

EVALUATION OF SUITABILITY OF 1,4-DIMETHYLPIPERAZINE AS A SUBSTITUTE CATALYST FOR POLYURETHANE FOAM PRODUCTION

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Dissertation submitted in partial fulfillment of the requirements for the degree of
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Declaration

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Abstract

The flexible polyurethane foams have been fabricated from polymeric 4,4'-di-phenylmethane diisocyanate (MDI) and polyols. Catalysts play a major role in polyurethane foam preparation controlling the reaction profile throughout the reaction time. As a substitute catalyst 1,4-dimethylpiperazine promotes gelling reaction as well as blowing reaction as predicted. Effect of 1,4-dimethylpiperazine on polyurethane foam formation was investigated by varying the additive concentration while keeping all the other factors constant. Sample of standard dimensions were prepared from the resultant foam. They were used for density test compression set test, tensile strength and elongation tests. The tests were carried out as per the ASTM -D3574 standards. The reaction profile has moved to slower direction in terms of gelling time, rise time, curing time in the presence of 1,4-dimethylpiperazine compared to the control catalyst. This is due to the less reactivity of the test catalyst. The resultant controlled behavior of the 1,4- dimethylpiperazine could be more useful in applications such as complex molding. Other physical properties such as foam density, hardness, tensile strength, compression set test value lie within the comparable range which could again be useful in molding conditions. It is concluded that 1,4-dimethylpiperazine is a good delayed action catalyst which is found to be better for in-mold flowability and slow cure times with comparable foam properties.

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List of Abbreviations

Abbreviation	Description
1,4-DMP	1,4-dimethylpiperazine
Mol wt	Molecular weight
MDI	Diphenyl methane diisocyanate
TDI	Toluenediisocyanate
HDI	Hexamethylene diisocyanate

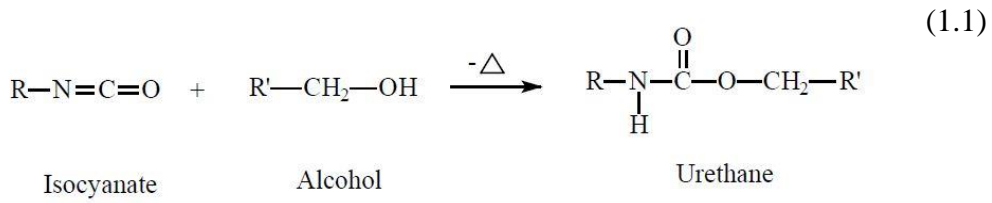
CHAPTER 1 INTRODUCTION

1.1 Introduction

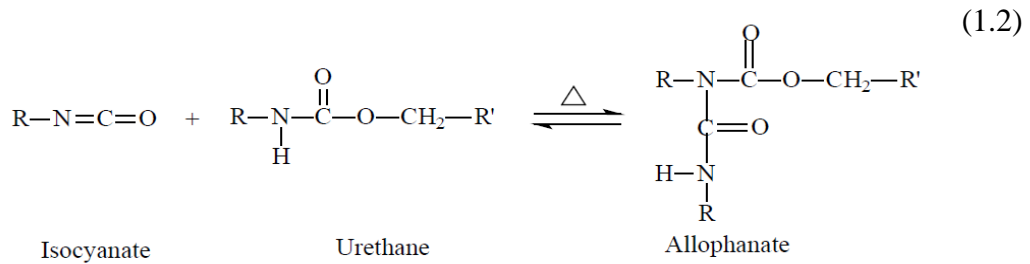
Out of the materials we use today polyurethanes have very broad application range. Polyurethanes are categorized into certain types depending on their physical nature. These types are namely Flexible polyurethane foam, Rigid polyurethane foam, Coating, Adhesive, Sealant and Elastomers (CASE), Thermoplastic polyurethane foam (TPU), Reaction injection molding(RIM), Binders, Waterborne polyurethane dispersions (PUDs). Flexible polyurethanes are used in bedding, furniture, automotive interiors. Rigid polyurethane foams are used as an effective insulation material which are used in walls and roofs. Thermoplastic polyurethanes (TPU) has many applications due its nature of highly elastic, flexible and resistant to abrasion. They are used in construction, automotive and foot wear. RIM is a technology which is highly useful in situation to achieve more intricate designs, it is applied in making thin and thick-walled parts, encapsulated inners, etc.

Polyurethane is a polymer produced by the mixing of two chemical components Polyol and Isocyanate. Mixing of these two raw materials gives a hard solid which is polyurethane polymer. The area of polyurethane foam chemistry is considered as a building block chemistry. Proper choice of polyol and poly isocyanate is required to the preparation of all types of polyurethane foams. Factors such as chemical structure, equivalent weight, and functionality of the raw materials are considered to obtain foams with desired properties. While growing the polymer, gas is introduced by either chemically or physically.

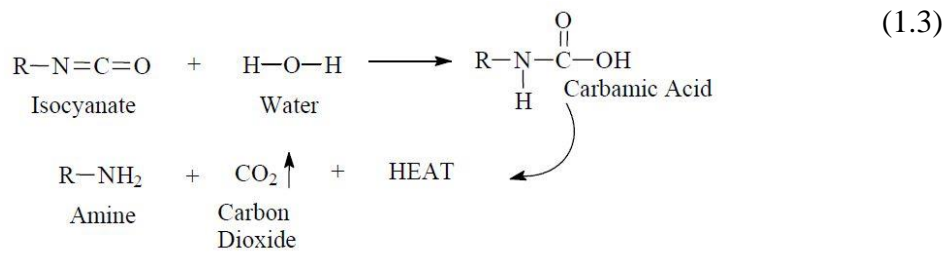
Generally polyurethane foam formation occurs through two basic reactions named as Gel reaction and Blow reaction. During the gel reaction, isocyanate group reacts with an alcohol group to give a urethane bond as illustrated in equation (1.1) given below: hence this is called polymerization reaction.



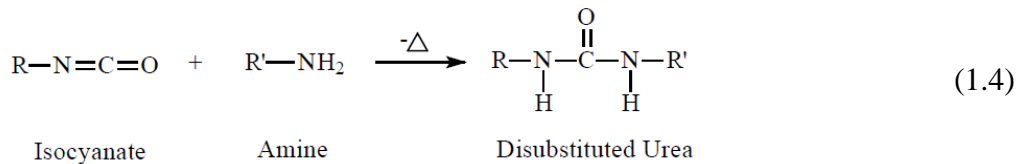
This urethane group reacts with an isocyanate molecule resulting an allophanate group. From this reaction growing polymer chain will further extend by cross linking each other. This is illustrated in equation 1.2



During blow reaction is the reaction between isocyanate and water. As given in equation 1.3 this will produce an amine functionality and carbon dioxide via carbamic acid which is unstable¹



Equation 1.4 shows formation of disubstituted urea. by reacting an amine group with isocyanate group disubstituted urea is formed. During this reaction additional heat is also generated.



Blow reaction does two functions as foam expansion and making urea hard segments. From the gel reaction these hard segments are bonded to polyol chains by formation of covalent bonds.

Obtaining optimum processing and end properties at the same time cannot usually be achieved using a single Polyol and the same holds for catalysts and blowing agents. Therefore, multiple components are being utilized during formulation development.

The Polyol system generally constitutes with polyols, catalysts, surfactants, chain extenders, cross linkers, water and blowing agents¹. Each constituent has specific function to produce a quality polyurethane foam. Polyols are derived from polyethers and polyesters. These polyols can be difunctional (diol), trifunctional (triol), tetrafunctional (tetrol), or polyfunctional. Polyols are molecules with large molecular weight range (Generally range from 300 to 10000 daltons). They react with isocyanate to produce polyurethane backbone which connects via urethane bonds.

Polyurethane is linear block copolymer which consists of three building blocks as polyol, diisocyanate and chain extender which is illustrated in figure 1.1. The properties of the resulting polyurethane polymer can be modified by varying the functionality of these building blocks⁸

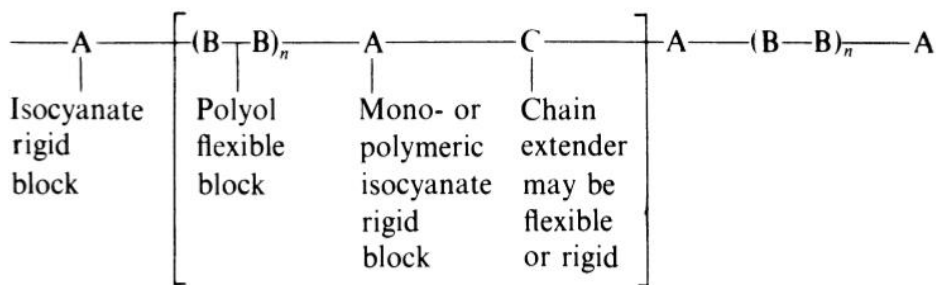


Figure1.1: The basic unit in a urethane block copolymer.

The properties of the polymer produced are related to segmented flexibility, chain entanglement, interchain forces and crosslinking.⁸

Isocyanate is one of the main raw material in polyurethane. There are two types isocyanates being utilized as toluene diisocyanate (TDI) and diphenylmethane

diisocyanate (MDI). There are two isomers as 2,4- and 2,6- TDI isomers in TDI. The proportion of the 2, 4- isomer in the product is indicated by the number following the TDI symbol. Compound named TDI-80 has 80% of 2,4-TDI and 20% of 2,6-TDI. Compared to TDI, MDI is less volatile. Hence toxicity of MDI is less compared to TDI when one is exposed to them. There are different types of MDI available in the market. These are namely 4, 4-, 2, 4-, 2, 2- and polymeric MDI which is given in Figure 1.2.¹

