.1.4. Molded test using reference and substituted PO polyol as cell opening agents in FPUR foam formulation

FPUR foam formulations using substituted PO polyol formulation in 4.1.3 were selected and prepared using molded test method to compare with the reference formulation. The mold used was aluminum mold with the dimension of 400 mm x 400 mm x 100 mm. The mold temperature was controlled in the range 60 – 65 ^{O}C.

Formulated polyol was prepared in 2 mixing step, which was the same as in previous experiment. The formulated polyol and isocyanate were mixed together by using mechanical stirrer at 5500 rpm for 7 seconds, then the mixture was poured into aluminum mold and kept in the mold for curing for 5.0 minutes. After 5.0 minutes, FPUR foams were de-mold and kept for 1.0 minute before performing force to crush measurement to measure the open cell content. After 24 hours, FPUR foams were submitted to physical and mechanical analysis. The core density of block foams was varied at 35.0 - 45.0 kg/m^3 ($\underline{+}$ 3.0 kg/m^3) depending on the %water content in FPUR foam formulations. The NCO index was varied at 90, 100 and 110.

4.1.4.1 Force to crush measurement

In force to crush measurement, the uncrushed block foams were place in Zwick/Roell universal testing machine. The machine presses the block foams to 25% and 50% of its original thickness using force of 5.0 N. Force required pressing the block foams to 25% and 50% of its thickness so called "force to crush". The force to crush represents the open cell content in block FPUR foams and related to the force requires to crush the foam during crushing process in automotive seating production. The higher force to crush means the block foam has the lower open cell content and therefore the higher force is required in crushing process, which may lead to not enough crushed foam and results in foam shrinkage. The force to crush measurement details is shown in Figure 4.25.

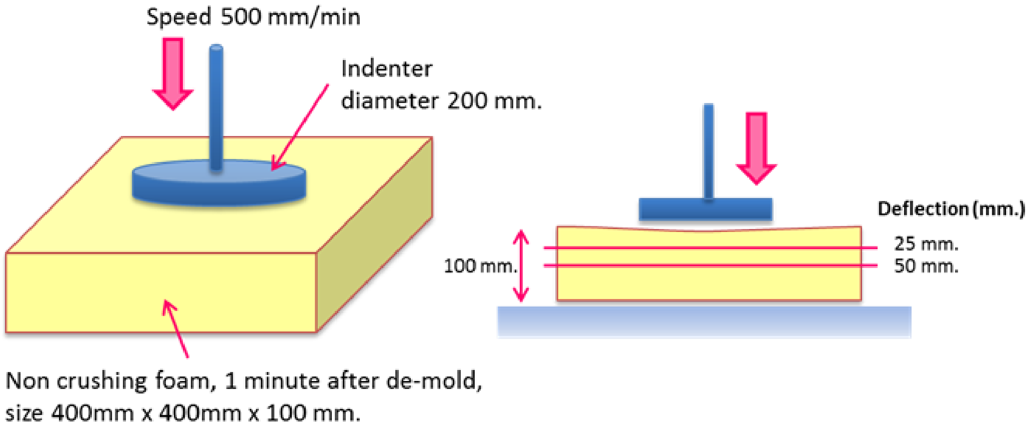


Figure 4.25 Schematic of force to crush measurement

4.1.4.1.1 Force to crush of block FPUR foams prepared using FPUR foam formulation with 3.5% water content

The block FPUR foams with core density of 40.0 kg/m^3 (± 3.0 kg/m^3) were prepared using reference, 10.0 and 15.0 pbw substituted PO polyol formulations at the NCO indexes of 90, 100 and 110. The prepared block FPUR foams were good and no foam collapse was observed. Table 4.16 shows the force to crush comparison between reference and substituted PO polyol formulation at all NCO indexes.

The result from Table 4.16 shows that the force to crush of 10.0 pbw substituted PO polyol formulation is higher than that of the reference formulation at all NCO indexes. This indicated that 10.0 pbw substituted PO polyol formulation has less performance in cell opening than the conventional cell opening agent in reference formulation. In the case of 15.0 pbw substituted PO polyol formulation, although it showed worse foam stability than other formulations at NCO index of 110 but no foam collapse was observed in block FPUR foam and the force to crush result showed that 15.0 pbw substituted PO polyol has the lower force to crush as compared to reference formulation. Thus, 15.0 pbw substituted PO polyol formulation can be used as cell opening agent in FPUR formulation instead of conventional cell opening agent.

Table 4.16 Force to crush comparison between reference and substituted PO polyol formulation with 3.5% water content

FPUR foam formulations	**%Compress**	**FTC (kgf) / NCO indexes**		
		90	**100**	**110**
Reference	25%	41.3	31.1	9.2
	50%	109.0	87.7	30.5
10.0 pbw substituted PO Polyol	25%	44.2	35.5	15.1
	50%	115.1	90.1	46.3
15.0 pbw substituted PO Polyol	25%	35.5	25.4	9.4
	50%	96.4	73.1	31.0

4.1.4.1.2 Force to crush of block FPUR foams prepared using FPUR foam formulation with 3.0% water content

According to the results from 4.1.4.1.1, force to crush of 10.0 pbw substituted PO polyol formulation was higher than that of reference formulation and 15.0 pbw gave good block FPUR foam with satisfied open cell content. Thus, 10.0 pbw substituted PO polyol formulation was not studied in this experiment. The block FPUR foams with core density 45.0 kg/m^3 (± 3.0 kg/m^3) were prepared using reference and 15.0 pbw substituted PO polyol formulations at NCO indexes of 90, 100 and 110. Table 4.17 shows the force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations at all NCO indexes.

Table 4.17 Force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations with 3.0% water content

FPUR foam formulations	%Compress	FTC (kgf) / NCO indexes		
		90	100	110
Reference	25%	39.0	29.7	8.2
	50%	106.0	84.6	25.1
15.0 pbw substituted	25%	39.8	29.3	9.8
PO Polyol	50%	111.3	83.5	31.9

The force to crush result shows that 15.0 pbw substituted PO polyol formulation has comparable force to crush with reference formulation at NCO index of 90 (within ± 5% of reference formulation value) and even lower at NCO index of 100. But the result at NCO index of 110 shows significantly higher force to crush especially at 50% compression than reference formulation. This result agrees with the %settling result in foam reactivity, which 15.0 pbw substituted PO polyol has equally %settling with reference formulation at NCO indexes of 90 and 100, but has lower %settling at NCO index of 110.

4.1.4.1.3 Force to crush of block FPUR foams prepared using FPUR foam formulation with 4.0% water content

As mentioned in 4.1.4.1.2, 10.0 pbw substituted PO polyol formulation was not studied in this experiment. The block FPUR foams with core density of 35.0 kg/m^3 (±3.0 kg/m^3) were prepared using reference and 15.0 pbw substituted PO polyol formulations at NCO indexes of 90, 100 and 110. All prepared block FPUR foams have good appearance with no foam collapse, especially in 15.0 pbw substituted PO polyol formulation at NCO index of 110, which has worst foam stability due to high %settling. Table 4.18 shows the force to crush comparison between reference and 15.0 pbw substituted PO polyol formulation at all NCO indexes.

Table 4.18 Force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations with 4.0% water content

FPUR foam formulations	%Compress	FTC (kgf) / NCO indexes		
		90	100	110
Reference	25%	58.9	47.0	21.3
	50%	142.5	114.1	67.4
15.0 pbw substituted	25%	40.7	34.7	14.4
PO Polyol	50%	108.9	93.3	46.7

The result from Table 4.18 shows significantly reduction in force to crush of block FPUR foams prepared using 15.0 pbw substituted PO polyol. The results are the same as those in 4.1.4.1.2, the force to crush result agrees with the %settling result in foam reactivity, which 15.0 pbw substituted PO polyol formulation has higher %settling than reference formulation at all NCO indexes.

4.1.4.2 Mechanical property analysis

The block FPUR foams from 4.1.4.1 were kept for 24 hours after force to crush measurement at 25 ^{O}C and then the foams were submitted to mechanical property analysis under ambient conditions with a Zwick/Roell universal testing machine. The core density, tensile strength, tear strength, elongation at break, ball rebound and compression set were performed according JIS 6400-1. The indentation force hardness test (25% ILD) was performed according to ASTM D3574-95. For tensile strength, tear strength and elongation at break; 5 samples were measured and averaged. For the core density, ball rebound and compression set; 3 samples were measured and averaged. For indentation force hardness test, the measurement was done with 1 sample.

4.1.4.2.1 Mechanical property analysis of FPUR formulation with 3.5% water content

The mechanical property of block FPUR foam samples prepared using reference and substituted PO polyol formulations at NCO indexes of 90, 100 and 110 are shown in Table 4.19, 4.20 and 4.21, respectively. The results from all NCO indexes show that FPUR foams prepared from substituted PO polyol formulation have higher foam hardness, tensile and tear strength, but have lower elongation at break and ball rebound. This indicated that the low molecular weight of PO polyol (Mw 3,000) which was used as cell opening agent instead of long chain based polyol (Mw 6,000), results in the harder foam, higher foam strength but give less foam flexibility and resilience.

Table 4.19 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations		
			Reference	10.0 pbw PO polyol	15.0 pbw PO polyol
Core density		Kg/m^3	37.6	37.0	37.1
Hardness (25% ILD)		N/314cm^2	123.6	129.5	138.3
Tensile strength		kPa	120.7	134.3	136.4
Tear strength		N/cm	7.45	7.55	7.55
Elongation at break		%	131	121	120
Ball Rebound		%	64	62	62
Compression set	Dry	%	7.3	8.1	8.6
	Wet	%	32.7	31.2	32.6

Table 4.20 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations		
			Reference	10.0 pbw PO polyol	15.0 pbw PO polyol
Core density		Kg/m^3	37.1	36.5	36.5
Hardness (25% ILD)		N/314cm^2	157.8	163.8	174.6
Tensile strength		kPa	145.2	149.1	150.5
Tear strength		N/cm	7.45	7.45	7.64
Elongation at break		%	120	111	110
Ball Rebound		%	65	63	62
Compression set	Dry	%	6.9	5.6	6.2
	Wet	%	24.2	28.6	30.0

Table 4.21 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 110

Mechanical properties		Unit	FPUR foam formulations		
			Reference	10.0 pbw PO polyol	15.0 pbw PO polyol
Core density		Kg/m^3	36.9	37.0	37.5
Hardness (25% ILD)		$N/314cm^2$	188.6	215.8	217.8
Tensile strength		kPa	154.0	162.8	167.8
Tear strength		N/cm	7.74	7.85	7.93
Elongation at break		%	105	96	95
Ball Rebound		%	64	63	62
Compression set	Dry	%	6.1	6.0	6.7
	Wet	%	23.0	22.6	23.0

4.1.4.2.2 Mechanical property analysis of FPUR formulations with 3.0% and 4.0% water content

The block FPUR foams prepared in 4.1.4.1.2 and 4.1.4.1.3 were submitted to mechanical property analysis according to 4.1.4.2.1. The mechanical properties of foams prepared using FPUR foam formulation with 3.0% water content at NCO indexes of 90, 100 and 110 are shown in Table 4.22, 4.23 and 4.24, respectively while the mechanical properties of foams prepared using FPUR foam formulation contained 3.0% water content at NCO indexes of 90, 100 and 110 are shown in Table 4.25, 4.26 and 4.27, respectively

Table 4.22 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	43.0	42.7
Hardness (25% ILD)		N/314cm^2	137.3	140.5
Tensile strength		kPa	130.4	134.4
Tear strength		N/cm	7.06	7.36
Elongation at break		%	117	110
Ball Rebound		%	68	65
Compression set	Dry	%	5.8	7.5
	Wet	%	24.5	28.9

Table 4.23 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	42.2	42.1
Hardness (25% ILD)		N/314cm^2	179.5	187.4
Tensile strength		kPa	140.2	163.8
Tear strength		N/cm	7.16	7.65
Elongation at break		%	113	104
Ball Rebound		%	68	65
Compression set	Dry	%	4.9	5.7
	Wet	%	25.4	30.8

Table 4.24 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 110

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	44.2	43.9
Hardness (25% ILD)		N/314cm^2	230.6	250.2
Tensile strength		kPa	152.1	172.6
Tear strength		N/cm	7.65	8.14
Elongation at break		%	98	94
Ball Rebound		%	68	64
Compression set	Dry	%	4.9	6.4
	Wet	%	19.9	27.5

Table 4.25 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulation with 4.0% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	33.1	33.6
Hardness (25% ILD)		N/314cm^2	132.4	141.7
Tensile strength		kPa	138.3	148.1
Tear strength		N/cm	6.96	7.45
Elongation at break		%	117	106
Ball Rebound		%	63	61
Compression set	Dry	%	12.4	35.0
	Wet	%	11.8	36.0

Table 4.26 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 4.0% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	32.8	32.5
Hardness (25% ILD)		N/314cm^2	165.7	173.6
Tensile strength		kPa	149.1	152.1
Tear strength		N/cm	7.02	7.55
Elongation at break		%	110	106
Ball Rebound		%	64	61
Compression set	Dry	%	10.3	11.4
	Wet	%	32.1	31.7

Table 4.27 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 4.0% water content at NCO index of 110

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	32.1	32.8
Hardness (25% ILD)		N/314cm^2	211.8	220.7
Tensile strength		kPa	149.3	168.7
Tear strength		N/cm	7.16	7.65
Elongation at break		%	98	90
Ball Rebound		%	64	60
Compression set	Dry	%	8.4	10.7
	Wet	%	31.7	30.0

From the results in Tables 4.22-4.27, both FPUR formulations with 3.0% and 4.0% water contents show the same mechanical properties. The substituted PO polyol causes FPUR foams to be harder but have less flexibility and resilience due to higher foam hardness and foam strength, but lower elongation at break and ball rebound. The results are same as those of 3.5% water content formulation in 4.1.4.2.1. However, the 3.0% water content formulation gives worse compression set than reference formulation at all NCO indexes. This is because substituted PO polyol makes FPUR foam to have higher crosslink density than reference formulation. The polyol chain of PO polyol is shorter as compared to long chain based polyol. While in 3.5% and 4.0% water content formulations, the crosslink density in FPUR foams structure contributes from the reaction between water and isocyanate rather than the short chain PO polyol.