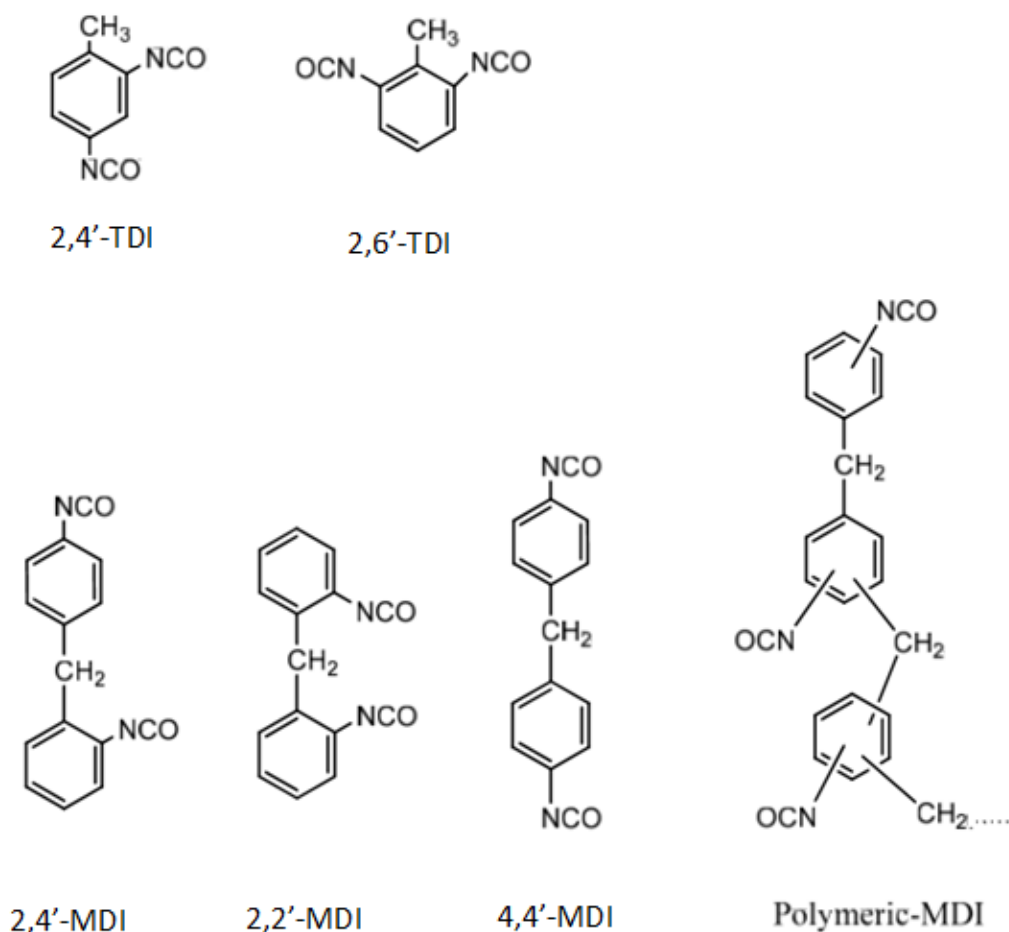


Figure 1.2: Structures of TDI and MDI¹

The aromatic diisocyanates lead to polyurethanes that turn yellow on exposure to light, and recent developments have been directed to intermediates in which the NCO groups are aliphatic or not attached directly to an aromatic nucleus. Hexa methylene diisocyanate (HDI) is, of course, an obvious isocyanate to consider in this respect, particularly with the finding that its activity can be promoted by use of catalysts.⁸

Compounds with active hydrogen react with isocyanates giving respective products along with carbon dioxide gas. Water, urethanes, urea and carboxylic acid are some of the active hydrogen containing compounds.

The reactivity of isocyanate group towards hydrogen active compounds can be explained using resonance structures of the isocyanate which is shown in Figure 1.3

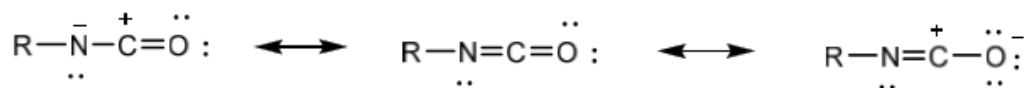
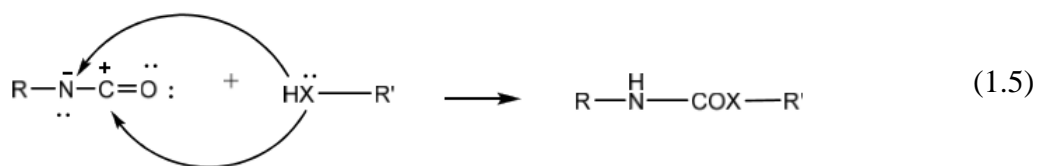


Figure 1.3: Resonance structures of isocyanate¹

As shown in equation 1.5 the reaction of isocyanates with hydrogen active compounds (HXR) is an addition reaction at the carbon-nitrogen double bond. Nucleophilic center of the active hydrogen compound attacks on electrophilic carbon of the isocyanate group. Then hydrogen atom bonds to the nitrogen atom of the -NCO group by taking electrons from it. There are certain factors which affects the reactivity of the -NCO groups. Type of R group attached to the -NCO group determines the reactivity of it. When it is an Electron withdrawing group the reactivity increases, when an electron donating group is attached it decreases the reactivity against hydrogen active compounds. When compared to aliphatic isocyanates, aromatic isocyanates are more reactive. This is due to the electron withdrawal nature of the aromatic ring. Steric hindrance at -NCO or HXR' groups reduce the reactivity.



Generally, catalysts are two types as gel catalysts and blow catalysts.¹ Amine based catalysts promote each reaction. Gel catalysts promote gel reaction between Polyol and Isocyanate while blow catalysts promote blow reaction which occurs between

isocyanate and water. Surfactants are non-ionic silicone based and they perform main functions such as cell regulation and cell stabilization. Water is used to promote blow reaction which produces CO₂ which act as a blowing agent to give foam properties to the polyurethane polymer. Polymer could be blown by carbon dioxide which produced from the water-isocyanate reaction. There are two types blowing agents as chemical blowing agents and physical blowing agents. Chemical blowing agents produce carbon dioxide by reacting with isocyanate. Water is the typical chemical blowing agent. Physical blowing agents are being added to the polyol blend to lower the foam density. Some of the physical blowing agents include low boiling solvents such as pentane and hexane. Some other physical blowing agents include CFC (Chloro Fluoro Carbon), HCFC (Hydro Chloro Fluoro Carbon), Methylene chloride, acetone and liquid carbon dioxide.

Another major component in polyurethane formulation are Cross-linking agents and chain extenders. These are molecules with low molecular weight which contains hydroxyl and/or amine groups. Absence of chain extender in polyurethane foam formation results low physical properties. Chain extenders in the polyol formulation increase the hard segment length of the polyurethane foam.

There are two classes of chain extenders used in polyurethane as aromatic diols and diamines and the corresponding aliphatic diols and diamines. Aliphatic diols produce softer polyurethane material compared to aromatic chain diols. Compared to diol chain extenders, diamine chain extenders are more reactive.

Examples of diol chain extenders (Table 1.1) include 1,6-hexanediol (HG), ethylene glycol (EG), 1,4-butanediol (BDO, BD or BG), diethylene glycol (DEG), diacetylene diols such as: 2,4-hexadiyne 1,6-diol or 5,7-dodecadiyne-1,12-diol and some aromatic diols: triazine diols or 4,4'-(ethane-1,2-diyl) bis(benzenethiohexanol).⁶

Table 1.1: Examples of diol chain extenders⁶

(EG) (ethylene glycol)	$\text{HO}-(\text{CH}_2)_2-\text{OH}$
(BG or BDO) (butylene glycol)	$\text{HO}-(\text{CH}_2)_4-\text{OH}$
(DEG) (diethylene glycol)	$\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}$

Examples of diamine chain extenders (Figure 1.4) include 2,5-bis-(4-aminophenylene-1,3,4-oxadiazole) (DAPO), 4,4'-diamino-dibenzyl(DAB), 2,6-diaminopyridine(DAPy) or 4,4'-methylene-dianiline(MDA).

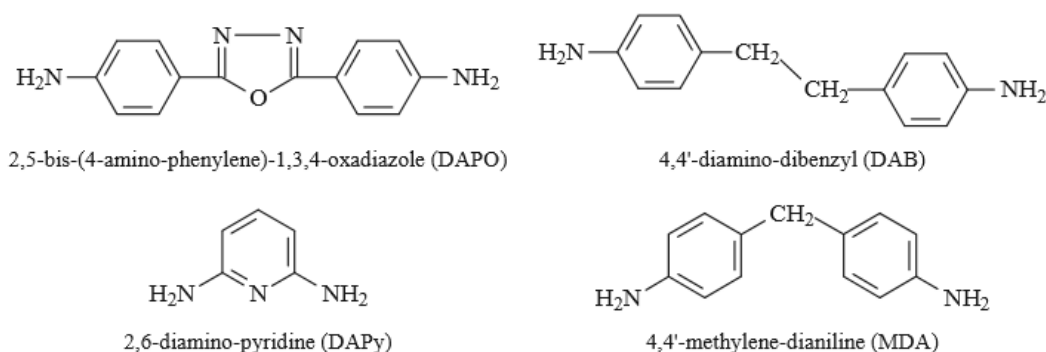


Figure 1.4: Examples of diamine chain extenders⁶

DEOA (Diethanol Amine) is another commercially used cross linking agent. Phase separation behavior of the foam is being interfered with additional covalent linkage resulting from the cross-linking agent.¹ Hence cross-linking agents reduce the stiffness of the foam. All these constituents should be formulated in a specific manner to produce stable foam. Perfect balance of the raw materials is an essential requirement to achieve this task.

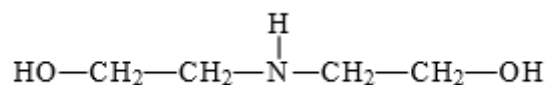


Figure 1.5: Structure of Diethanolamine (DEOA)

When a diamine chain extender is being used, stronger interchain interactions produce at the urea linkage. This results polyurethane with better physical properties. Aliphatic glycol containing aromatic structure leads to the formation of materials with higher modulus and hardness.

Flexible polyurethane foams are made with non-ionic, silicone-based surfactants. Different grades of silicone surfactants are available to the manufacturer to meet specific needs. Silicone surfactants carry out few main functions. They reduce of surface tension for improved chemical affinity with polyol, Silicone surfactants provide control of cell size through the promotion of homogenous fine cells. This phenomenon is known as 'emulsification'. Silicone provide bubble breakage at full rise. If this action does not occur, the foam is bound to shrink during cure. In this case, the resulting foam is said to be 'dead' or 'closed'. Of all these factors, the most important function is stabilization of the cell walls.

Other than above constituents, there are certain other additives which are used in polyol formulation depending on special requirements. Additives are materials introduced into a foam formulation system to achieve specific or desired properties for end uses. They do not interfere with the basic foaming chemistry. Some of the most common additives are pigments, fillers, flame retardants, antioxidants, cell openers, plasticizers, anti-bacterial agents, anti-static agents, UV stabilizers, colorants, foam hardeners.⁹

Foams made from general foam formulation systems are colourless or 'white'. Pigments are added to foam systems for easy identification of products. Yellow is the preferred colour for hiding UV action on foam, and coloured foam also helps the aesthetics of the product.

Fillers are usually finely divided inert inorganic compounds and are added to foam formulations to increase density, load-bearing and sound absorption, and results in cost reduction for the foam. The use of fillers may affect certain physical properties of foams.

Foam scorching is one of the major problems of flexible urethane foam. The causes of scorching include high water level, high isocyanate index, low-acidity isocyanates, Flame retardants are often added to reduce this flammability, as measured by small-scale laboratory tests. The choice of flame retardant for any specific foam is often dependent upon the intended service application of that foam and the attendant flammability testing results governing that application.

Polymer degradation prevents by anti oxidents. These are two types of anti oxidents as primary and secondary antioxidants. BHT (2,6 Di-tert-butyl-4-methylphenol) is a radical scavenger type of antioxidant which is recognized to be an excellent antioxidant.

Some flexible foams are used in packaging, clothing and other applications where it is desired to reduce the electrical resistance of the foam so that buildup of static electrical charges is minimized. This has traditionally been accomplished through the addition of ionisable metal salts, carboxylic salts and phosphate esters. These anti-static agents function by being inherently conductive or by absorbing moisture from the air. The desired net result is achieved by the surface resistivity of the foam.

In some PUR foams it is necessary to add cell-openers to prevent cells from shrinking upon cooling. Additives used for inducing cell opening are silicone-based additives, waxes, finely divided solids, paraffin oils, long-chain fatty acids and certain polyether polyols made using a high concentration of ethylene oxide.⁹

All PUR based on aromatic isocyanates turn dark shades of yellow upon aging with prolonged exposure to light. This yellowing is a surface phenomenon that is not a problem for most foam applications. Light-protection agents such as zinc dibutyl thiocarbamate, hindered amines, and phosphites can be used to improve the light stability of PUR or colouring the foam yellow is also effective.⁹

Hardeners are highly viscous polyol-based additives designed specifically to produce high load-bearing flexible foams. They are polyether or polyester polyols with high functionality crosslinkers and copolymers to improve foam hardness and reduce the production cost while maintaining good physical properties.

Once the isocyanate and polyol blend are mixed there is typically an increase in volume and the formation of individual cells is related to the nuclei present in the mixture.³ The stages in the foaming process are described by many characteristic

times, such as cream time, gel time, rise time and the curing time. Cream time is the time at which the clear mixture turns creamy and starts to expand (point a in Figure 1.6). The viscosity of the foaming liquid increases with reaction time due to the cross-linking reactions. Gel time is the time which the expanding foam start to pull away when it is touched with spatula. Gel time is shown in point b in figure 1.6. Rise time is the time which foam reaches of complete expansion of the foaming.³ When the chemical reaction inside is completed foam reaches its final curing Now foam surface does not show any stickiness when touched with a spatula. (point d in Figure 1.6).

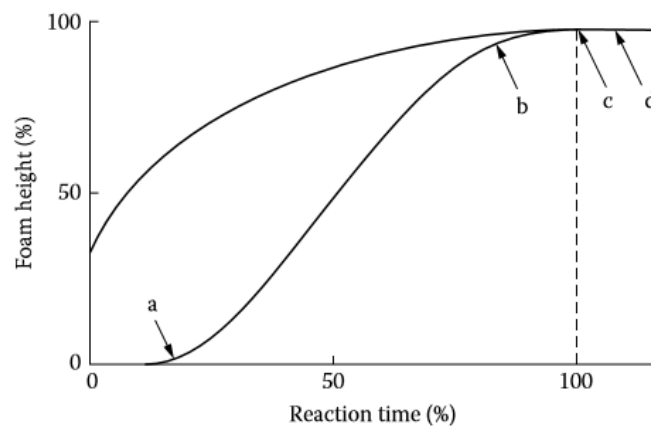


Figure 1.6: Stages of foaming process³

There are some basic requirements which should be monitored throughout the foam formation process to obtain quality product. These includes temperature conditioning, accurate metering or weighing, freedom from contaminants, effective mixing, curing environment.²

Moulded foam formation is a complicated chemical process which involves several reactions occurring simultaneously. During this process, volume and temperature increases rapidly. Also, there is concurrent development of phase separated polymer networks takes place. Generally, catalyst and surfactant chemistries affect the foam properties. Several techniques are used to identify key performance benefits and issues. Cell openness is determined by the force to crush (FTC) detection device.

Mass-loss/rate-of-rise is run to understand rate of rise and height measurements, weight loss from carbon dioxide generation and temperature profiles.⁵

There are two types of flexible urethane foams according to the polyol type used in polyurethane foam formation as polyether foams and polyester foams. Classification based on the process used being slab stock foams and molded foams. Slabstock foams include conventional polyether foam, high-resilience (HR) foam, viscoelastic foam, super-soft foam, energy-absorbing (EA) foam, semiflexible foam, and flexible polyester foam. Molded foams are classified in two classes: hot molded foam and cold molded foam.¹

During the process of Slabstock foam formation, continuous pouring of liquid foaming mixture is being added on to the moving conveyor belt which results continuous loaf of foam. Then segments are cut from this which is called a bun foam. Both polyether and polyester foams are made using this process.

Products with complicated designs and shapes such as automotive parts, head restraints, vibration damping for automobiles, arm rests and furniture cushions are produced by molded flexible urethane foams by the process of RIM (Reaction Injection Molding).

Viscoelastic (VE) foams generally called memory foams has a characteristic property which is slow recovery after compression. The resilience of this type of foam is very low. The situations where deformation occurs viscoelastic foams are applied. As an example, these are used in car seats, where deformation occurs to a large extent by heavy parts of the body such as hips, but is deformed to a small extent by light body parts such as backs. For the preparation of viscoelastic foams polyol blend with of high- and low-molecular weight are reacted with either TDI or polymeric MDI at low isocyanate index. Generally, TDI-based VE foams are characterized by softness, low resilience and slow recovery whereas MDI-based foams are characterized by their low tensile strength, high resiliency, high compression set, easy processing and at a wider range of isocyanate indexes.

Super soft foams are made by using High-molecular weight polyether triols.

Foams with open cell skeleton without having cell membranes are known as Reticulated foams. By dissolving membranes with an alkaline solution, these cell membranes can be removed. There are several other cell membrane removal methods which includes compressed air treatment and explosion of hydrogen gas. Reticulated foams applied in various filters, mats, and pads.

Integral skin foams can be differentiating by characteristic high-density skin. These are also called self-skin foams. These foams have sandwich structure which consist of skin and low-density core foam. Open mold process or reaction injection (RIM) process are used to prepare integral skin foams.¹ These are widely used in automotive interiors, furniture components, household leisure goods and health care products, such as wheelchairs.

Open cast molding involves pouring liquid polyurethane into a mold, or a setting. During setting this mold is immediately closed to allowed to foam expansion and curing. This is a low-cost option that results in an extremely durable product, but it is not suitable for any designs that require any fine details.

Foaming system composed of two reactive components is injected into a closed mold through a high-pressure impinging mixer during closed mold process (RIM Process). Thin and large automotive parts such as bumper covers, air spoilers, deck lids, fenders, and steering wheel covers can be produced using this process.

RIM foam consists of high-density skin and low-density core foam. An advantage of integral skin foam is that the structure gives more stiffness to molded foams. Another advantage of the RIM molding process is lower molding pressure than thermoplastic resins, for example, polypropylene and polystyrene. This advantage allows the use of a simple, light-weight mold and small-sized equipment; Hence the investment costs are lower than for thermoplastic resins. Another advantage is that light-weight, large and thin molded products are obtained under relatively lower molding pressure than that of thermoplastic polymers.

1.2 Objectives

The objectives of this research work have been to;

- Evaluate the suitability of 1,4-dimethylpiperazine as gelling and blowing catalyst substitute.

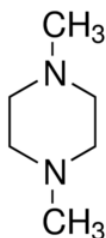


Figure 1.7: Structure of 1,4-dimethylpiperazine

The evaluation of the capability is done through the process of testing the new catalyst along with the normal foam formation process.

- Compare the reactivity of 1,4- dimethylpiperazine against commercially available catalyst triethylene diamine. The reactivity analysis is done through kinetic study of both compounds.
- Evaluate the physical properties such as foam density, hardness, compression set value, air permeability and tensile properties of the polyurethane foam obtained in the presence of 1,4-dimethylpiperazine against the standard foam which is produced using triethylene diamine as a catalyst.
- Determine the behavior of the 1,4-dimethylpiperazine in polyurethane foam formation and understand the limitations of each catalyst and identify suitable applications based on reaction profile and processing conditions.

CHAPTER 2 LITERATURE REVIEW

2.1 Catalysts

There are different types of catalysts used in polyurethane industry to fulfill different purposes. These include gelling catalysts, blowing catalysts, cyclotrimerization catalysts, oxazolidone catalysts, and carbodiimide catalysts.³ Only the gelling catalysts and blowing catalysts are considered during this study. Generally during the manufacture of polyurethane foam at least one type of catalyst being occupied. Out of all amines and organometallics are widely used in flexible foam industry. Optimum balance between the chain propagation (isocyanate with hydroxyl) reaction and the blowing reaction (isocyanate with water) is established by using various combinations of catalysts. Polymer formation rate and gas formation rate needs to be balanced to produce stable polyurethane polymer. This helps to entrap evolving gas efficiently in the growing polymer and to develop cell walls with sufficient strength which leads to maintain their structure without collapse or shrinkage. When the gel reaction takes place too slowly, the growing polymer will not have sufficient viscosity maintain the cellular structure when the cells open. This will result collapse of the foam. In contrast, fast gel reaction may lead to increase of the viscosity in the growing polymer too fast and slow down the bubble expansion. If the gelation reaction proceeds too quickly, the viscosity will rise too fast. This will prevent the cells from opening at all. Catalysts also perform the action on curing of the foam.⁴

The gas generated by the blow reaction may expand the polymer before the polymer is strong enough to contain it when the blow reaction takes place faster. Hence the resulting polymer will consist of internal splits and foam collapse. In contrast, when the gelling occurs faster than the gas-producing reaction, the cells of the growing polymer will remain closed. This will cause the foam to shrink as it cools. Uniform open cells will dominate the foam structure when these two reactions are balanced properly. This balance between both reactions needs to be developed by understanding the behavior of the additives in the formulation.

Amines and tin compounds catalyze different reactions within the foaming reactions. These two could be mixed to obtain a better foam. They do not behave completely independently. Both reactions in the foaming process are influenced by each catalyst. Appropriate balance between the two foaming reactions can be greatly influenced by the composition and selection of specific catalysts.⁹

When consider industrial productivity catalyst play a major role. The reactions between isocyanate group and alcohols, water and itself takes place very slowly in the absence of catalyst. Obtaining an appropriate profile among the several reactions that can occur during PU production processes is fulfilled by the choice of catalyst. All types of polyurethanes namely cellular polyurethanes (flexible, semi-rigid and rigid foams, microcellular elastomers) and solid polyurethanes (elastomers, coatings, sealants, adhesives, etc) are made by use of catalysts. Different catalyst types are used for the reaction of isocyanate with water and polyols. These catalysts are categorize into two as tertiary amines (aliphatic or aromatic) and organometallic compounds. Generally tertiary amines catalyse both gel reaction and the blow reaction whereas organometallic compounds catalyse only the gel reaction.