4.1.4.3 Scanning electron microscope (SEM) analysis

The FPUR foam samples prepared using reference and substituted PO polyol formulations from 4.1.4.2.1 and 4.1.4.2.2 were submitted to SEM analysis. Figure 4.26 shows SEM micrographs of FPUR foams from 4.1.4.2.1 which prepared using FPUR foam formulations having 3.5% water content.

From Figure 4.26, SEM micrographs of FPUR foams prepared using reference formulation (Figure 4.24 (a) and (b)) and 10.0 pbw substituted PO polyol formulation (Figure 4.24 (c) and (d)) show similar cell structure, cell size and cell size distribution. While the SEM micrographs of FPUR foams prepared using 15.0 pbw substituted PO polyol formulation (Figure 4.24 (e) and (f)) shows similar cell structure, but smaller cell size and wider cell size distribution were observed as shown in Figure 4.24(e) and (f). The SEM micrographs of FPUR foams prepared using formulation having 3.0% and 4.0% water contents from 4.1.4.2.2 are shown in Figures 4.27 and 4.28, respectively.

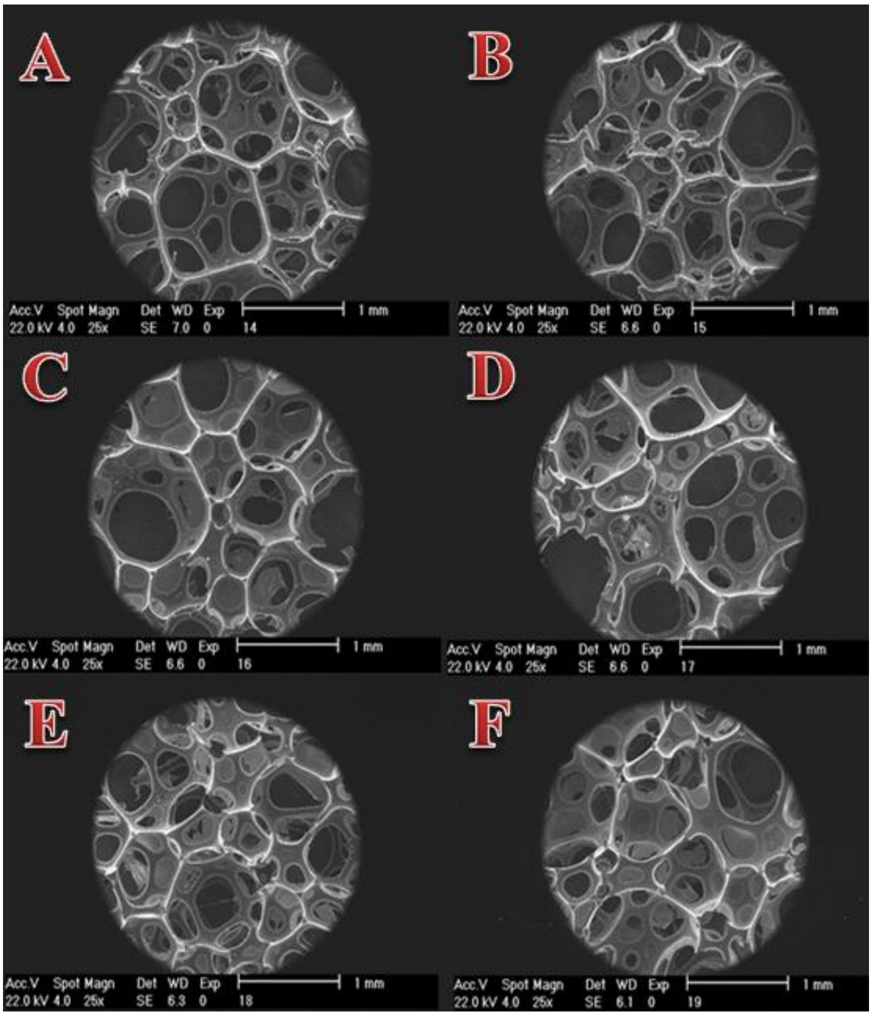


Figure 4.26 SEM of FPUR foams prepared using 3.5% water content formulation; (a), (b) reference formulation; (c), (d) 10.0 pbw substituted PO polyol formulation; (e), (f) 15.0 pbw substituted PO polyol formulation

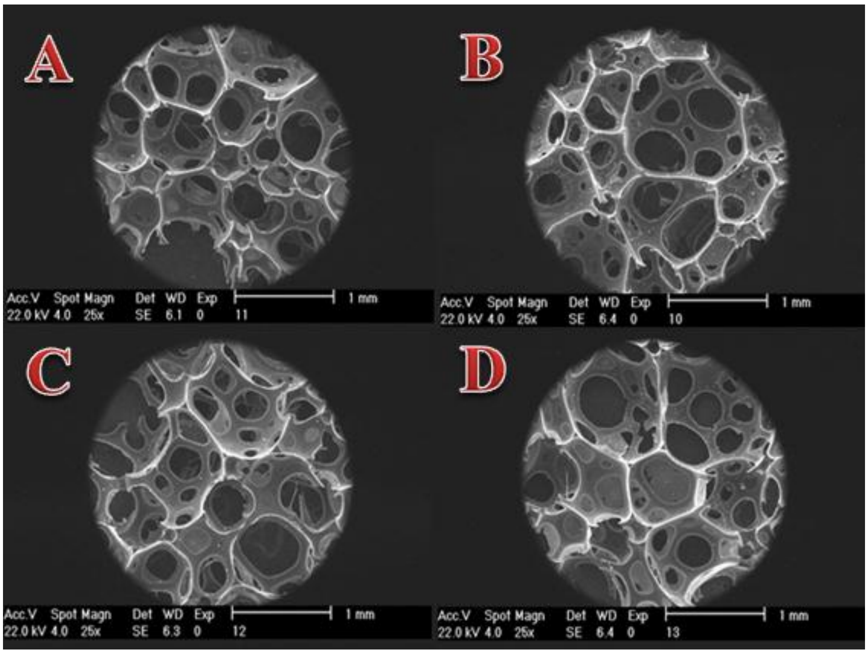


Figure 4.27 SEM of FPUR foams prepared using 3.0% water content formulation; (a), (b) reference formulation; (c), (d) 15.0 pbw substituted PO polyol formulation

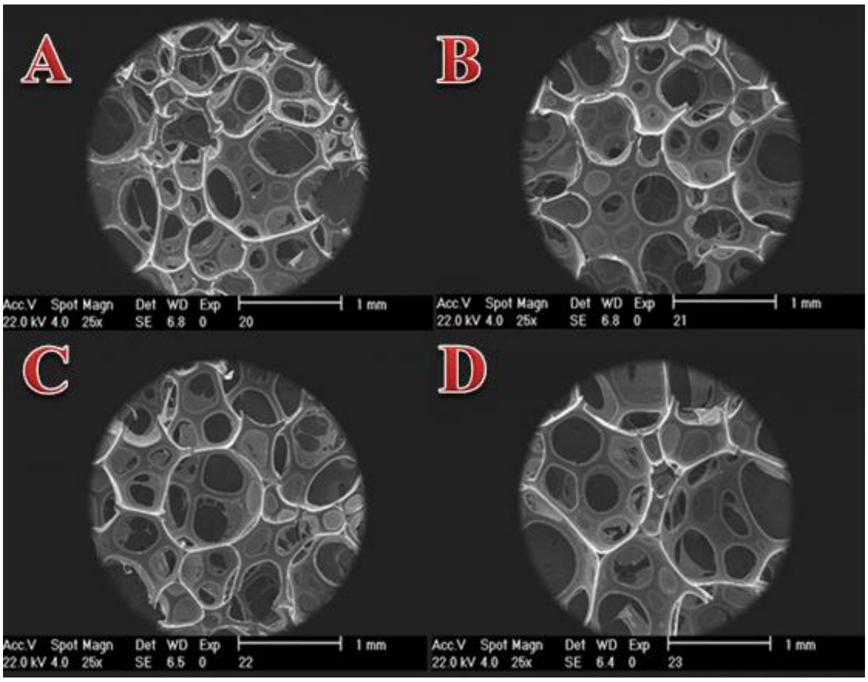


Figure 4.28 SEM of FPUR foams prepared using 4.0% water content formulation; (a), (b) reference formulation; (c), (d) 15.0 pbw substituted PO polyol formulation

The SEM micrographs comparison between FPUR foams prepared using reference and 15.0 pbw substituted PO polyol formulations having 3.0% water content (Figure 4.27) show the same cell size and cell size distribution while the SEM micrographs comparison from those of formulation having 4.0% water content (Figure 4.28) show the different. The SEM micrographs from FPUR foams prepared using 15.0 pbw substituted PO polyol formulation (Figure 4.28 (c) and (d)) have larger cell size and wider cell size distribution than those prepared using reference formulation (Figure 4.28 (a) and (b)).

4.2 Preparation of flexible polyurethane (FPUR) foams for furniture application

4.2.1. Cup test experiments using reference FPUR foam formulations

The FPUR foams were prepared in 2 steps as described in 4.1.1. In the case of furniture formulation, methylene diphenyl diisocyanate (MDI) was used as isocyanate part. The %water contents were varied at 2.5%, 3.0% and 3.5% while the NCO indexes were varied at 70, 80 and 90. The lower NCO indexes was used due to the demand of soft feeling and comfort ability in furniture application Table 4.28 shows the reference FPUR foam formulations for furniture application.

Table 4.28 FPUR foam formulations prepared using conventional cell opening agent (reference formulation) for furniture application

Formulations (pbw)	**Reference formulation**		
	#1	**#2**	**#3**
Arcol Polyol® 1362	90.0	90.0	90.0
Hyperlite® E-850	10.0	10.0	10.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	5.0	5.0	5.0
Surfactant	1.0	1.0	1.0
Catalyst	0.6	0.6	0.6
Blowing agent (water, %)	2.5	3.0	3.5
Isocyanate (P-MDI) : 100 pbw formulated polyol			
NCO index 70	30.4	39.0	44.5
NCO index 80	34.7	44.6	50.8
NCO index 90	39.1	50.1	57.2

4.2.1.1 FPUR foam reactivity and rise profiles

The reactivity of all reference formulations were shown in Table 4.29. The FPUR foam appearances were shown in Figure 4.30. In general, the reactivity of FPUR foam formulations prepared using MDI is faster than that of TDI. This is because the NCO groups on MDI molecules are more reactive due to less steric hindrances. As illustrated in Figure 4.29, the NCO groups on both 2,4 TDI isomer and 2,6 TDI isomer have steric effect, especially in 2,6 TDI isomer, which make it less reactive.

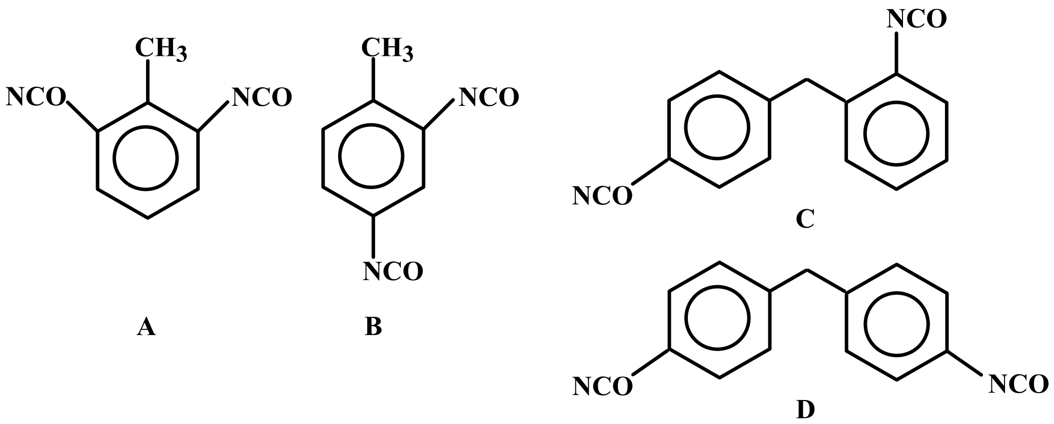


Figure 4.29 The chemical structures of TDI and MDI; (a) 2,6 TDI; (b) 2,4 TDI; (c) 4,4 MDI; (d) 2,4 MDI

Table 4.29 Reactivity of FPUR foam prepared by using reference formulation at different blowing agent contents (%) and NCO indexes

Water content (%)	**2.5**			**3.0**			**3.5**		
NCO indexes	**70**	**80**	**90**	**70**	**80**	**90**	**70**	**80**	**90**
Cream time (s)	12	12	12	12	12	12	12	12	12
Gel time (s)	81	83	84	76	70	72	70	68	69
Rise time (s)	148	135	135	114	104	103	95	89	83
Settling (%)	4.0	5.3	6.9	4.9	7.7	10.7	5.9	19.1	19.6
Foams density (kg/m^3)	52.3	47.8	47.9	44.4	42.9	44.3	49.0	45.3	49.2

From Table 4.29, at low NCO index (NCO index 70), the amount of isocyanate groups is too small to react with water in FPUR foam formulations to perform blowing reaction, therefore, this causes the delay in foam reactivity, too low %settling and too high foam density. Thus, the NCO indexes were changed from 70, 80 and 90 to 80, 90 and 100. Table 4.30 shows the reactivity of reference formulations at NCO indexes of 80, 90 and 100. The foam appearances were shown in Figure 4.30.