2.2 Tertiary amine catalysts

The most commonly used flexible polyurethane foam catalysts are tertiary amines. Most amines have similar contributions to gelling reaction as well as blowing reaction. Presence of a free electron pair on the nitrogen atom causes the catalytic activity of amines. This lone pair of electrons on the nitrogen atom provides a strong nucleophile which can attack the carbon of the isocyanate group.⁴ (Figure 2.1)

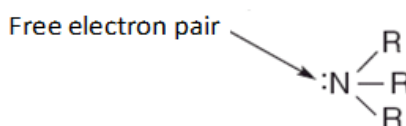


Figure 2.1: Reactive lone pair on the tertiary amine

Factors affecting reactivity of tertiary amine could be vary with the chemical structure of the amine. When the basicity increases reactivity increases while the steric hindrance which is the presence of bulk groups around the reactive center of the amino nitrogen reduces the reactivity of it⁸

Lone pair of the electrons from the tertiary nitrogen atom is donated to the isocyanate group during the catalysis mechanism leading to the formation of an intermediate complex. (Figure 2.2)

With aromatic isocyanates the carbonyl and aromatic groups both have moderate electron-withdrawing effects.⁴ With the formation of an amine complex, the nitrogen atom of the isocyanate group is activated and readily reacts with hydrogen atoms from any water or polyol sources in the vicinity.⁴

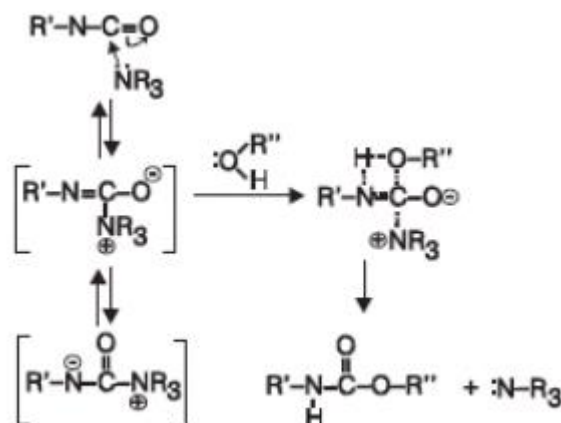


Figure 2.2: Catalytic mechanism Formation of Isocyanate-Amine Complex⁴

Availability of the electrons is a function of two scenarios as the steric hindrance caused by the substituent groups, as well as the electron withdrawing or electron releasing nature of the substituent groups. Groups which tend to withdraw electrons reduce the catalytic activity by reducing the accessibility of the electrons.⁴ In some foam systems, more than one amine is utilized to obtain optimum balance between the gelation and blow reactions.

Process requirements such as cream time, rise profiles, gel time and even cure of the outer surface skin are being affected by the type and concentration of amines catalysts

being utilized in the polyol formulation. Properties such as airflow and Tensile strength is influenced by the type of amine used.

Good catalyst should have certain characteristic features such as nucleophilic enough to attack the carbon of the isocyanate group, ability to form an active hydrogen amine complex and solubility in water with the ability to form hydrogen bonds with water.⁴

When the basicity increases, the catalytic activity is found to increase. Hence catalytic activity increases with pH. Triethylenediamine (Figure 2.3) is an exception to this behavior. This higher reactivity is due to the availability of lone pair of electrons on the active nitrogen atoms. The substituent groups on the nitrogen are pulled back, which reduces the steric strain. Hence electron pair on the nitrogen atom easily accessible which leads to have high reactivity towards the isocyanate reaction.

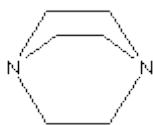


Figure 2.3: Structure of Triethylene diamine

The critical factor of these catalysts is that their applications are determined by the desired performance in a specific manufacturing processes. For example, during molded foam production, highest rates of polymerization and easy curing has been achieved by using higher levels of both kinds of catalysts. The other factors which needs to be considered are the reactivity of the polyols being used and the solubility of the catalysts in water. The exact amount of catalyst needs to be added to the polyurethane system is determined by after doing the production scale pilot run.

Other than electronic effects, there are other physical and chemical properties which determines the catalytic activity of amine. These include boiling point, volatility, reactivity of the amine with polymer. Dimethylaminoethanol which contain hydroxyl groups will chemically react with the growing polymer chain. Hence the molecules are

unable to find their way to a reaction site. This leads to lose the catalytic activity. These issues could be eliminated by using mixture of catalysts with different functionalities.

Chemical structures of several tertiary amines are listed in figures 2.4, 2.5 and 2.6.

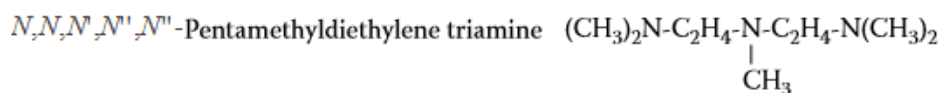
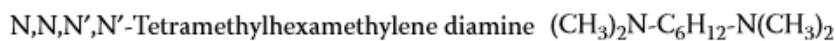
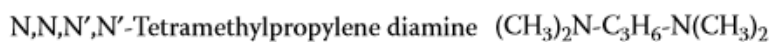
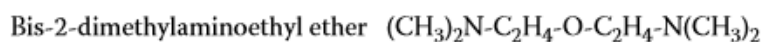


Figure 2.4: Molecular formula of aliphatic tertiary amines³

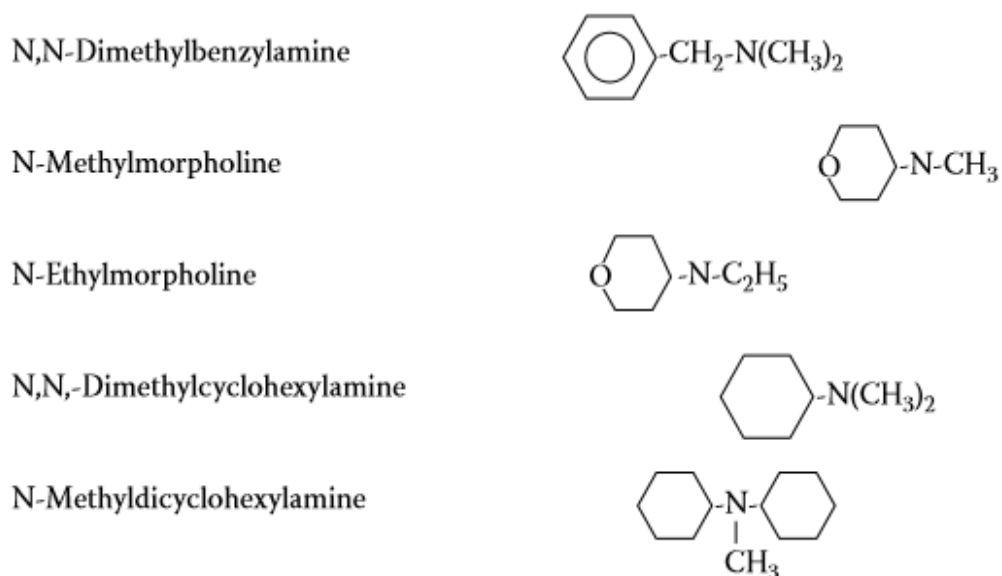
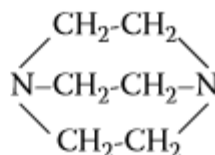
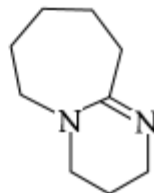


Figure 2.5: Molecular formula of aromatic tertiary amines³

Triethylenediamine
(1,4-diazabicyclo-2,2,2,octane),
(DABCO™)



1,8-Diazabicyclo,5,4,0,undecene-7



2-Methyl-2 azanorbornane,

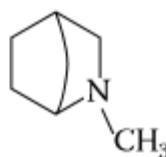


Figure 2.6: Molecular formula of heterocyclic tertiary amines⁴

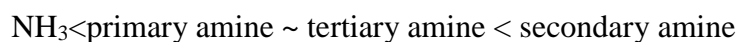
Amines are considered as alkyl or aryl derivative of ammonia (NH₃). These are categorized depending on the number of alkyl or aryl groups substituted for the hydrogen. Amines are bases due to the presence of lone pair of electrons on the nitrogen atom of amines. Hydroxyl ions are formed by reacting these with water. Bases are those species that donate OH⁻ ions (hydroxyl ions). The basicity of amines increases by the increase of the availability of the hydroxyl ions.¹¹

Both alkyl amines and ammonia contain nitrogen atom which has a lone pair of electrons. Alkyl amine become more basic in the presence of alkyl groups. This is due to the electron releasing property of alkyl groups.

The electron density around the nitrogen atom increases due to the alkyl groups attached to the nitrogen of the amine which will increase the electron releasing ability., the molecule becomes more basic than ammonia due to the greater and easier release of electrons in the alkyl amine. When the basicity of the aliphatic amines is compared

it is expected to have higher basicity of tertiary amines and then followed by secondary amine and then primary amine.

But this is not so. The order of basicity is



This “unexpected” order of basicity is due to following reasons:

Steric hindrance is one of the major reasons. The size of an alkyl group is larger than a hydrogen atom. Hence an alkyl group would hinder the attack of a hydrogen atom, thus decreasing the basicity of the molecule. Hence the basicity decreases with the number of alkyl groups attached.¹¹

Hence the decreasing order of basicity will be:

Primary amine > secondary amine > tertiary amine

The same steric effect applies when the basicity of triethylenediamine is compared with that of 1,4-Dimethylpiperazine. Lone pair on the nitrogen atom of triethylenediamine is more available to reaction via electrophilic addition or substitution while lone pair of nitrogen atom on 1,4-Dimethylpiperazine is less available due to steric hindrance caused by the methyl groups.

2.3 Organometallic catalysts

Literature shows many tin catalysts. Some representative tin-catalysts are shown in Figure 2. 7 These compounds act as Lewis acids and they are generally associated with the basic sites of the isocyanate and polyol groups.¹ According to one hypothesis, the Lewis acidic nature of the carbon in the isocyanate group is enhanced by this interaction which makes it more reactive towards the oxygen of the polyol hydroxyl functionality.

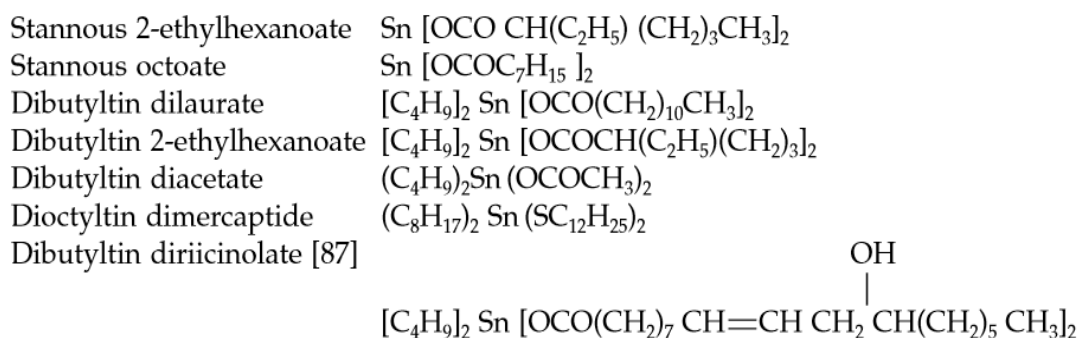


Figure 2.7 Tin catalysts³

2.4 Delayed action catalysts

Delayed action catalysts are three types as blocked amines, thermo-activated amines, and thermo-sensitive amines. when the amines partially or totally neutralized with carboxylic acids they are called blocked catalysts.³ Isocyanate groups react with These acids and the resulting primary amines. Better in-mold flowability and faster cure times has been achieved by using these catalysts. The concept of delay action is to use additives at low activity at room temperature but when the foaming reactions heat up the system they become activated¹. The most frequently utilized catalysts of this type are tertiary amine salts in a solvent such as low molecular weight glycol or water. These catalysts are added in combination with organic acids

such as carbonic, formic, and acetic acids. There are certain disadvantages in these catalysts. One is they produce phase incompatibility and metal corrosion problems when used in combination with standard tertiary amine catalysts.¹

Flowability of the foaming liquid is very important to achieve completely filling of the mold, especially with large and complicated profiles. Delayed action catalysts have been developed to achieve short demolding times and to avoid fingerprinting when the molded piece is taken out of the mold. Delayed action blow catalysts should be employed when starting reactivity is too high, on the other hand, viscosity build-up of the foaming mixture is delayed by the delayed action gelation catalysts. This leads to flow the polyurethane mixture which is in the liquid state easily in the mold cavity. Delayed action catalysts are manufactured by reacting a specified tertiary amine with

a carboxylic acid. The resulting compound is composed of a salt and an excess of the starting amine. The salt has limited or no catalytic activity. Free amine launches the reaction. The salt dissociates to yield back the amine and the acid when the reactions have progressed with heat generation. Now the catalyst is de-blocked and has recovered the original activity. The released organic acid reacts with isocyanate - forming carbon dioxide and carbon monoxide, supplying an auxiliary source of blowing agent, resulting in less dense with more open cell foams. Normally, carboxylic acids such as formic and 2-ethylhexanoic acids are used as blocking agents. The unblocking temperature depends on the acid used. Strong acids require higher temperature than weak acids.¹⁰

CHAPTER 3 EXPERIMENTAL

3.1 Materials

Polyols used in Polyol system are composed of Arcol Polyol 1375 and Hyperlite E-850 provided by chemical company COVESTRO. Arcol Polyol 1375 is a tri functional polyether polyol with a hydroxyl value 23 ± 3 mg KOH/g. Hyperlite E-850 is a polymer polyol, which is used in a broad range of urethane foam and other applications. This has a hydroxyl value of 18.2-22.2 mg KOH/g and molecular weight 88600 daltons. Testing catalyst used is 1,4-DMP. (1,4- Dimethylpiperazine) from Sigma Aldrich. Control catalyst is Tegoamine 33 (Triethylenediamine) provided by chemical company Evonik. Apart from them crosslinker Tegoamine DEOA (Diethanoylamine) and surfactant Tegostab B 4690 is added to the polyol blend. Isocyanate utilized is Desmodur CDC from COVESTRO and it has 4, 4'- MDI > 25 %, NCO content 29.5%.

3.2 Methods

Preliminary trials were carried out by varying test catalyst (1,4-DMP) and control catalyst (Tegoamine 33) level from 0.5 to 7 pphp according to the Table 3.1 Conventional flexible molded foams were made using 100 g of polyol and the other constituents as per the formulation given table 3.1. For each experiment water, catalysts and silicone surfactants were added to the polyol and mixed together by stirring at 2000 rpm for 30 s. The resultant liquid mixture was conditioned at 25 °C for 5 min. Then the isocyanate was added and the mixture was stirred at 2000 rpm for 5 seconds. The resultant liquid material was then poured into the ATC unit of the FOAMAT instrument and the program was run to obtain the kinetic data.

Table 3.1: General foam formulation

Chemicals	Parts per hundred parts of polyol (pphp)
Arcol Polyol 1375	80
Hyperlite E-850	20
1,4 DMP (test) or Tegoamine 33 (control)	Variable
TegostabB 4690	2
Tegoamine DEOA	1.5
Water	3.5
Desmodur CDC ratio (amount of iso to 100g of polyol)	35

3.3 Preparation of samples

Polyol mix was prepared by adding catalysts, surfactants, cross-linkers, distilled water to the polyol mix. This was mixed thoroughly for 30 seconds and finally measured amount of MDI was added, this was rapidly mixed for 5 seconds and then material was transferred into the prepared mould box. When the foam is fully cured, this was cut and used for further analysis.

3.3.1 Sample Machining

The foam block was produced using a box mold with dimensions of 17 cm × 17cm × 5cm. (Figure 3.1) The resultant solidified foam (Figure 3.2) was used to produce standard test samples for each test to investigate the physical properties of the foam.

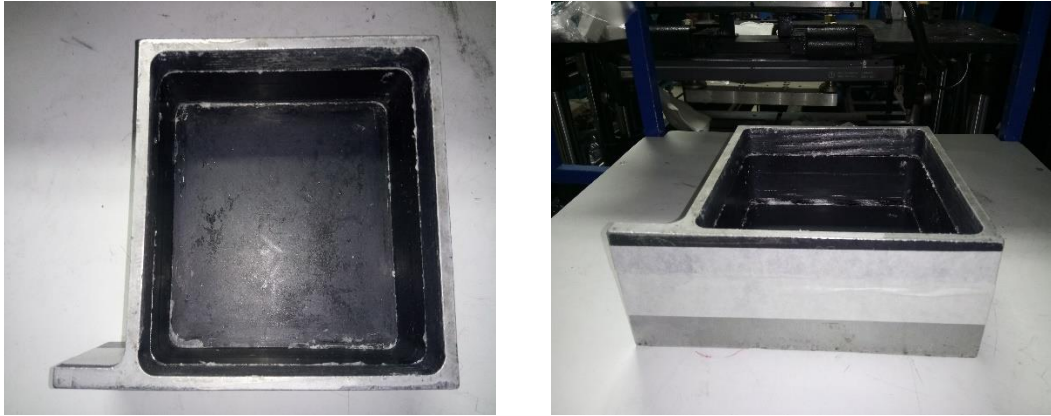


Figure 3.1 Standard box mold with dimensions (17 cm × 17cm × 5cm)



Figure 3.2: Polyurethane foam produced in the Standard box mold

3.3.2 Investigation of various properties

Three test samples were used to measure each property and the average value was calculated and recorded. Each of the test was carried out as outlined in the ASTM-D3574.

3.3.2.1 Density

The density measurement is an apparent or bulk density, not the true polymer density. This physical property is important because of its parallel relationship with cost and loadbearing. In general, high densities result in higher costs and improved loadbearing properties.⁹ Flat surface cubes with dimensions (5cm × 5cm × 2.5 cm) were cut out

from each of the samples of foam produced. (Figure 3.2). By measuring weight and the volume of these pieces density was calculated.



Figure 3.3: Foam piece for density measurement

3.3.2.2 Hardness

Foam hardness was measured using the durometer Asker F (Figure 3.4). Accurate readings are given by durometer Type F (Asker F) for much softer specimens (low hardness) as it features a larger indenter and pressure foot. The durometer is used exclusively for various foam materials such as urethane foam, sponge, etc. Durometer is just needed to place onto the specimen, it should not be pressed to get a reading. As it is soft, the weight of the durometer constitutes the pressure to the specimen.⁷



Figure 3.4: Durometer Asker F⁷

As the minimum thickness to obtain a reliable hardness measurement is 25mm, the thickness of the foam piece was kept for 25mm (Figure 3.5). Then three hardness measurements were taken and averaged to calculate the final hardness.



Figure 3.5: Flat foam sheet used for hardness measurement



Figure 3.6: Reading hardness measurement of foam

3.3.2.3 Compression set test

The test sample for this test should be with dimensions 50 mm × 50 mm × 25 mm. After measuring the thickness of the sample, it is placed between the horizontal plates of a compression device. The horizontal plates of the compression device have greater surface area than the sample being tested. The compression plates were arranged to hold the samples to be parallel to each other, and the space between them is adjusted to the required deflected height.

The sample is compressed to 75 % of its original thickness while maintaining this known condition for 72 hours. The final thickness is measured and recorded after sample is removed and kept recovering for 30 minutes. The compression set is calculated using following equation. Compression set = $100 (T_0 - T_r)/T_0$

Where : T_0 is the original thickness of sample

T_r is the thickness of sample after recovery



Figure 3.7: Foam compression device

3.3.2.4 FOAMAT (Foam Qualification System)

The foam qualification system **FOAMAT** is an electronic device based on ultrasound and other sensor techniques for measuring the rise profile, the reaction temperature, the rise pressure and the dielectric polarization of foams generated in a test cup or specially designed containers. Rise height (H), dielectric polarization (D), rise pressure (P), and reaction temperature (T) is simultaneously recorded by the software FOAM.

The **FOAMAT** system enables one to characterize foams by their rise profile, temperature increase, pressure generation and dielectric properties. Master curves can be generated from all measurement curves for use in the QC mode of the software **FOAM**. **FOAMAT** is a versatile tool for quality control in the production line of all kinds of foam items. In the development of new foam systems, it provides valuable physical data for new foam formulations meeting one's demands.

During this study FOMAT machine was utilized to get foam kinetic data using the rise profile. The following measurements were taken and recorded: rise time, gel time, foam density and shrinkage of the foam.

The Foam Qualification System FOAMAT comprises the ultrasonic fan sensor PFT on a stand, the Foam Pressure Measurement devices FPM 2 and FPM 150, and the controller unit (Figure 3.7). The reaction temperature is measured with a thermocouple.



Figure 3.8: Basic parts of the FOMAT equipment

3.3.2.5 Air flow

Airflow is a measurement of the openness or porosity of a foam. Airflow values are affected by the orientation of the samples and two values are typically recorded. One airflow measurement is taken to parallel to the foam rise while other airflow measurement is taken to perpendicular to foam rise. In moulded foams, airflow through the surface skin is also critical.⁹

Air permeability of the foam samples are measured according to the ASTM D 736-96 method. The air flow test implies the ability to pass air through a cellular structure of the foam. Cell structure can be explained using the air flow value.

Air flow of the polyurethane part can be taken as the degree of cell openness of polyurethane foam. High air flow values indicate the foam has less tendency to shrink

and hence it is dimensionally stable as compared to a foam with low air flows. Foam with high air flow is much easier to crush-out by breaking many of the cell windows.

During the test flexible foam core specimen is placed in a cavity over a chamber and creates a specified constant air pressure differential. The rate of flow of air required to maintain this pressure differential is the air flow through the foam. Alternative methods are required to measure air flow of molded skin foam or extremely high air flow products. Cell openness is qualitatively evaluated using airflow measurements. Air permeability machine is used to carry out the analysis and readings are given in the units of CFM (Cubic feet squared per minute).

3.3.2.6 Physical properties

Physical properties of polyurethane foam such as tensile strength, breaking strength, elongation percentage is measured using Elongation testing machine (Figure 3.9) which basically measures the strength of the foam material. A die with standard dimensions is used to prepare samples for tensile test (Figure 3.10).