Table 4.30 Reactivity of FPUR foam prepared by using reference formulation at different blowing agent contents (%) and NCO indexes (80 – 100)

Water content (%)	**2.5**			**3.0**			**3.5**		
NCO indexes	**80**	**90**	**100**	**80**	**90**	**100**	**80**	**90**	**100**
Cream time (s)	12	12	12	12	12	12	12	12	12
Gel time (s)	83	84	85	70	72	75	68	69	69
Rise time (s)	135	135	136	104	103	103	89	83	80
Settling (%)	5.3	6.9	8.9	7.7	10.7	17.3	19.1	19.6	22.3
Foams density (kg/m^3)	47.8	47.9	46.1	42.9	44.3	46.8	45.3	49.2	52.9

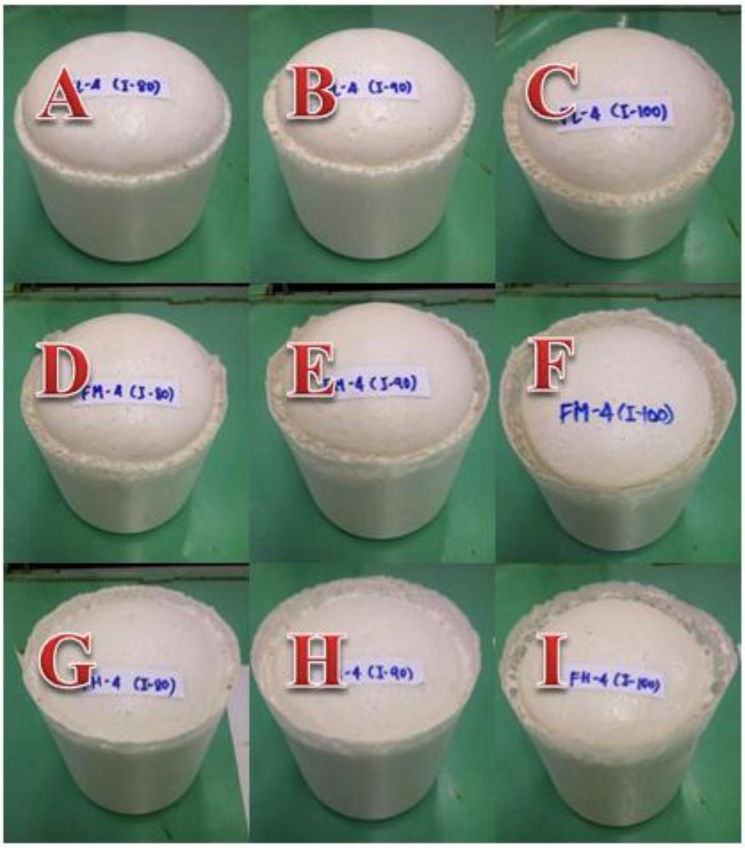


Figure 4.30 FPUR foam appearances for furniture application; (a), (b) and (c) 2.5% water content at NCO indexes of 80, 90 and 100, respectively; (d), (e) and (f) 3.0% water content at NCO indexes of 80, 90 and 100, respectively; (g), (f) and (I) 3.5% water content at NCO indexes of 80, 90 and 100, respectively

Too high %settling results at all NCO indexes from formulation having 3.5% water content (19% - 22%) potentially cause the foam to have poor stability. Therefore, the cell opening agent was decreased from 5.0 pbw to 4.0 pbw in order to obtain the more stable foam. The reference formulations were changed according to Table 4.31. The reactivity and foam appearances of new reference formulations are shown in Table 4.32 and Figure 4.31, respectively.

Table 4.31 FPUR foam formulations prepared using conventional cell opening agent (reference formulation) for furniture application

Formulations (pbw)	**Reference formulation**		
	#1	**#2**	**#3**
Arcol Polyol® 1362	90.0	90.0	90.0
Hyperlite® E-850	10.0	10.0	10.0
Crosslinker	0.5	0.5	0.5
Cell opening agent	5.0	5.0	4.0
Surfactant	1.0	1.0	1.0
Catalyst	0.6	0.6	0.6
Blowing agent (water, %)	2.5	3.0	3.5
Isocyanate (P-MDI) : 100 pbw formulated polyol			
NCO index 70	30.4	39.0	44.5
NCO index 80	34.7	44.6	50.8
NCO index 90	39.1	50.1	57.2

Table 4.32 Reactivity of FPUR foam prepared by using reference formulation at different blowing agent contents (%) and NCO indexes

Water content (%)	**2.5**			**3.0**			**3.5**		
NCO indexes	**80**	**90**	**100**	**80**	**90**	**100**	**80**	**90**	**100**
Cream time (s)	12	12	12	12	12	12	12	12	12
Gel time (s)	83	84	85	70	72	75	67	69	70
Rise time (s)	135	135	136	103	103	103	88	86	89
Settling (%)	5.3	6.9	8.9	7.7	10.7	17.3	11.5	16.1	19.1
Foams density (kg/m^3)	47.8	47.9	46.1	42.9	44.3	46.8	40.13	44.1	48.7

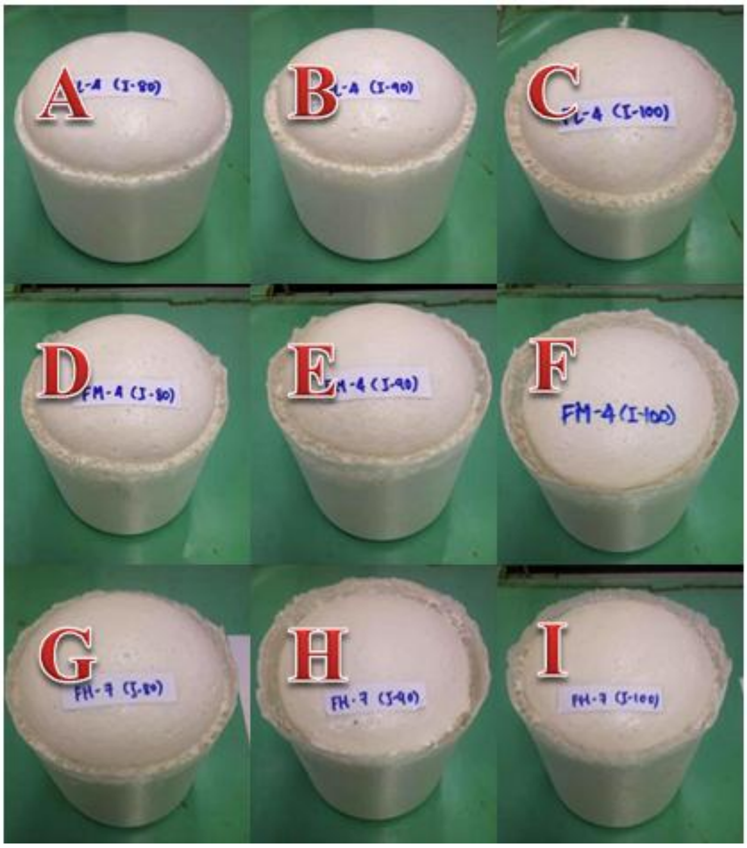


Figure 4.31 FPUR foam appearances of the reference formulation; (a), (b) and (c) 2.5% water content at NCO indexes of 80, 90 and 100, respectively; (d), (e) and (f) 3.0% water content at NCO indexes of 80, 90 and 100, respectively; (g), (f) and (I) 3.5% water content at NCO indexes of 80, 90 and 100, respectively

4.2.2. Cup test experiments using substituted PO polyol as cell opening agent in FPUR foam formulation

PO polyol was partially substituted in FPUR foam formulation using the same amount as the experiment in 4.1.3. (15.0 pbw substituted PO polyol) by varying the amount of %water content at 2.5%, 3.0% and 3.5%. The NCO indexes were varied at 80, 90 and 100. Table 4.33 shows the formulation in comparison between reference and 15.0 pbw substituted PO polyol formulation at variable % water content.

Table 4.33 FPUR foam formulations prepared using conventional cell opening agent (reference formulation) for furniture application

Formulations (pbw)	**Reference formulation**			**Substituted PO polyol formulation**		
	#1	**#2**	**#3**	**#1**	**#2**	**#3**
Arcol Polyol® 1362	90.0	90.0	90.0	75.0	75.0	75.0
Hyperlite® E-850	10.0	10.0	10.0	10.0	10.0	10.0
PO polyol	-	-	-	15.0	15.0	15.0
Crosslinker	0.5	0.5	0.5	0.5	0.5	0.5
Cell opening agent	5.0	5.0	4.0	-	-	-
Surfactant	1.0	1.0	1.0	1.0	1.0	1.0
Catalyst	0.6	0.6	0.6	0.6	0.6	0.6
Blowing agent (water, %)	2.5	3.0	3.5	2.5	3.0	3.5
Isocyanate (P-MDI) : 100 pbw formulated polyol						
NCO index 80	34.7	40.5	46.2	35.5	41.3	47.0
NCO index 90	39.1	45.6	51.9	40.0	46.4	52.9
NCO index 100	43.4	50.6	57.7	44.4	51.6	58.8

4.2.2.1 Effect of substituted PO polyol to foam reactivity and rise profiles in FPUR foam formulation with 3.0% water content

The reactivity after partially substitution of base polyol with 15.0 pbw of PO polyol is shown in Table 4.34, while the foam appearances comparison between reference and 15.0 pbw substituted PO polyol are shown in Figure 4.32. Figures 4.33

and 4.34 show the rise profiles and rising speed of 15.0 pbw substituted PO polyol formulation in comparison with reference formulation at NCO index of 90.

Table 4.34 FPUR foam reactivity of reference and 15.0 pbw substituted PO polyol formulations with 3.0% water content at the NCO indexes of 80, 90 and 100

Foam reactivity	**Reference formulation**			**15.0 pbw substituted PO polyol formulation**		
NCO indexes	**80**	**90**	**100**	**80**	**90**	**100**
Cream time (s)	12	12	12	12	12	12
Gel time (s)	70	72	75	66	68	73
Rise time (s)	103	103	103	100	88	81
Settling (%)	7.7	10.7	17.3	1.9	2.1	6.5
Foam density (kg/m^3)	42.9	44.3	46.8	47.1	45.5	49.8

The results from Table 4.34 show that the reactivity of 15.0 pbw substituted PO polyol formulation is significantly faster than that of reference formulation. The result is in contrast to the result which observed in 4.1.3. It is also in contrast to the assumption about secondary -OH in PO polyol which cause the delay in foam reactivity. The possible explanation for the reverse result is because of the reactive NCO group in MDI molecules. These NCO groups are more reactive than those in TDI due to less steric hindrances. Although the PO polyol has only secondary –OH, however, it has significantly lower molecular weight as compared with long chain base polyol. Therefore, MDI can react with PO polyol very fast and results in faster gel time. The NCO group also reacts with water molecules very fast which causes the faster rise time.

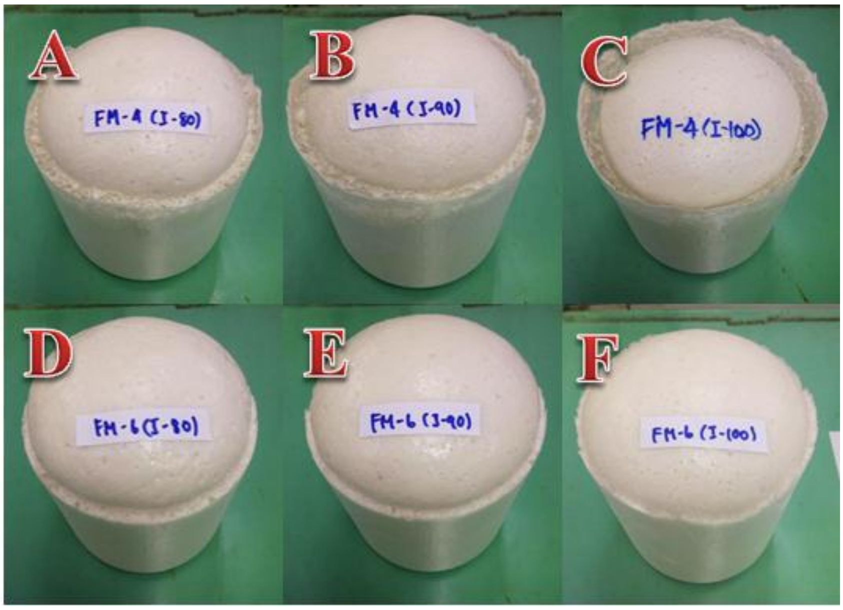


Figure 4.32 FPUR foam appearances of the reference and 15.0 pbw substituted PO polyol formulation with 3.0% water content; (a), (b) and (c) reference formulation at the NCO indexes of 80, 90 and 100, respectively; (d), (e) and (f) 15.0 pbw substituted PO polyol formulation at the NCO indexes of 80, 90 and 100, respectively

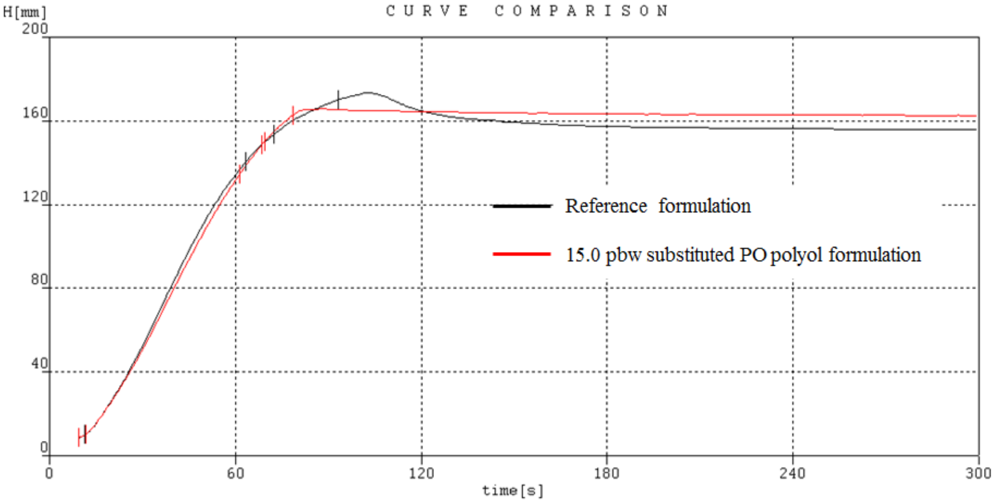


Figure 4.33 Rise profiles comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 3.0% water content at the NCO index of 100

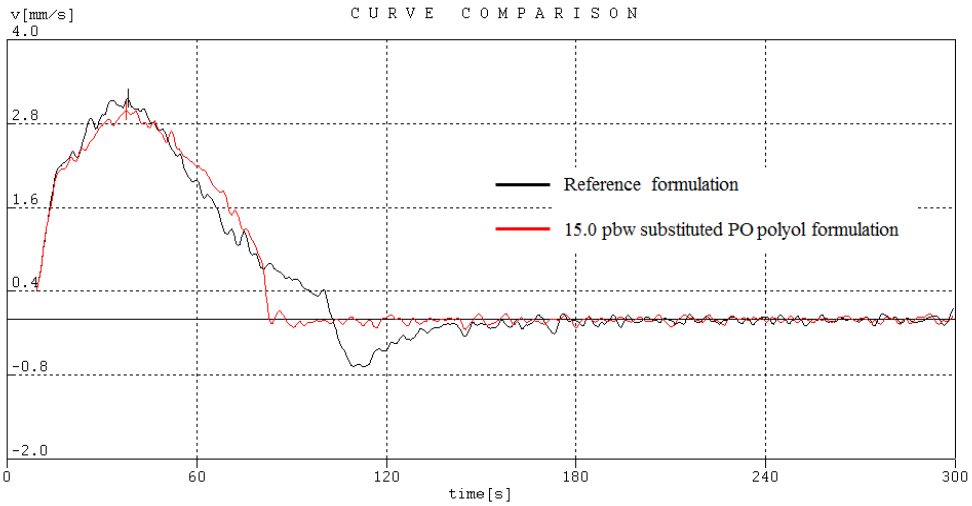


Figure 4.34 Rising speed comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 3.0% water content at the NCO index of 100

Comparison between rise profiles in the reference and 15.0 pbw substituted PO polyol formulation at the NCO index of 100 (Figure 4.33) shows that the faster gel reaction in 15.0 pbw substituted PO polyol formulation causes FPUR foam to have enough strength to resist the foam expansion. This results in lower maximum height and too low %settling in 15.0 pbw substituted formulation when compared with reference formulation, however, there is no foam shrinkage presented during reactivity testing (Figure 4.32 (d), (e) and (f)). Both of reference and 15.0 pbw substituted PO polyol formulations have the same reaction speed (Figure 4.34).

4.2.2.2 Effect of substituted PO polyol in FPUR foam formulation having 2.5% water content (low water content FPUR foam formulation)

The water content in reference FPUR foam formulation in 4.2.2.1 was decreased from 3.0% to 2.5%. The amount of PO polyol was fixed at 15.0 pbw same as in 4.2.2. Table 4.33 shows the reference and 15.0 pbw substituted PO polyol formulations. Table 4.35 shows FPUR foam reactivity of reference and 15.0 pbw substituted PO polyol formulations.

Table 4.35 FPUR foam reactivity of reference and 15.0 pbw substituted PO polyol formulation with 2.5% water content at the NCO indexes of 80, 90 and 100

Foam reactivity	**Reference formulation**			**15.0 pbw substituted PO polyol formulation**		
NCO indexes	**80**	**90**	**100**	**80**	**90**	**100**
Cream time (s)	12	12	12	12	12	12
Gel time (s)	83	84	85	69	71	75
Rise time (s)	135	135	136	95	110	123
Settling (%)	5.3	6.9	8.9	3.7	2.7	2.3
Foam density (kg/m^3)	47.8	47.9	46.1	57.8	52.9	51.1

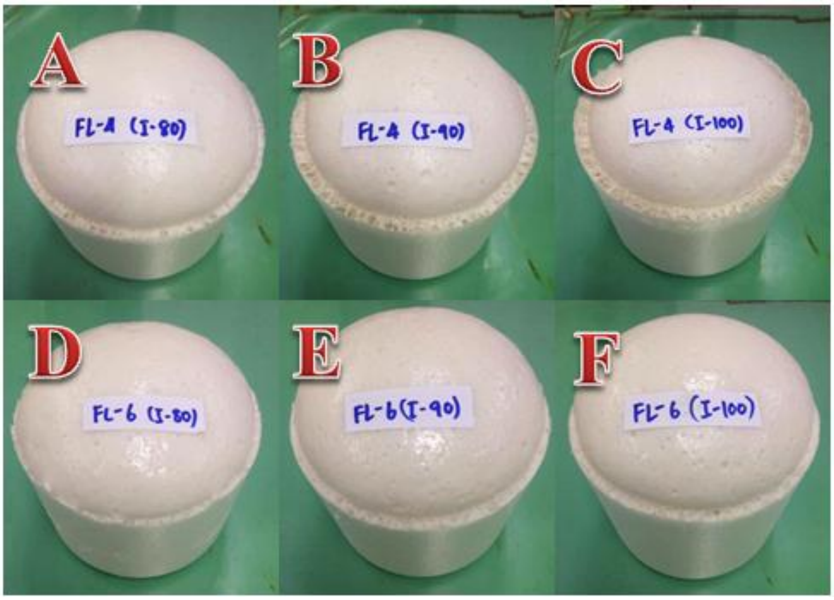


Figure 4.35 FPUR foam appearances of the reference and 15.0 pbw substituted PO polyol formulation with 2.5% water content; (a), (b) and (c) reference formulation at the NCO indexes of 80, 90 and 100, respectively; (d), (e) and (f) 15.0 pbw substituted PO polyol formulation at the NCO indexes of 80, 90 and 100, respectively

The reactivity results show the same trend as those in 4.2.2.1, which the reactivity of 15.0 pbw substituted PO polyol formulation show faster gel time, rise time and lower %settling than reference formulation. The explanation is the same as described above. Both reference and 15.0 pbw substituted PO polyol formulations have good foam appearances with no shrinkage observed (Figure 4.35).

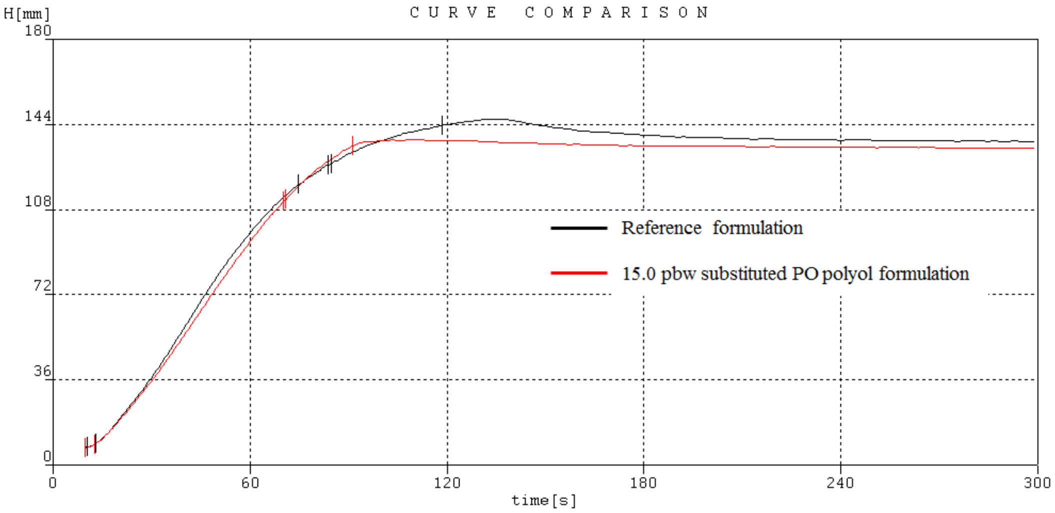


Figure 4.36 Rise profiles comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 2.5% water content at the NCO index of 100

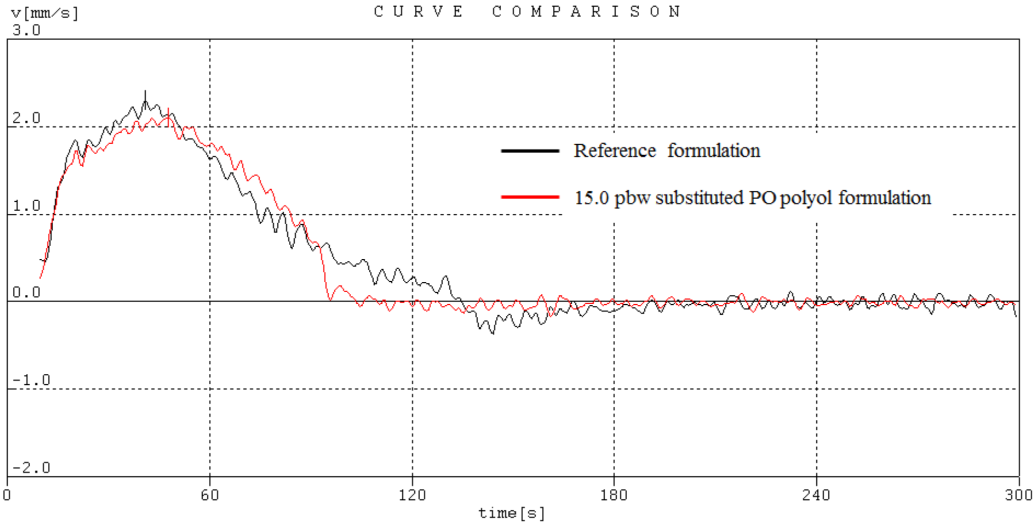


Figure 4.37 Rising speed comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 2.5% water content at the NCO index of 100

Comparison between rise profiles in the reference and 15.0 pbw substituted PO polyol formulation (Figure 4.36) shows the same trend as in 4.2.2.1. However, the rising speed (Figure 4.37) is different. The rising speed of 15.0 pbw substituted PO polyol is slightly slower than that of reference formulation, although it has faster foam reactivity. It may because of too fast gel reaction causes the foam to resist the expansion from blowing reaction.

4.2.2.3 Effect of substituted PO polyol in FPUR foam formulation having 3.5% water content (high water content FPUR foam formulation)

The water content in reference FPUR foam formulation in 4.2.2.1 was increased from 3.0% to 3.5%. 15.0 pbw Substituted PO polyol was employed as same as in previous experiment. The formulations were shown in 4.2.2 (Table 4.33). The FPUR foam reactivity, FPUR foam appearances, rise profiles and rising speed of the reference and 15.0 pbw substituted PO polyol formulation are shown in Table 4.36, Figures 4.38, 4.39 and 4.40, respectively.

Table 4.36 FPUR foam reactivity of reference and 15.0 pbw substituted PO polyol formulations with 3.5% water content at the NCO indexes of 80, 90 and 100

Foam reactivity	**Reference formulation**			**15.0 pbw substituted PO polyol formulation**		
NCO indexes	**80**	**90**	**100**	**80**	**90**	**100**
Cream time (s)	12	12	12	12	12	12
Gel time (s)	67	69	70	66	69	71
Rise time (s)	88	86	89	82	78	75
Settling (%)	11.5	16.1	19.1	2.4	12.4	19.5
Foam density (kg/m^3)	40.13	44.1	48.7	43.3	47.4	50.3

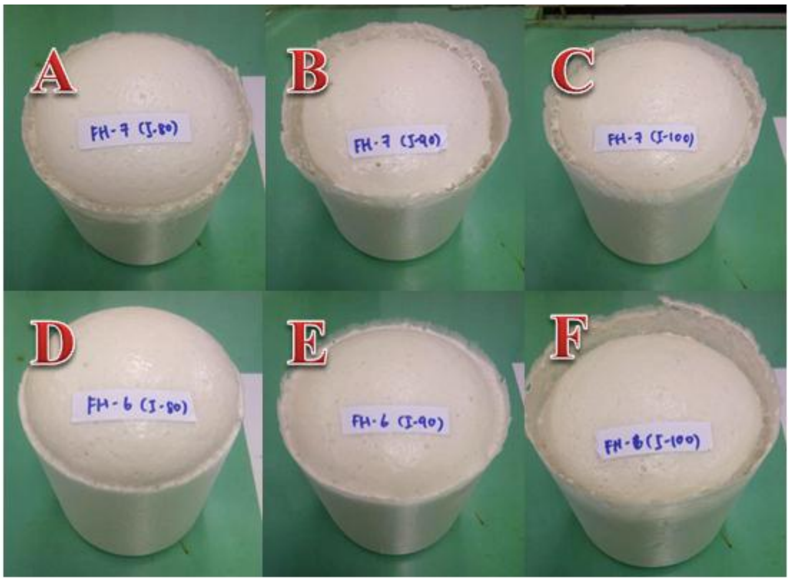


Figure 4.38 FPUR foam appearances of the reference and 15.0 pbw substituted PO polyol formulation with 3.5% water content; (a), (b) and (c) reference formulation at the NCO indexes of 80, 90 and 100, respectively; (d), (e) and (f) 15.0 pbw substituted PO polyol formulation at the NCO indexes of 80, 90 and 100, respectively

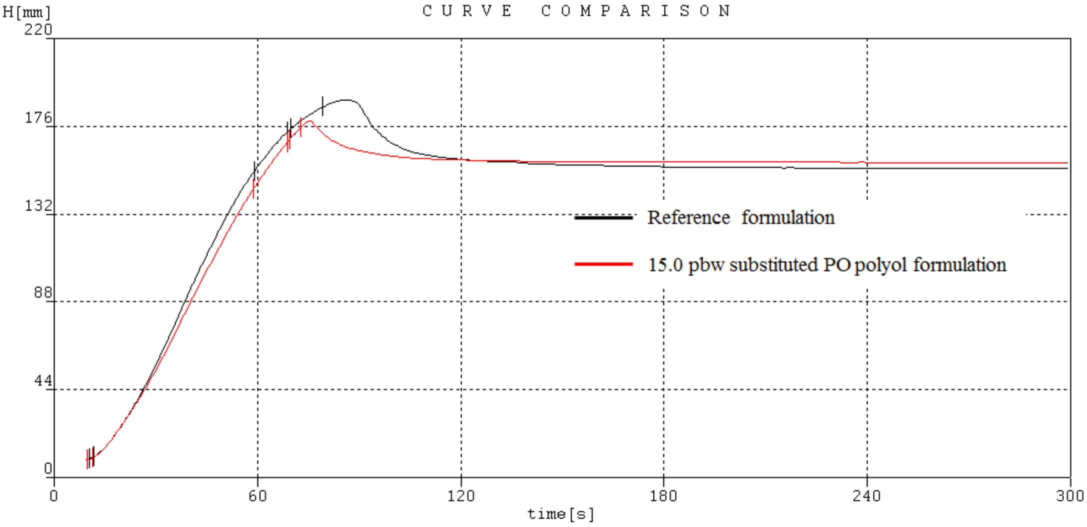


Figure 4.39 Rise profiles comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 3.5% water content at the NCO index of 100