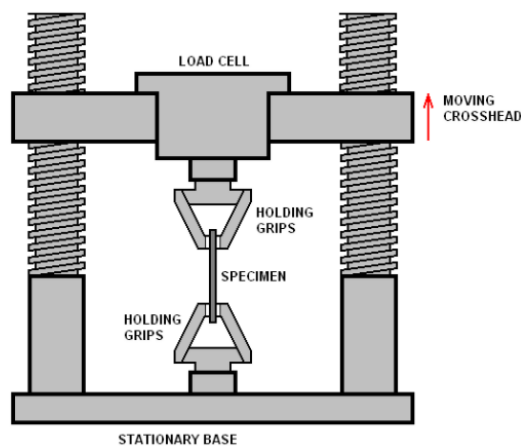


Figure 3.9: Tensile testing machine

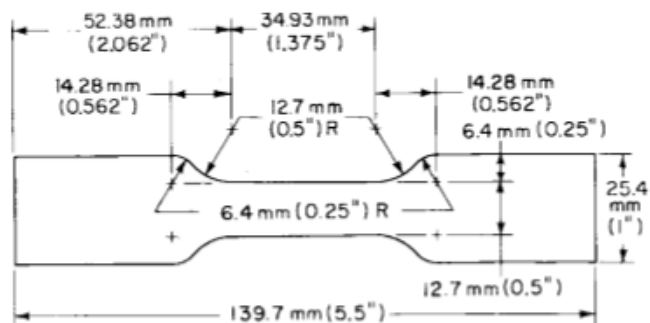


Figure 3.10: Dimensions of the standard die for the tensile test

Figure 3.11 shows the flat polyurethane foam prepared for the test and the test specimen (Figure 3.12) is cut from it for the tensile test.



Figure 3.11 flat foam piece



Figure 3.12 test specimen for Elongation test

Elastic properties of the sample could be obtained using this test. Tensometer was utilized to perform the tensile test. Test piece is pulled at a constant rate until it breaks. This is done on a machine, and the force recorded at the breaking point is the tensile strength of the foam, and is usually expressed in kPa. The fracture load, diameter at the point of fracture and the final gauge length is noted.

3.3.2.7 Cellular structure and solid morphology

Examination and analysis of the microstructural characteristics of solid objects is done by scanning electron microscope (SEM) which has high resolution. Hence SEM is useful when bulk objects are examined.

SEM is used to evaluate and compare the general cellular structure of the molded foams. These comparisons are useful to document any differences in the cellular structure of polyurethane foams which are significantly influences the physical properties of these foams. Differences in cell structure and cell distribution caused by changes in the catalyst and surfactant chemistries could be determined using SEM.⁵ During this study Zeisssoevo Is 15 machines was utilized to obtain the images. During

the analysis thin slices (3 - 4 mm) of foam is adhered to aluminum stubs using silver paint and allowed to dry. Then using a SPI model 13131 sputter coater a thin layer of gold is then applied to the surface of the foam. With the help of stereoscan 100 SEM (ZEISS EVO LS 15) operating at 20 kV and at a magnification from 50x to 500x micrographs are taken.

4 RESULTS AND DISCUSSION

4.1 Variation of Foam density with catalyst level

Variation of Foam density with catalyst level has been displayed in figure 4.1. The foam density has decreased with catalyst level as expected.

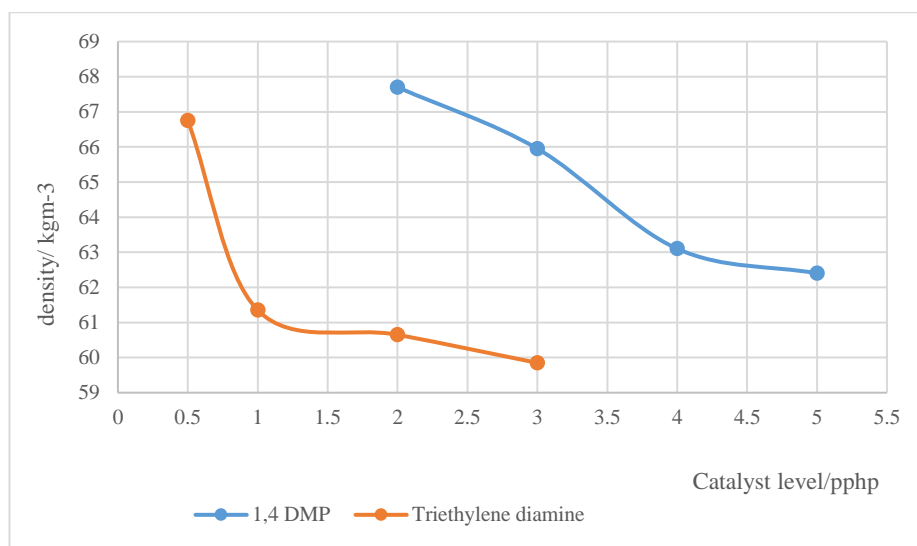


Figure 4.1 Effect of varying catalyst content on foam density of the polyurethane sample

With the increase of catalyst level, the foam density has been reduced due to the increase of the reaction rate. This occurs due to the formation of CO₂ gas from the blowing reaction which results in increase in foam volume compared to the mass of the foam. For the control catalyst (Triethylene diamine) density has been varied from $63 \pm 3 \text{ kgm}^{-3}$ at the range of 0.5 to 3 pphp where as for the test catalyst (1,4- DMP) this has become $65 \pm 3 \text{ kgm}^{-3}$ for the range of 2 to 5 pphp. This shows that to obtain the performance of the control catalyst, test catalyst level must be increased to a certain level as illustrated by figure 4.1. Nearly the reaction window has been shifted towards right side with approximately 4 times high compared to control catalyst. This may be a result of the availability of free lone pair on triethylene diamine unlike on 1,4- DMP.

4.2 Variation of foam Hardness with catalyst level

Foam hardness has decreased with catalyst content. The variation of the foam hardness is different for each catalyst, Triethylene diamine and 1,4-DMP as illustrated in figure 4.2.

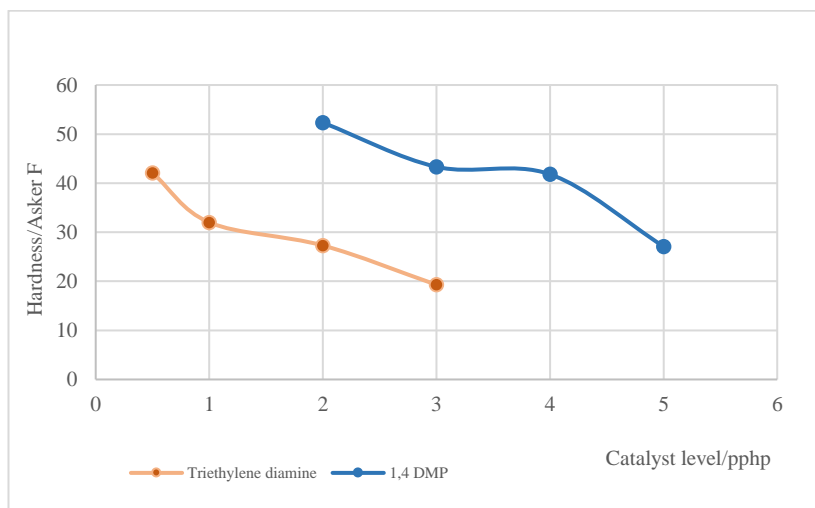


Figure 4.2 Effect of varying catalyst content on foam Hardness of the polyurethane sample

In the presence of 0.5 to 3 pphp of Triethylene diamine, foam hardness has been varied within 30 ± 10 Asker F whereas for 1,4-DMP it has been varied within 40 ± 10 Asker F at the level from 2 to 5 pphp. Hence this shows that to obtain the comparative hardness performance to triethylene diamine, the test catalyst level (1,4-DMP) must be increased up to certain level as shown in the graph. This is approximately 4 times high for 1,4- DMP compared to Triethylene diamine.

4.3 Variation of Compression set test of foam with catalyst level

Variation of compression set with catalyst level has been shown in the figure 4.3. Compression set of the foam is calculated by obtaining the compressed thickness values.

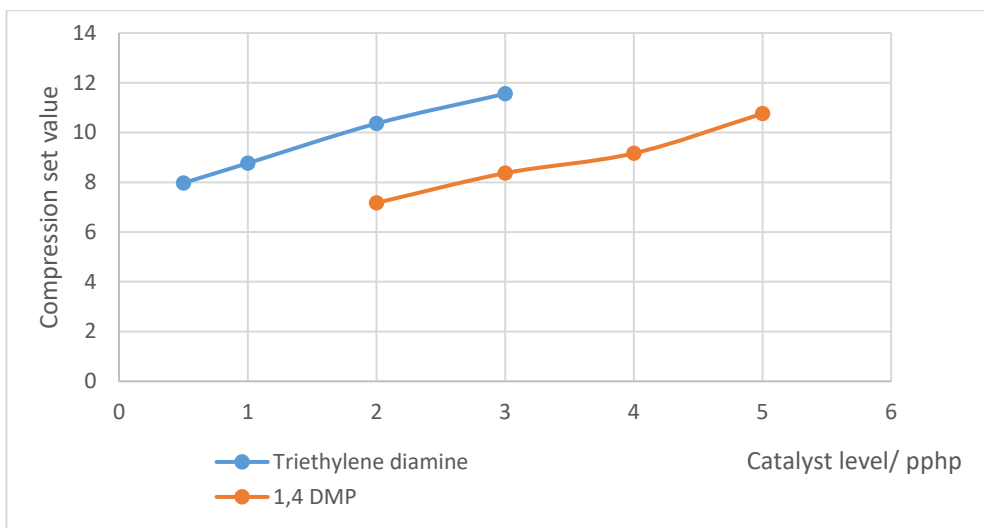


Figure 4.3 Effect of varying catalyst content on Compression set value of the polyurethane sample.

According to the figure 4.3 compression set value of the polyurethane foam sample has been increased with the increasing catalyst level. The polyurethane foam made use of Triethylene diamine and foam made use of 1,4 – DMP had undergone the same compression conditions during the test. The resultant foams were observed for compression set measurements and according to the data obtained, the compression set value has been varied for the range of 10 ± 2 for the sample with Triethylene diamine where it has become 9 ± 2 for the sample with 1,4- DMP which shows approximately same performance at their respective workable catalyst level range.

4.4 Variation of FOMAT data (Kinetic parameters of the foam)

Kinetic data is obtained using rise profile of the fomat curve. Gel time, rise time and curing time has been recorded as the kinetic parameters of the foam. Those are the main three turning points of the rising foam. The variation of the gel time, rise time and the curing time has been illustrated for the Triethylene diamine and the catalyst to be investigated (1,4- DMP) for the range given. At gelling point the liquid mixture starts to convert into solidified state of the final product and to identify this transition, the rising foam should be continuously touched. Then there is a point that start strings come off from the foam, this is the gel point. Even it reached the gel point foam is still

foaming, the point where foam finishes rising is the rising time. The curing time is the time where the foam finishing it is complete reaction and it loses its tackiness at that time.

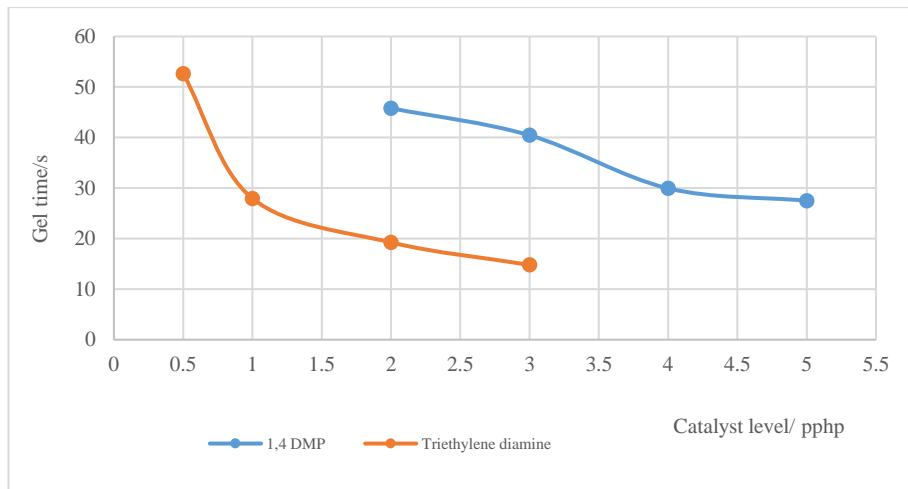


Figure 4.4: Effect of varying catalyst content on gel time of the polyurethane sample

Gel time has been reduced in the presence of each catalyst. Variation of the gel time is 52s to 14 s for Triethylene diamine for the range of 0.5 to 3 pphp while this has been reduced from 45s to 27s for the test catalyst range from 2 to 5 pphp. This shows that the gel time has been significantly affected by control catalyst compared to the test catalyst. Reaction is comparatively slow in the presence of 1,4-DMP and to achieve the same performance as Triethylenediamine, the amount of 1,4-DMP which is needed to be added is high. This is approximately 4 times according to the figure 4.4.

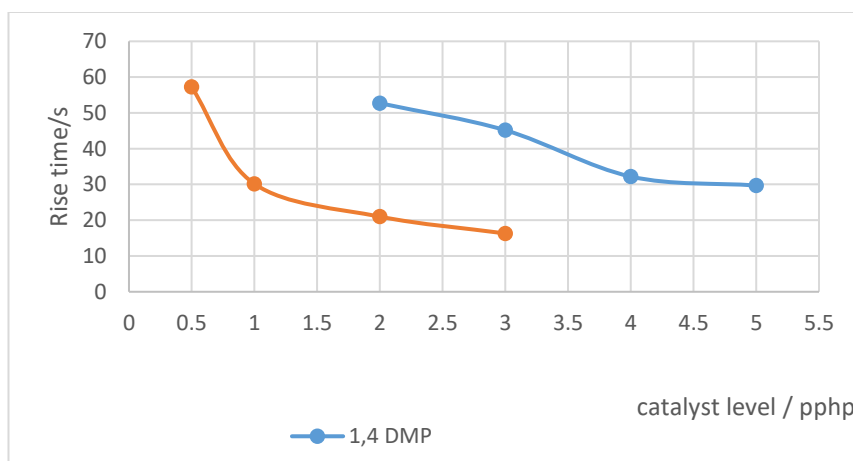


Figure 4.5: Effect of varying catalyst content on Rise time of the polyurethane sample

Rise time also has been reduced in the presence each catalyst. For Triethylene diamine, it has reduced from 58s to 16 s for the range of 0.5 pphp to 3 pphp whereas for 1,4-DMP, rise time has reduced from 52s to 30 s for the range of 2 to 5 pphp. This shows that compared to Triethylene diamine, performance of 1,4-DMP is low and it gives similar performance when the level is increased by approximately 4 according to the figure 4.5.

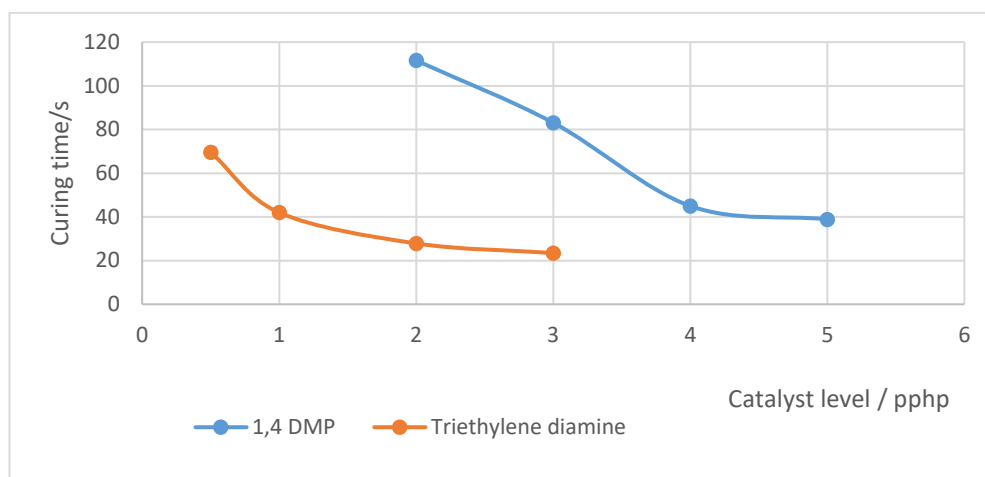


Figure 4.6: Effect of varying catalyst content on curing time of the polyurethane sample

Figure 4.6 shows that the performance of test catalyst has become low compared to the control catalyst. Curing time profile has been shifted to slower direction for 1,4-DMP compared to Triethylene diamine.

Generally, reaction rate increases with the catalyst level. As the catalyst which is available in the polyol system accelerates the reaction in other words it changes the reaction pathway where it lowers the energy barrier of the complete reaction. Hence it results in increase in reaction rate. Therefore all the kinetic data has been reduced with the increase of the catalyst level for control as well as test catalyst. The performance of the 1,4-DMP has been evaluated only for the range of 2 to 5 pphp. When the 1,4-DMP level is reduced to less than 2 pphp, the reaction rate become extremely low where it cannot be monitored using laboratory method followed during the study. When the 1,4-DMP level is increased up to more than 5 pphp, the reaction rate become too fast where it cannot be also monitored as well as those reactions are not suitable

for practical PU molding applications. The relative performance or the reactivity window lies within that test range only. For Triethylene diamine, this relative performance range lies within 0.5 to 3 pphp range. This difference is due to the difference in relative reactivity of the active ingredient present in each which was described earlier as the difference in availability of lone pair on the catalyst.

The variations of gel time, rise time and curing time for forming process with the level of control catalyst and test catalyst are shown in figure 4.7 and 4.8 respectively.

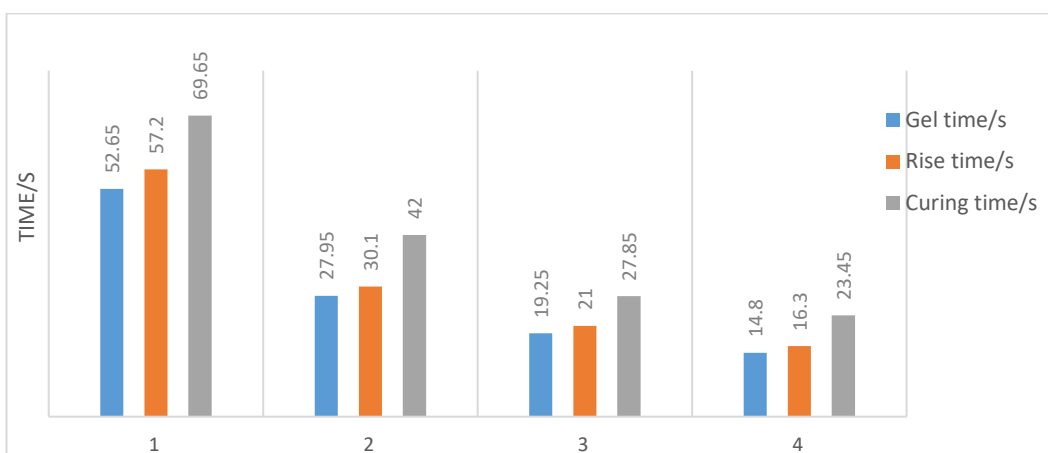


Figure 4.7: Stages of foaming process in the presence of Triethylene diamine (1,2,3,4 illustrates each level of Triethylene diamine present in the medium as 0.5 pphp, 1 pphp, 2 pphp and 3 pphp respectively)

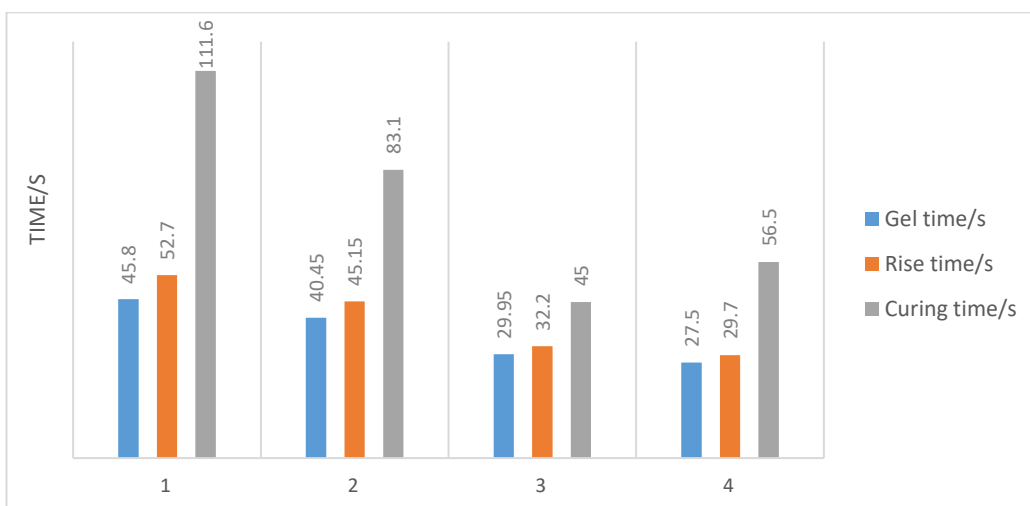


Figure 4.8: Stages of foaming process in the presence of 1,4- DMP (1,2,3,4 illustrates each level of 1,4-DMP present in the medium as 2 pphp, 3 pphp, 4 pphp and 5 pphp respectively)

Stages of the foaming processes are illustrated in above figures for test catalyst (Figure 4.8) and the control catalyst (Figure 4.7). According to them performance of the rising profile at 4 pphp level of 1,4-DMP is comparable with the rising profile of the 1 pphp level of Triethylene diamine which is elaborated in figure 4.9.