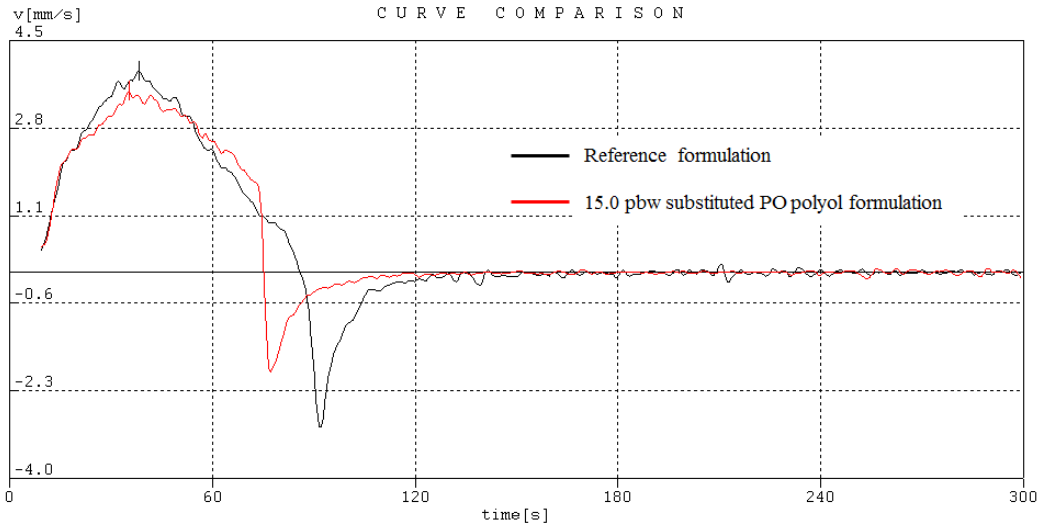


Figure 4.40 Rising speed comparison of FPUR foams prepared by using reference and 15.0 pbw substituted PO polyol formulations with 3.5% water content at the NCO index of 100

In 3.5% water content formulation, the gel time of 15.0 pbw substituted PO polyol and reference formulation is the same at all NCO indexes, however, the faster rise time is still observed in 15.0 pbw substituted PO polyol formulation. The %settling of 15.0 pbw substituted PO polyol formulation at NCO indexes of 90 and 100 are as high as that in the reference formulation. This indicated that the higher water content causes 15.0 pbw substituted PO polyol formulation to have the comparable amount of open cell content as reference formulation. However, the rise profiles (Figure 4.39) and rising speed (Figure 4.40) shows the different results. The rise profiles show that 15.0 pbw substituted PO polyol formulation still has stronger gel strength which resists the foam expansion. This causes lower maximum height and the faster rise time in 15.0 pbw substituted PO polyol formulation. The rising speed shows the sudden drop in rising speed since the foam expansion is resisted by the higher foam strength in 15.0 pbw substituted PO polyol formulation. The higher foam strength may come from the higher crosslink density from low molecular weight PO polyol.

4.2.3. Molded test using reference and substituted PO polyol as cell opening agents in FPUR foam formulation

Reference and 15.0 pbw substituted PO polyol formulations were selected to prepare FPUR block foam samples by use of mold test. Foam samples were subjected to the force to crush measurement and mechanical property analysis according to the method described in 4.1.4. The core density of block foams was varied at 45 – 55 kg/m^3 ($\pm$ 3.0 kg/m^3). After mechanical property analysis, FPUR foams were further submitted to SEM analysis.

4.2.3.1 Force to crush measurement

4.2.3.1.1 Force to crush of block FPUR foams prepared using FPUR foam formulation with 3.0% water content.

The block FPUR foams with core density of 50.0 kg/m^3 ($\pm$ 3.0 kg/m^3) were prepared using reference and 15.0 pbw substituted PO polyol formulations at the NCO indexes of 80, 90 and 100. The prepared block FPUR foams show good appearances. Table 4.37 shows the force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations at all NCO indexes.

The result from Table 4.37 shows that the force to crush of 15.0 pbw substituted PO polyol formulation is significant higher than that of reference formulation. Although 15.0 pbw substituted PO polyol formulation gives good foam appearance and no foam shrinkage during reactivity testing by cup test method, however, the force to crush results indicates that 15.0 pbw substituted PO polyol gives less open cell content than reference formulation.

Table 4.37 Force to crush comparison between reference and substituted PO polyol formulation with 3.0% water content

FPUR foam formulations	**%Compress**	**FTC (kgf) / NCO indexes**		
		80	**90**	**100**
Reference	25%	14.1	14.1	12.1
	50%	25.2	24.6	21.1
15.0 pbw substituted	25%	32.9	33.7	16.6
PO Polyol	50%	82.1	79.9	29.1

4.2.3.1.2 Force to crush of block FPUR foams prepared using FPUR foam formulation with 2.5% water content.

The block FPUR foams with core density 55.0 kg/m^3 (± 3.0 kg/m^3) were prepared using reference and 15.0 pbw substituted PO polyol formulations at NCO indexes of 80, 90 and 100. Both reference and 15.0 pbw substituted PO polyol formulations give good foam appearance. Table 4.38 shows the force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations at all NCO indexes.

Table 4.38 Force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations with 2.5% water content

FPUR foam formulations	**%Compress**	**FTC (kgf) / NCO indexes**		
		80	**90**	**100**
Reference	25%	15.5	16.7	11.7
	50%	30.3	32.8	21.9
15.0 pbw substituted PO Polyol	25%	13.1	34.4	29.9
	50%	27.2	87.2	77.3

The result shows that 15.0 pbw substituted PO polyol formulation gives higher force to crush than reference formulation at the NCO indexes of 90 and 100. However, at the NCO index of 80, the result of 15.0 pbw substituted PO polyol formulation shows lower force to crush than reference formulation. This result comes from the effect of too high free rise density of 15.0 pbw substituted PO polyol formulation at NCO index of 80, which causes less over-packing of FPUR foam in mold. This is not due to the higher open cell content in 15.0 pbw substituted PO polyol than reference formulation at the NCO index of 80.

4.2.3.1.3 Force to crush of block FPUR foams prepared using FPUR foam formulation with 3.5% water content.

The block FPUR foams with core density 45.0 kg/m^3 (± 3.0 kg/m^3) were prepared using reference and 15.0 pbw substituted PO polyol formulations at NCO indexes of 80, 90 and 100. For reference formulation, all FPUR block foams have good appearance with no shrinkage.

The force to crush results of formulation having 3.5% water content (Table 4.39) shows the same results as in previous experiment. The 15.0 pbw substituted PO polyol formulation has higher force to crush than reference formulation at all NCO indexes. This clearly shows that substituted PO polyol cannot give enough open cell structure in furniture formulation which MDI is used as isocyanate part.

Table 4.39 Force to crush comparison between reference and 15.0 pbw substituted PO polyol formulations with 3.5% water content

FPUR foam formulations	**%Compress**	**FTC (kgf) / NCO indexes**		
		80	**90**	**100**
Reference	25%	15.4	15.2	12.1
	50%	27.1	26.7	21.1
15.0 pbw substituted	25%	39.3	22.9	21.8
PO Polyol	50%	100.2	43.3	36.6

4.2.3.2 Mechanical property analysis

The block FPUR foams from 4.2.3.1 were kept for 24 hours after force to crush measurement at 25 ^{O}C and then the foams were submitted to mechanical property analysis under ambient conditions as described in 4.1.4.2.

4.2.3.2.1 Mechanical property analysis of FPUR formulation with 3.0% water content

The mechanical properties of FPUR foam formulation having 3.0% water content prepared using FPUR foam furniture formulation shows opposite results from automotive FPUR foam formulation. Tables 4.40, 4.41 and 4.42 show mechanical properties of FPUR foams from furniture formulation having 3.0% water content at the NCO indexes of 80, 90 and 100, respectively.

Table 4.40 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 80

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	48.8	48.5
Hardness (25% ILD)		N/314cm^2	138.2	124.5
Tensile strength		kPa	65.6	99.8
Tear strength		N/cm	4.02	5.19
Elongation at break		%	82	118
Ball Rebound		%	61	57
Compression set	Dry	%	5.8	9.6
	Wet	%	7.9	16.7

Table 4.41 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	49.1	48.6
Hardness (25% ILD)		N/314cm^2	175.7	173.9
Tensile strength		kPa	85.2	113.7
Tear strength		N/cm	4.80	7.06
Elongation at break		%	85	105
Ball Rebound		%	60	55
Compression set	Dry	%	5.5	8.8
	Wet	%	11.0	15.9

Table 4.42 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.0% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	49.1	49.4
Hardness (25% ILD)		N/314cm^2	240.1	263.9
Tensile strength		kPa	98.0	155.8
Tear strength		N/cm	5.88	7.93
Elongation at break		%	80	102
Ball Rebound		%	60	55
Compression set	Dry	%	4.6	6.9
	Wet	%	10.6	14.1

In the previous automotive FPUR foam formulation, PO polyol causes the decrease in FPUR foam flexibility and resilience, which results in lower elongation and ball rebound while increase the FPUR foam hardness and foam strength. However, the mechanical properties of FPUR foam in furniture formulation are different. The fast gel reaction between low molecular weight PO polyol and MDI causes the FPUR foams structure to have harder soft segment and higher hard segment ratio [21]. This result in high cell structure modulus, higher foam strength and higher elongation in 15.0 pbw substituted PO polyol formulation. On the other hand, the harder soft segment from shorter molecular weight PO polyol may result in the mixed phase between soft and hard segments. The phase separation between soft and hard segment leads to poor compression set property [22]. The high modulus from harder soft segment and high hard segment ratio in 15.0 pbw substituted PO polyol formulation also reduce the ball rebound properties.

In the case of FPUR foams hardness, the results are much related to isocyanate in the system. Since the MDI reacts with PO polyol fast, the blowing reaction between MDI and water are less than those in reference formulation. Therefore, in systems which have lower isocyanate amount (NCO indexes of 80 and 90), there are less di-substituted urea and biuret group since there is small isocyanate amount to react with amine, which is a product from blowing reaction. Hence, there is lower crosslink density in 15.0 pbw substituted PO polyol formulation which results in lower foam hardness. Significant difference in hardness (> 10.0 N) is observed in the NCO index of 80. When the isocyanate amount is higher in NCO index of 90, the hardness of 15.0 pbw substituted PO polyol foam is still lower than that of reference formulation but the difference is not significant (< 2.0 N). At the NCO index of 100, where the isocyanate amount is high enough, there is no difference in crosslink density from the reason described above. 15.0 pbw Substituted PO polyol foam has higher hardness than reference formulation due to harder soft segment and high amount of hard segment.

4.2.3.2.2 Mechanical property analysis of FPUR formulation with 2.5% water content

In 2.5% water content formulation, the mechanical properties results at the NCO indexes of 80, 90 and 100 are shown in Tables 4.43, 4.44 and 4.45, respectively. The PO polyol in 15.0 pbw substituted PO polyol formulation causes FPUR foam to have higher elongation, tensile strength and tear strength, however, worse ball rebound and compression set are obtained. The reason is the same as described in 4.2.3.2.1. In the case of hardness, 15.0 pbw substituted PO polyol formulation has lower hardness than reference formulation at all NCO indexes. The explanation is the same as the lower hardness results observed at the NCO index of 80 in 3.0% water content formulation.

Table 4.43 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 2.5% water content at NCO index of 80

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	55.5	54.5
Hardness (25% ILD)		N/314cm^2	115.6	96.1
Tensile strength		kPa	51.9	60.7
Tear strength		N/cm	2.94	3.43
Elongation at break		%	115	150
Ball Rebound		%	62	61
Compression set	Dry	%	2.6	3.5
	Wet	%	4.5	8.9

Table 4.44 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 2.5% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	54.6	55.4
Hardness (25% ILD)		N/314cm^2	153.9	134.3
Tensile strength		kPa	55.9	78.4
Tear strength		N/cm	3.63	4.12
Elongation at break		%	110	135
Ball Rebound		%	64	60
Compression set	Dry	%	2.2	4.3
	Wet	%	6.0	11.5

Table 4.45 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 2.5% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	54.8	54.9
Hardness (25% ILD)		N/314cm^2	227.4	216.6
Tensile strength		kPa	77.4	105.8
Tear strength		N/cm	4.31	4.90
Elongation at break		%	110	115
Ball Rebound		%	62	57
Compression set	Dry	%	2.9	4.7
	Wet	%	4.9	11.0

4.2.3.2.3 Mechanical property analysis of FPUR formulation with 3.5% water content

In 3.5% water content formulation, the results are different from 2.5% water content formulation, the higher mechanical properties observed at all NCO indexes. Unlike in 2.5% water content formulation, in 3.5% water content formulation, the water amount is high enough to perform blowing reaction with MDI. Therefore, there is no different in crosslink density between 15.0 pbw substituted PO polyol and reference formulations. Moreover, the harder soft segment and higher amount of hard segment unit in 15.0 pbw substituted PO polyol foam, which was mentioned above, lead to higher foam hardness, elongation and foam strength in 15.0 pbw substituted PO polyol than in reference formulation, however, worse ball rebound and compression set are obtained. Tables 4.46, 4.47 and 4.48 show the mechanical properties of FPUR foam prepared using 3.5% water content formulation at NCO indexes of 80, 90 and 100, respectively.

Table 4.46 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 80

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	45.3	45.4
Hardness (25% ILD)		N/314cm^2	152.9	159.8
Tensile strength		kPa	96.1	128.3
Tear strength		N/cm	4.98	6.76
Elongation at break		%	95	115
Ball Rebound		%	56	53
Compression set	Dry	%	5.5	8.9
	Wet	%	10.8	23.9

Table 4.47 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 90

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	44.4	45.1
Hardness (25% ILD)		N/314cm^2	202.9	219.5
Tensile strength		kPa	106.8	148.9
Tear strength		N/cm	6.47	7.74
Elongation at break		%	85	105
Ball Rebound		%	54	53
Compression set	Dry	%	5.2	8.8
	Wet	%	12.7	25.4

Table 4.48 Mechanical properties of FPUR foams prepared using reference and substituted PO polyol formulations with 3.5% water content at NCO index of 100

Mechanical properties		Unit	FPUR foam formulations	
			Reference	15.0 pbw PO polyol
Core density		Kg/m^3	44.1	44.2
Hardness (25% ILD)		N/314cm^2	258.7	298.9
Tensile strength		kPa	130.3	177.4
Tear strength		N/cm	7.15	10.29
Elongation at break		%	80	85
Ball Rebound		%	50	49
Compression set	Dry	%	6.9	10.6
	Wet	%	17.8	25.6

4.2.3.3 Scanning electron microscope (SEM) analysis

The FPUR foam samples prepared using reference and 15.0 pbw substituted PO polyol formulations were submitted to SEM analysis using the accelerating voltage of 20 kV. Figures 4.41, 4.42 and 4.43 show SEM micrographs in comparison between FPUR foams prepared from reference and 15.0 pbw substituted PO polyol formulation having water content of 2.5%, 3.0% and 3.5% and using the NCO index of 100.

The SEM micrographs in Figures 4.41, 4.42 and 4.43 show that FPUR foams using 15.0 pbw substituted PO polyol formulation give the same open cell structure as those obtained from the reference formulation. However, FPUR foams from 15.0 pbw substituted PO polyol formulation (Figures 4.41 (b), 4.42 (b) and 4.43(b)) show larger cell size distribution than those obtained from reference formulation (Figures 4.41 (a), 4.42 (a) and 4.43(a)).

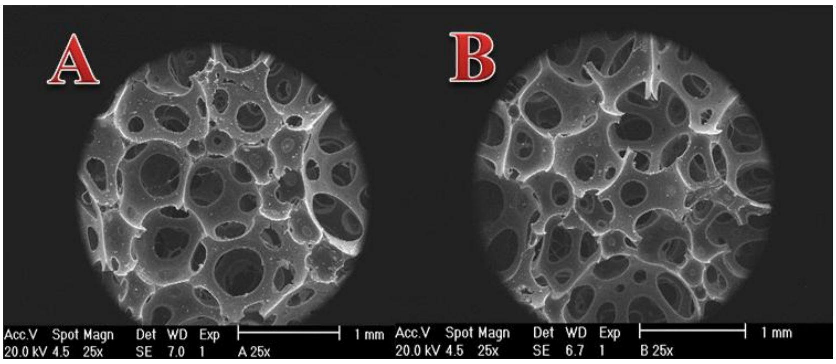


Figure 4.41 SEM of FPUR foams prepared using 2.5% water content formulation at the NCO index of 100; (a) reference formulation; (b) 15.0 pbw substituted PO polyol formulation

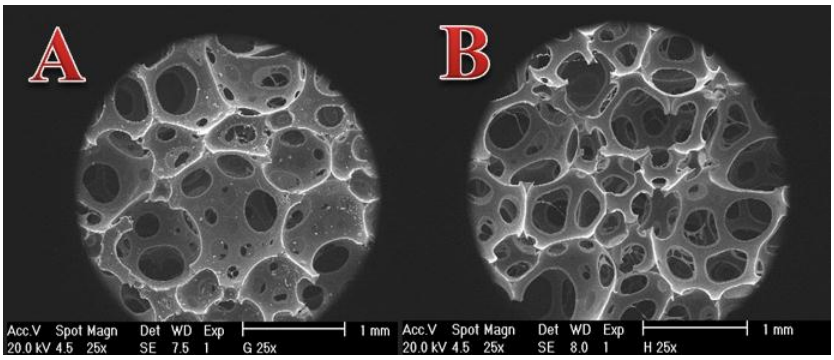


Figure 4.42 SEM of FPUR foams prepared using 3.0% water content formulation at the NCO index of 100; (a) reference formulation; (b) 15.0 pbw substituted PO polyol formulation

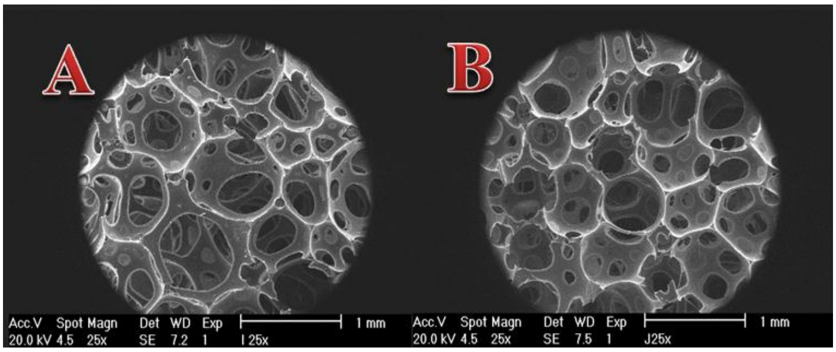


Figure 4.43 SEM of FPUR foams prepared using 3.5% water content formulation at the NCO index of 100; (a) reference formulation; (b) 15.0 pbw substituted PO polyol formulation

4.3 Phase separation of formulated polyol prepared using conventional cell opening agent and substituted PO polyol.

The phase separation was measured using aging test method, which is developed at Bayer (Thailand) Co., Ltd. This test was done by filling the glass test tubes with formulated polyol prepared using various amount of conventional cell opening agent (1.0, 2.0, 3.0, 4.0 and 5.0 pbw) and 15.0 pbw substituted PO polyol as cell opening agent. These test tubes were put it into the hot air oven at the temperature of 70 °C. This is to accelerate the interaction between high polarity groups in formulated polyol with water molecules. The method represents the phase separation which normally occurs in formulated polyol upon storage. The formulated polyol were taken out to measure the phase separation using visual observation every day for 6 days.

The phase separation results show that at the amount of ≥ 3.0 pbw of conventional cell opening agent, phase separation could be observed as the yellowish liquid at the bottom of the test tube. This separation comes from the reaction between high polarity and hydrophilic conventional cell opening agent and water after aging at 70 ^{O}C for 4 days. Upon increasing the amount of conventional cell opening agent to 4.0 or 5.0 pbw, the phase separation occurs faster. The phase separation occurs after aging for 3 days. In the case of using 15.0 pbw substituted PO polyol as cell opening agent, there is no phase separation observed even though the aging was done at 70 °C for 6 days.

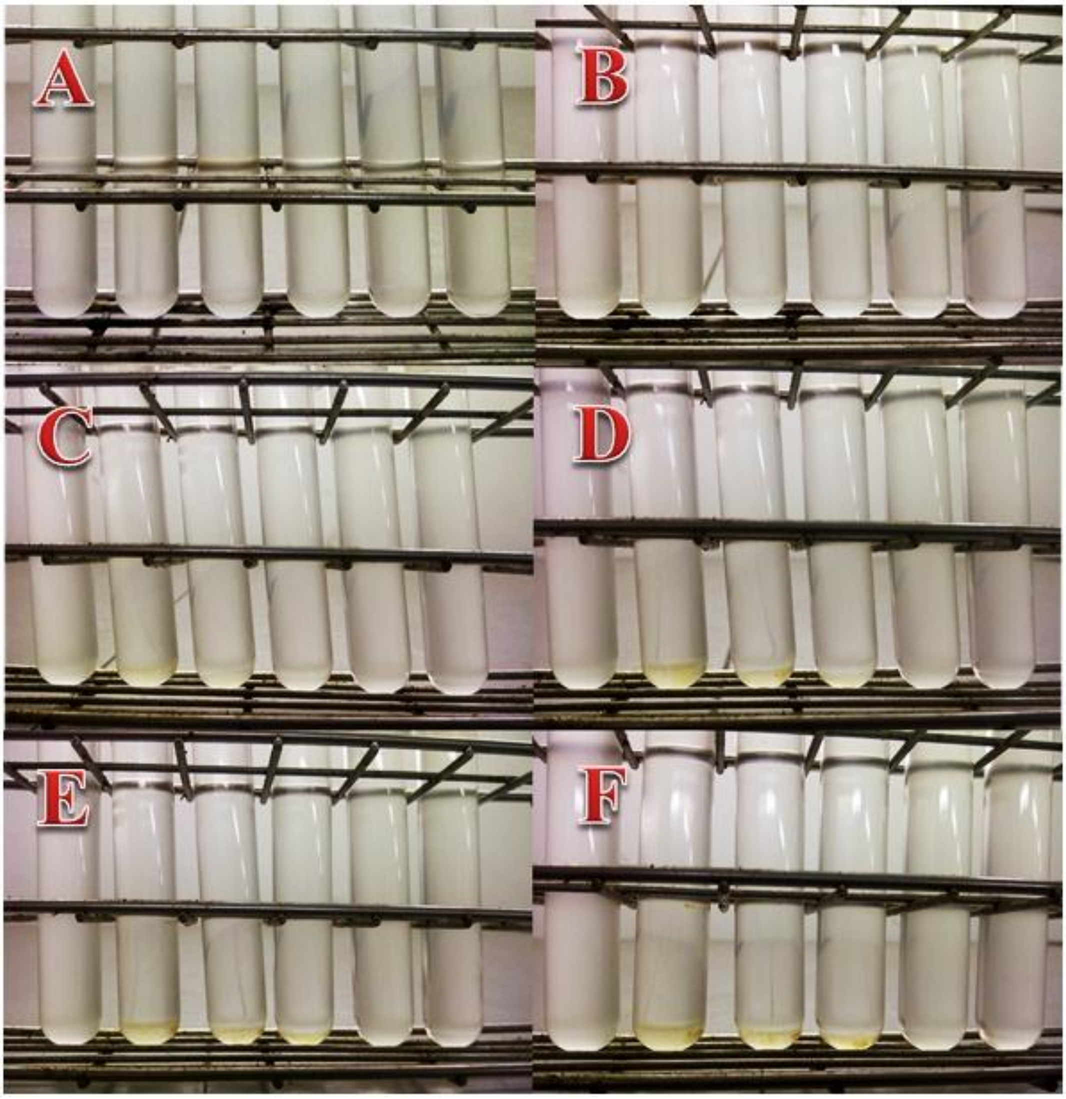


Figure 4.44 Phase separation of formulated polyol prepared using various cell opening agent types and amount after aging in oven having temperature of 70 ^{O}C; (a) 1 day aging; (b) 2 days aging; (c) 3 days aging; (d) 4 days aging; (e) 5 days aging and (f) 6 days aging. From left to right; 15.0 pbw substituted PO polyol as cell opening agent, 5.0 pbw, 4.0 pbw, 3.0 pbw, 2.0 pbw and 1.0 pbw of conventional cell opening agent, respectively

CHAPTER V
CONCLUSION

5.1 Conclusion

Pure polypropylene oxide (PO) polyol was used as new cell opening in FPUR foam formulations for automotive seating and furniture applications. The FPUR foams prepared using new cell opening agent were compared with those obtained from conventional cell opening agent which is high ethylene oxide (EO) content polyol (reference formulation). The isocyanate used in automotive formulation is toluene diisocyanate (TDI) while the isocyanate used in furniture formulation is diphenylmethane diisocyanate (MDI). The FPUR foams were prepared using cup test method to measure the reactivity and molded test method to measure the mechanical properties. The open cell content measurement was performed using force to crush measurement on FPUR foam samples prepared using molded test method. Cell morphology of FPUR foams was investigated by scanning electron microscopy (SEM).

In automotive seating formulation, the experiment was done on the formulation having 3.0%wt., 3.5% wt. and 4.0%wt. water content at the NCO indexes of 90, 100 and 110. The results from cup test method show that the additional PO polyol at least 10.0 pbw result in open cell FPUR foams, which is same result as the use of conventional cell opening agent. However, the additional polyol diluted the catalyst concentration in FPUR foam formulation results in the delayed reactivity. Partial substitution of PO polyol instead of long chain based polyol was further studied.

Use of 10.0 pbw and 15.0 pbw substituted PO polyol in FPUR foam formulation results in open cell FPUR foams without significant effect of FPUR foams reactivity by using cup test method. In addition, the force to crush result in molded test method shows that 10.0 pbw substituted PO polyol formulations have significantly higher force to crush than reference formulation. This indicates that 10.0 pbw substituted PO polyol gives less open cell content than reference formulation while the similar or even lower force to crush is obtained in 15.0 pbw substituted PO polyol formulation. This shows that 15.0 pbw PO polyol (partially substituted in long chain based polyol) can be used as cell opening agent in FPUR foam formulation for automotive seating application and gives the comparable amount of open cell content as the use of conventional cell opening agent.

The mechanical properties analysis shows that the use of substituted PO polyol increases the foam hardness and foam strength while decreases the elongation and ball rebound. This is because PO polyol has lower molecular weight than conventional long chain based polyol, which results in the smaller soft segment and high crosslink density. The SEM micrograph shows that both of reference and substituted PO polyol formulation give the similar open cell structure FPUR foams. However, in the case of substituted PO polyol formulation, larger cell size distribution was observed.

In furniture application, 15.0 pbw substituted PO polyol was used based on the results from automotive seating application. The experiments were done on furniture formulation having water at 2.5%wt, 3.0%wt and 3.5%wt water content at the NCO indexes of 80, 90 and 100. The foam reactivity shows that 15.0 pbw substituted PO polyol give a significantly faster reactivity than reference formulation. This is the effect from the high reactive isocyanate (MDI) used in furniture formulation react with low molecular weight PO polyol very fast. The force to crush results of 15.0 pbw substituted PO polyol is significantly higher than reference formulation. This indicates that PO polyol has less cell opening performance than conventional one.

In mechanical properties point of view, the substituted PO polyol formulation gives superior foam strength and elongation than the reference formulation due to high molecular weight built up from polyol-isocyanate reaction. However, the compression set results from the substituted PO polyol formulation is much worse compared to the reference formulation. In the case of hardness, it is much depended on the crosslink density from isocyanate-water reaction. The system which has lower water content and NCO index, the hardness of substituted PO polyol formulation is lower than those obtained from the reference formulation while the hardness of substituted PO polyol formulation is higher than those obtained from reference formulation in the system which has high water content and NCO index. The SEM micrographs of the 15.0 pbw substituted PO polyol show smaller cell size and larger cell size distribution than those obtained from reference formulation.

The phase separation results show that there is no phase separation in formulated polyol using substituted PO polyol as cell opening agent after aging at 70 ^{O}C for 6 days, while the formulations contained 3.0 pbw of conventional cell opening agent and above have the phase separation after past 3 days aging. This indicated that PO polyol has more homogeneity in the formulated polyol than conventional cell opening agent.

5.2 Suggestion for future work

Pure polypropylene oxide (PO) polyol was effectively used as cell opening agent in FPUR foams for automotive application which TDI was used as isocyanate. By contrast, in furniture application which MDI was used as isocyanate part, PO polyol alone is not as effective as the results obtained in automotive application. This is because the highly reactive NCO groups in MDI react with PO polyol faster than those from TDI. The suggestion for future work is to utilize the PO polyol as co-cell opening agent together with conventional cell opening agent in furniture application in order to balance the open cell content, improve phase separation and alter the mechanical properties, especially compression set which is significantly higher when PO polyol was used as sole cell opening agent.

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APPENDICES

APPENDIX A

NCO index calculations

NCO index calculation

Example : Calculate the parts by weight (pbw) of toluene diisocyanate (TDI) blend with diphenylmethane diisocyanate (MDI) in the ratio of 80:20 (TM-20) at NCO indexes of 90, 100 and 110 required to react with the FPUR foam formulation for automotive application having 3.5% water content as following:

Formulations	**OHV**	**pbw**
Arcol Polyol® 1362 (A-1362)	28	60
Hyperlite® E-850 (E-850)	20	40
Crosslinker	1830	0.5
Cell opening agent	37	2.0
Surfactant	-	0.6
Catalyst	560	0.6
Blowing agent (water, Mw =18 g/mole, functionality =2)		3.76
TM-20 (NCO content = 44.8)		??

Calculation step

1. Sum the parts of all components to get total polyol formulation weight.

Total formulation weight = 60 + 40 + 0.5 + 2 + 0.6 + 0.6 + 3.76 = 107.46

2. Calculate the equivalent weight of each component in polyol formulation.

$$\textbf{\textit{Equivalent weight}}_{\textit{A-1362}} = \frac{56.1 \times 1000}{28} = 2003.6$$

$$\textbf{\textit{Equivalent weight}}_{\textit{E-850}} = \frac{56.1 \times 1000}{20} = 2805.0$$

$$\textbf{\textit{Equivalent weight}}_{\textit{crosslinker}} = \frac{56.1 \times 1000}{1830} = 30.7$$

$$\textbf{\textit{Equivalent weight}}_{\textit{cell opening agent}} = \frac{56.1 \times 1000}{37} =1516.2$$

$$\textbf{\textit{Equivalent weight}}_{\textbf{\textit{catalyst}}} = \frac{56.1 \text{ x } 1000}{560} = 100.2$$

$$\textbf{\textit{Equivalent weight}}_{\textbf{\textit{water}}} = \frac{18}{2} = 9.0$$

3. Calculate number equivalent of each component in polyol formulation.

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{A-1362}}} = \frac{60}{2003.6} = 0.0299$$

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{E-850}}} = \frac{40}{2805.0} = 0.0143$$

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{crosslinker}}} = \frac{0.5}{30.7} = 0.0163$$

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{cell opening agent}}} = \frac{2.0}{1516.2} = 0.0013$$

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{catalyst}}} = \frac{0.6}{100.2} = 0.0060$$

$$\textbf{\textit{Number Equivalent}}_{\textbf{\textit{water}}} = \frac{3.76}{9.0} = 0.4177$$

4. Sum the total number equivalent in polyol formulation.

$$\begin{aligned}\textbf{\textit{Number Equivalent}}_{\textbf{\textit{total}}} &= 0.0299+0.0143+0.0163+0.0013+0.0060+0.4177 \\ &= 0.4855\end{aligned}$$

5. Calculate the equivalent weight of isocyanate.

$$\textbf{\textit{Equivalent weight}}_{\textbf{\textit{isocyanate}}} = \frac{42 \text{ x } 100}{44.8} = 93.75$$

6. Calculate the parts isocyanate to react with total polyol.

$$\textbf{\textit{Parts Isocyanate}}_{\textbf{\textit{(TM-20)}}} = 0.4855 \text{ x } 93.75 = 45.5$$

Note: 45.5 defines the isocyanate quantity at total polyol 107.46 at the NCO index of 100

Hence;

$$\textbf{\textit{Parts isocyanate}}_{\textbf{\textit{(per 100 g. polyol)}}} = \frac{45.5 \text{ x } 100}{107.46} = 42.3 \text{ g.}$$

Where;

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

Thus;

#Isocyanate index = 100

$$\textbf{\textit{Actual amount of isocyanate used}} = \frac{42.3 \text{ x } 100}{100} = 42.3 \text{ g.}$$

#Isocyanate index = 90

$$\textbf{\textit{Actual amount of isocyanate used}} = \frac{42.3 \text{ x } 90}{100} = 38.1 \text{ g.}$$

#Isocyanate index = 110

$$\textbf{\textit{Actual amount of isocyanate used}} = \frac{42.3 \text{ x } 110}{100} = 46.5 \text{ g.}$$

APPENDIX B

FPUR foam rise profiles and rising speed

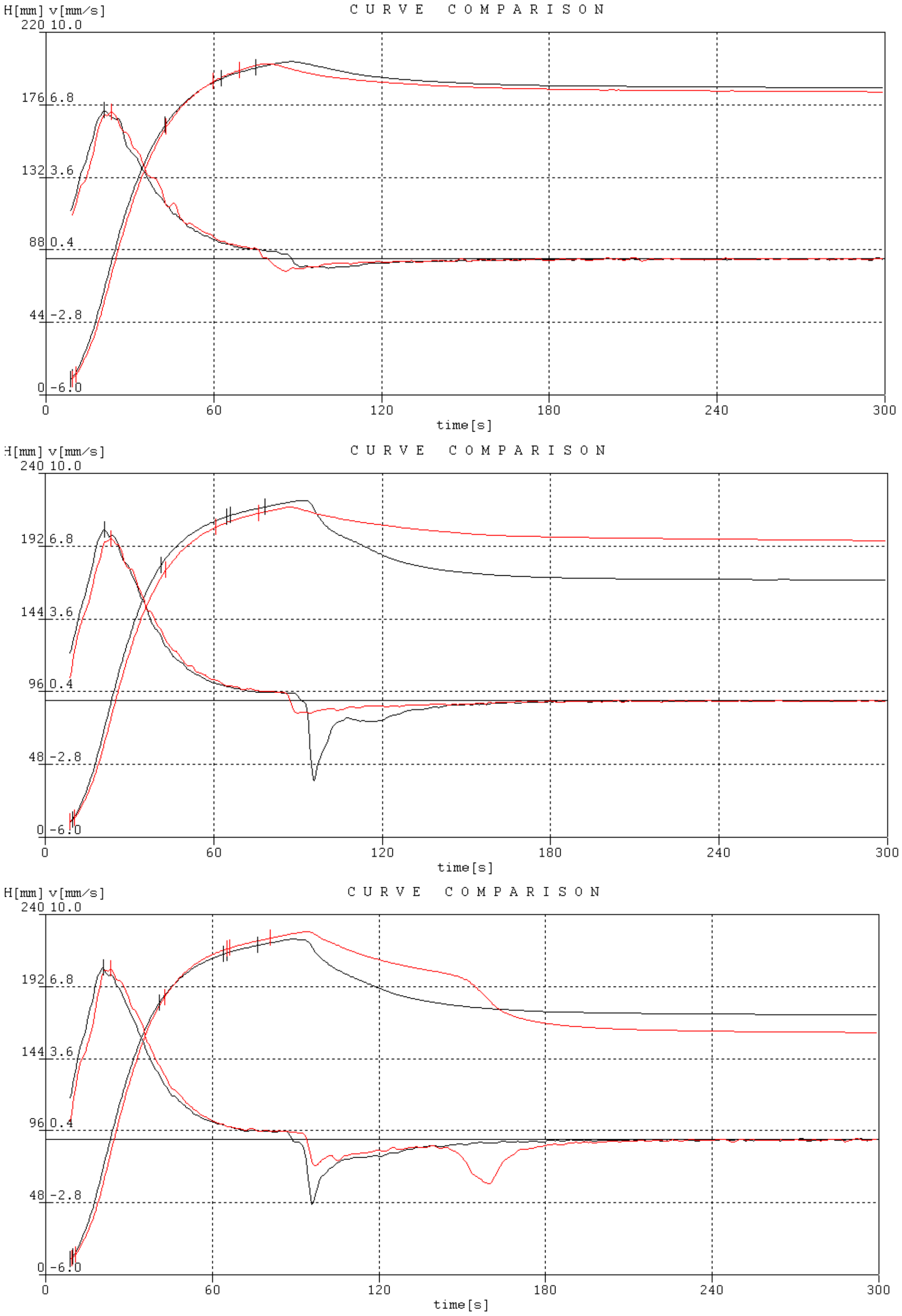

Figure B1 FPUR foam rise profiles and rising speed of FPUR foam automotive formulation having 3.5% water content at the NCO indexes of 90 (top), 100 (middle) and 110 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

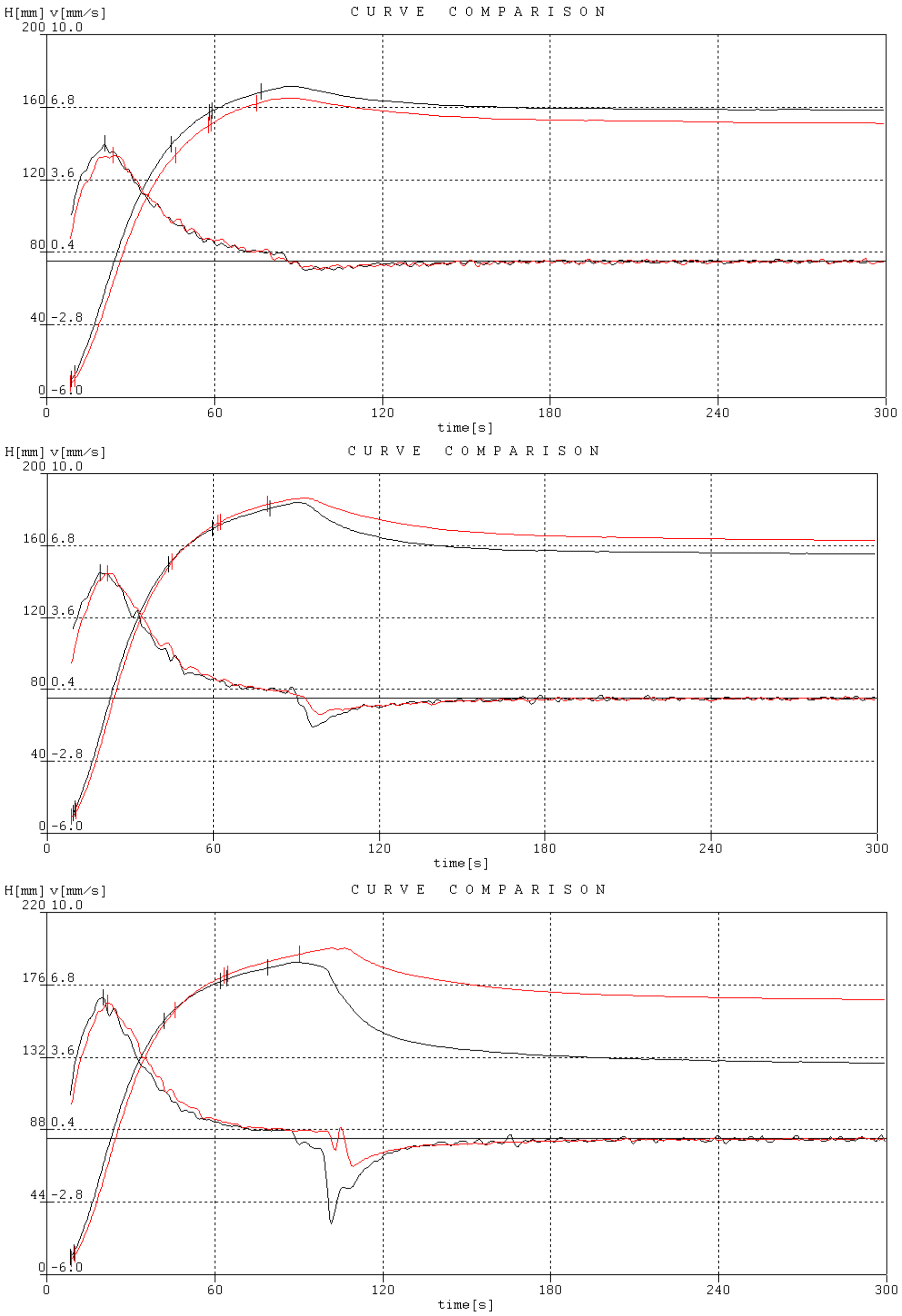

Figure B2 FPUR foam rise profiles and rising speed of FPUR foam automotive formulation having 3.0% water content at the NCO indexes of 90 (top), 100 (middle) and 110 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

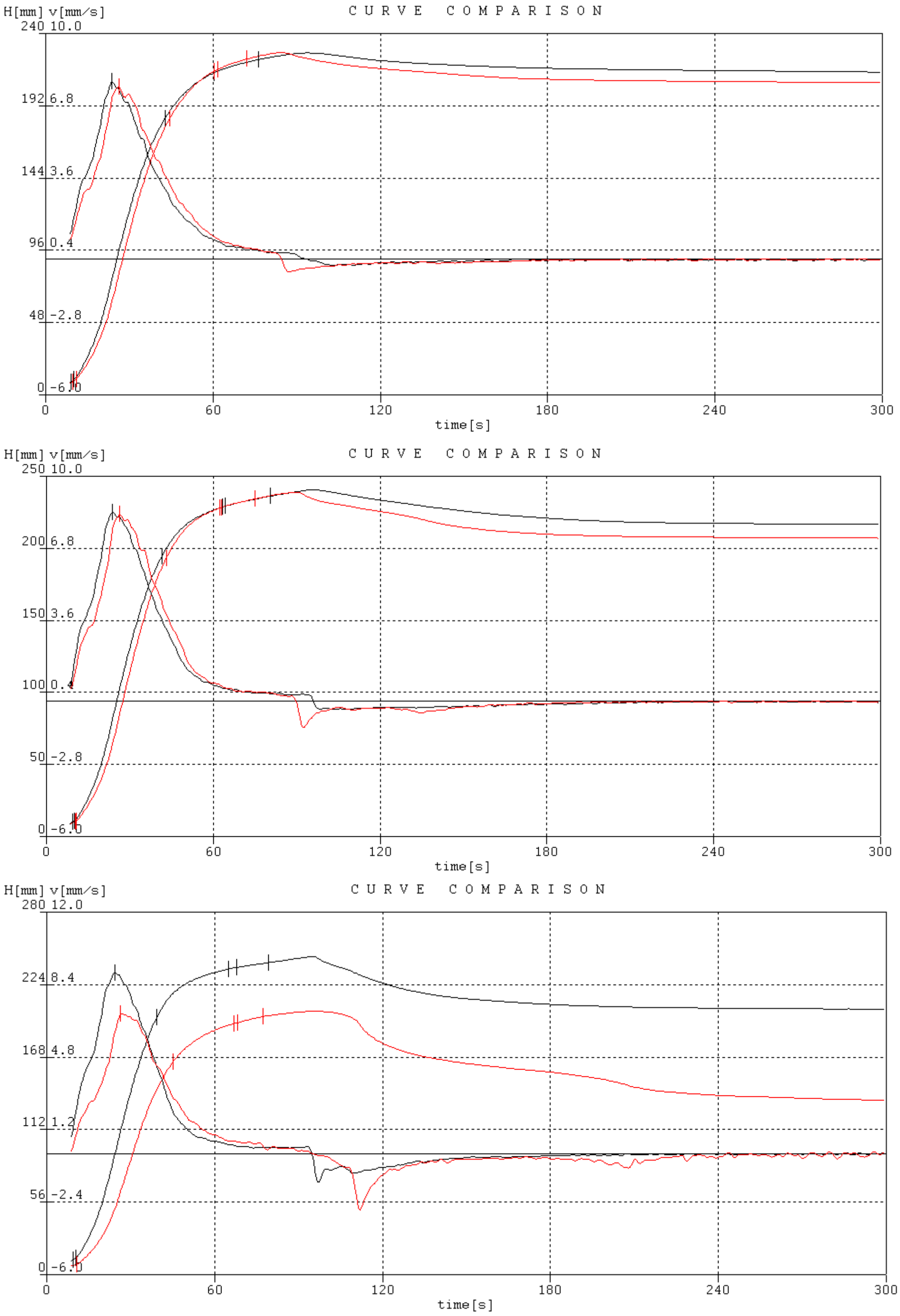

Figure B3 FPUR foam rise profiles and rising speed of FPUR foam automotive formulation having 4.0% water content at the NCO indexes of 90 (top), 100 (middle) and 110 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

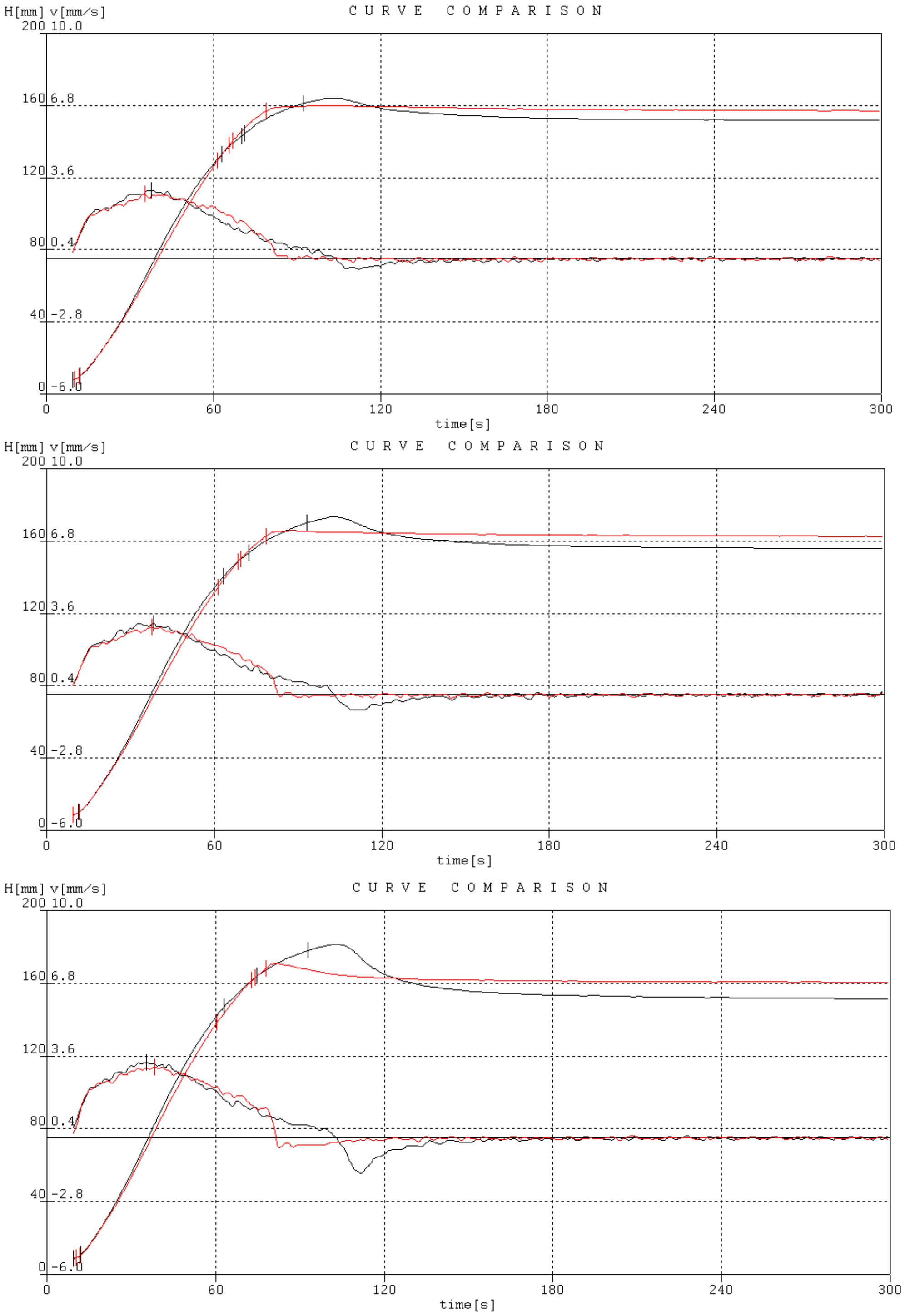

Figure B4 FPUR foam rise profiles and rising speed of FPUR foam furniture formulation having 3.0% water content at the NCO indexes of 80 (top), 90 (middle) and 100 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

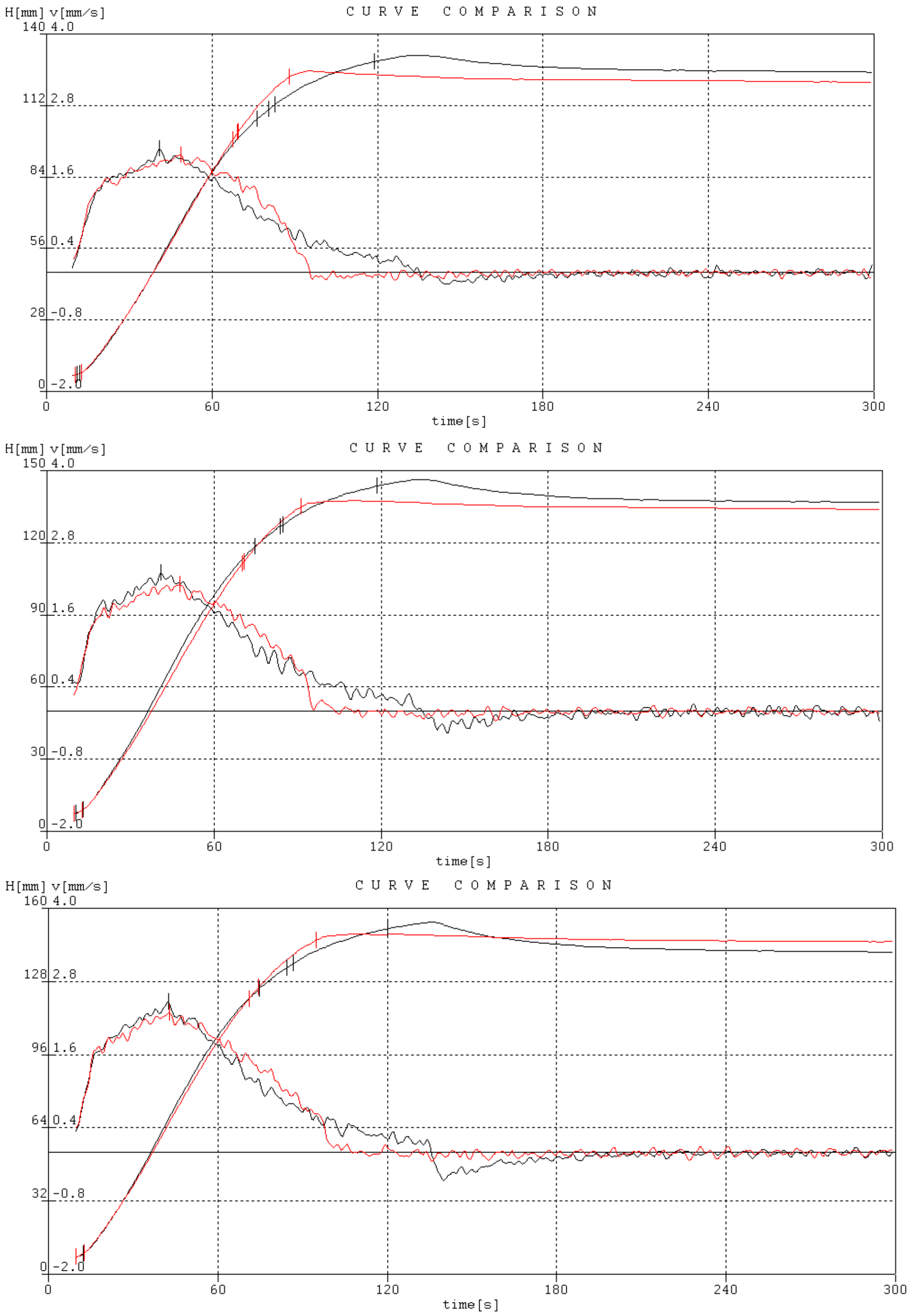

Figure B5 FPUR foam rise profiles and rising speed of FPUR foam furniture formulation having 2.5% water content at the NCO indexes of 80 (top), 90 (middle) and 100 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

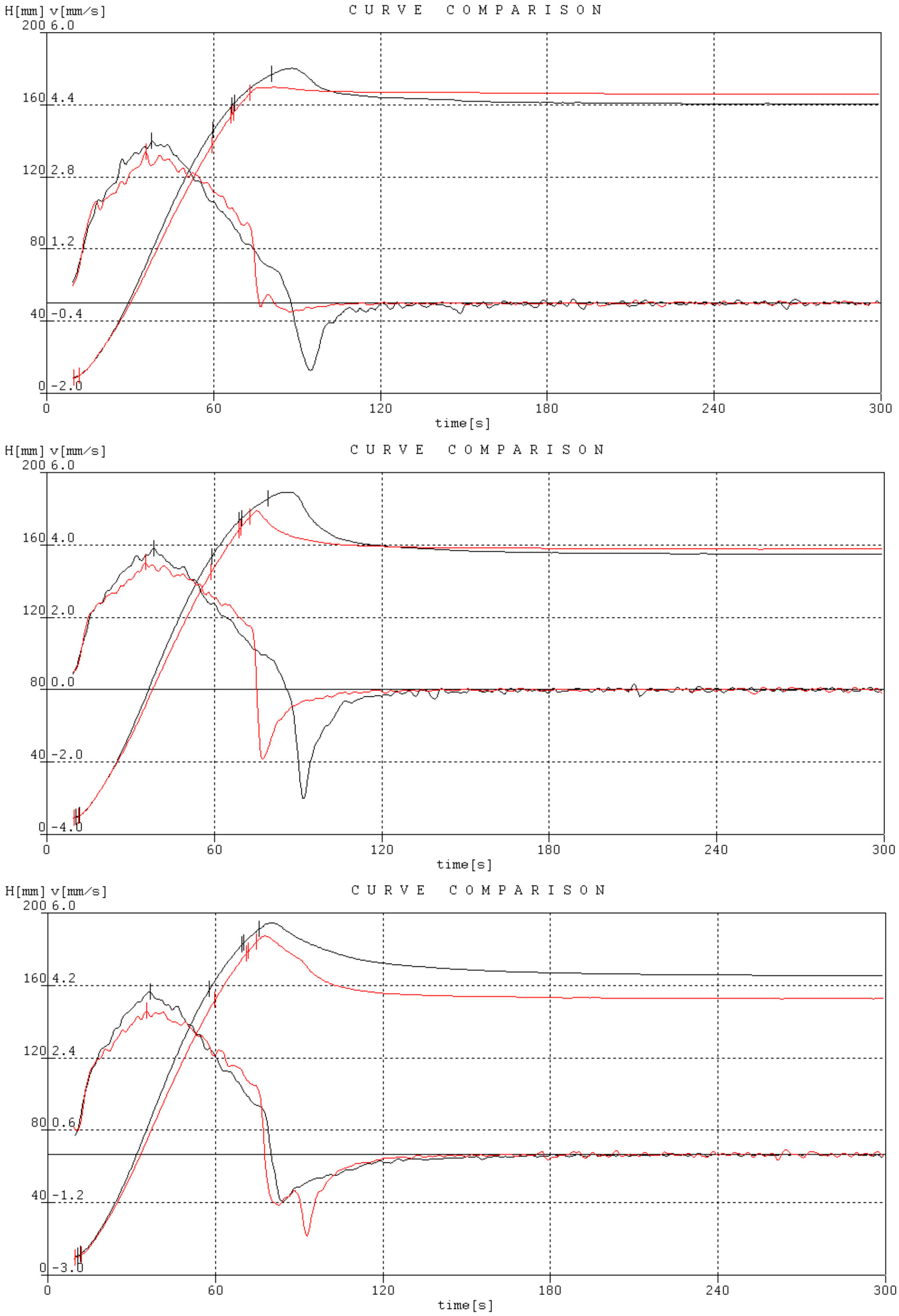

Figure B6 FPUR foam rise profiles and rising speed of FPUR foam furniture formulation having 3.5% water content at the NCO indexes of 80 (top), 90 (middle) and 100 (bottom), respectively. Black line is reference formulation while red line is 15.0 pbw substituted PO polyol formulation

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