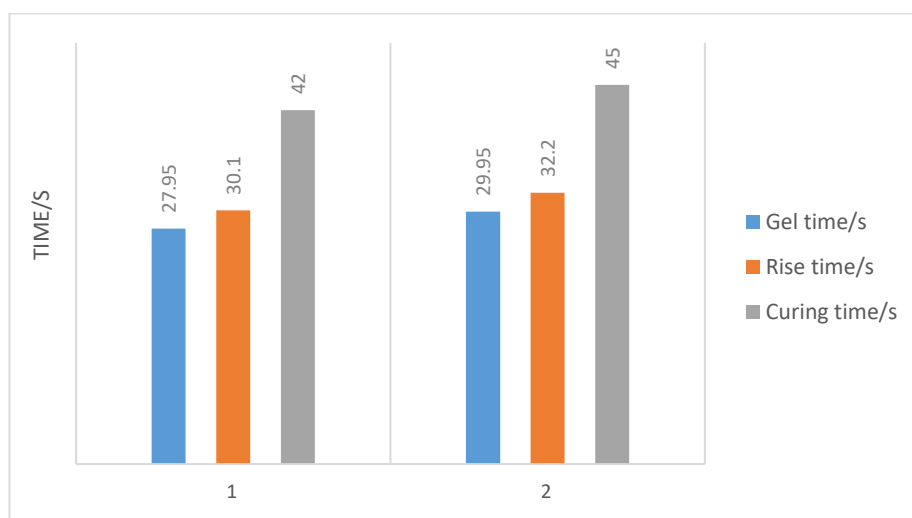


Figure 4.9: Stages of foaming process at comparable catalyst levels (1,2 illustrates 1 pphp of Triethylene diamine and 4 pphp of 1,4-DMP present in the medium respectively)

Hence the above relationship of comparative performance could be proved using the figure 4.9. This could be explained from the help of the chemical structure of each catalyst as follows; as there is no steric hindrance over the reactive nitrogen atoms in Triethylene diamine, it reacts comparatively faster. Due to the presence of a free methyl group on each reactive hydrogen atom in 1,4- dimethylpiperazine its reactivity has retarded in all the aspects. This methyl group reduces the accessibility to the lone pair of nitrogen atoms in 1,4- dimethylpiperazine. This is the most suitable explanation for the shifting reactivity of the 1,4 -DMP to the lower side (approximately 4 times lower compared to triethylene diamine) in all the aspects discussed earlier such as foam density, foam hardness, compression set test, kinetic parameters (gel time, rise time, curing time) as well as the properties like foam

shrinkage, air flow properties and physical properties (Elongation %, Tensile strength, Breaking strength) which will be discussed in section below. Hence the reactivity window of the 1,4-DMP has been shifted to low direction as illustrated by the respective graphs.

The reaction rate is directly proportional to the flowability of the material inside the mold. When the reaction rate is high, its flowability inside the mold is less due to fast curing. If the reaction is slow enough, then it completely flows inside the mold. This has massive impact on larger molds with complicated designs compared to simple molds. In simple molds material flow does not have high impact as the mold is small. If the reaction is too fast and it is not under control, the resulting molded piece processed in complicated mold will be full of quality defects such as foam holes, pin holes, foam breaking, blow off, uneven foam hardness throughout the surface, etc. if the reaction is under control, the flowability inside the mold will be increased which will result molded piece with minor defects. Hence it could be concluded that while having moderate reaction rate 1,4 dimethyl piperazine is a potential catalyst which would be useful as a delayed action catalyst. Figure 4.10 shows some simple mold designs and figure 4.11 shows complicated mold designs.





Figure 4.10: Simple mold designs



Figure 4.11: Complicated mold designs

4.5 Variation of the shrinkage of the foam with catalyst level

The shrinkage of the polyurethane foam bun is measured by deducing the final height from the initial height of the foam bun. Once it is fully cured, the bun reduces its volume into certain level due to gas release and other factors. Hence the shrinkage measurement is just a measure of how much foam is stable once it is cured. This variation of the foam shrinkage with catalyst level has been illustrated in figure 4.12

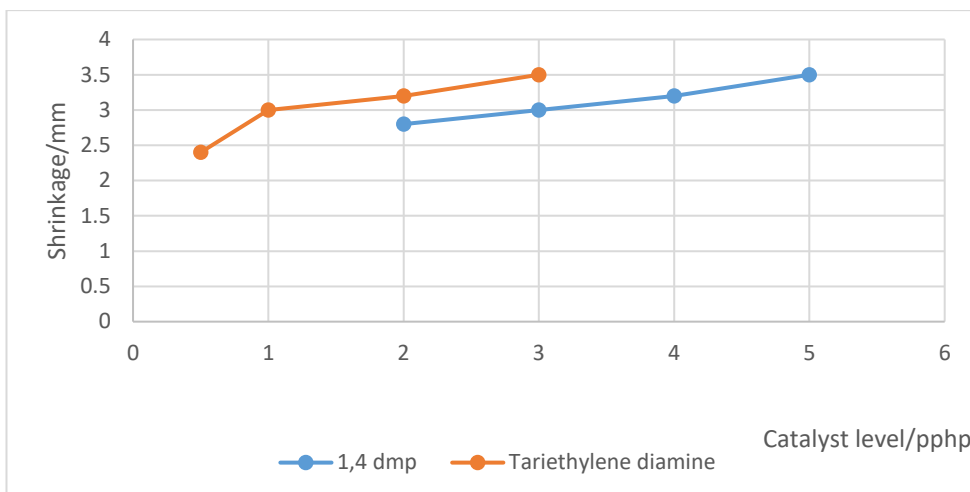


Figure 4.12 Effect of varying catalyst content on Shrinkage of the polyurethane sample

When the catalyst level increases, the blow reaction increases which results release of more carbon dioxide gas. This collects inside the foaming bun which will lead to increase in shrinkage of the foam once curing takes place. Hence when the formulation is developed the catalyst level needs to be adjusted to minimize the shrinkage. According to the above data, shrinkage measurement has become comparative for 1 pphp level of triethylene diamine compared to the 4 pphp level of the 1,4-DMP.

4.6 Variation of the Air flow of the foam with catalyst level

Air permeability is a measurement of the cell structure of the polyurethane foam. How well the cells are packed in the structure and how much the cells are open and closed. The catalyst level in the polyol mixture influences on the air permeability in the way it affects the blowing reaction. When the blow reaction takes place, it will release more carbon dioxide gas which leads to increase the cell size and number of open cell content in the polymer. Hence, generally, the Air permeability of the foam has been increased with increasing catalyst content for both 1,4-DMP and Triethylene diamine as shown in figure 4.13. Reactivity of the catalyst affects the extent of blow reaction during the foam formation. This directly affects air permeability of the foam. To achieve similar air permeability performance of the resulting foam produced by the presence of 1 pphp level of Triethylene diamine, approximately 4 times of the 1,4-DMP needs to be added to the polyol formulation.

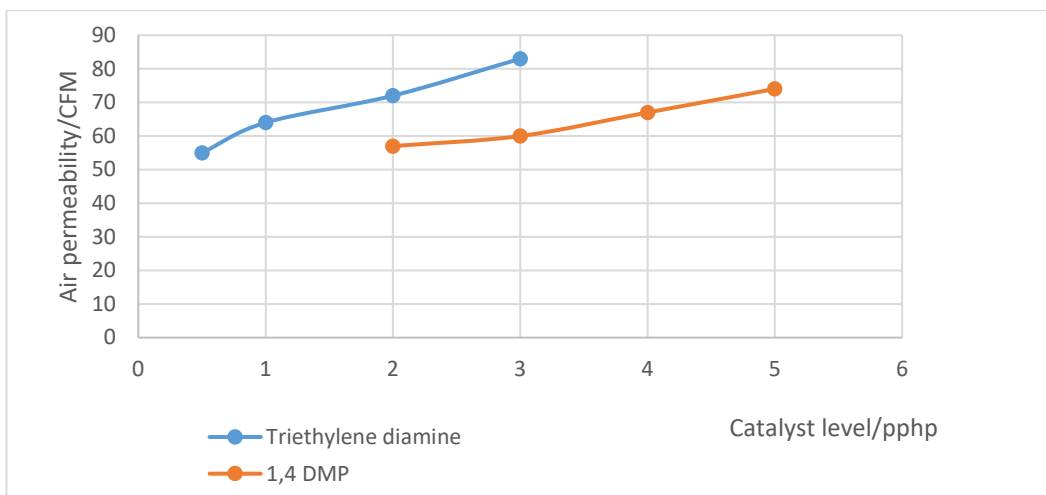


Figure 4.13 Effect of varying catalyst content on Air permeability of the polyurethane sample

4.7 Variation of the physical properties of the foam with catalyst level

Physical properties such as Breaking strength, Elongation % and the Tensile strength of the foam at each catalyst level are shown in figures 4.16, 4.17, 4.18 respectively.

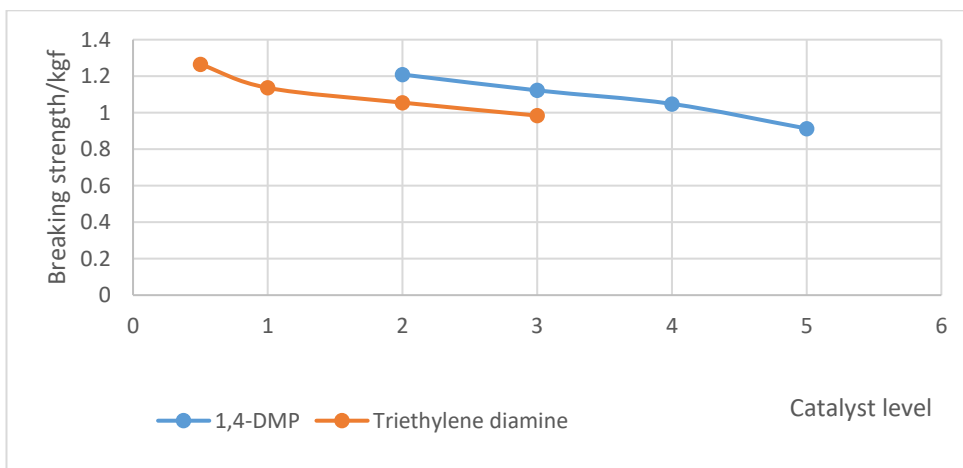


Figure 4.16: Effect of varying catalyst content on Breaking strength of the polyurethane sample

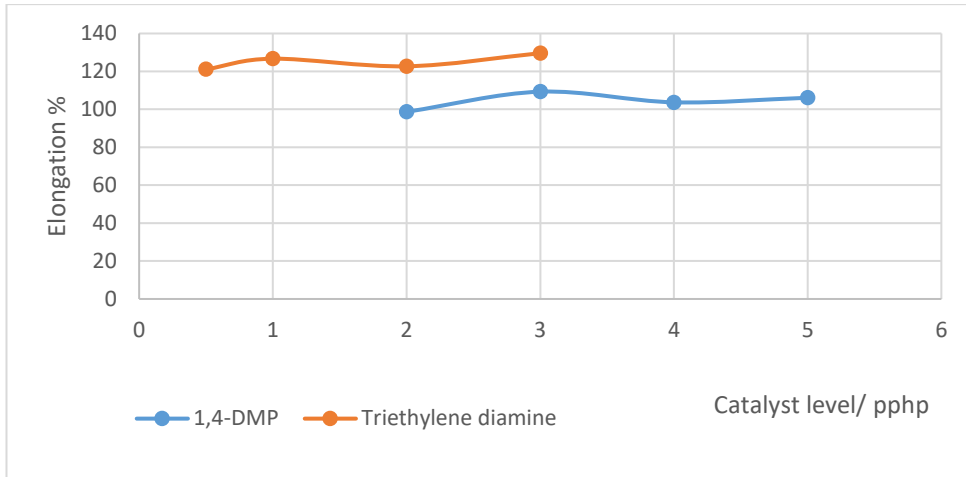


Figure 4.17: Effect of varying catalyst content on Elongation % of the polyurethane foam sample

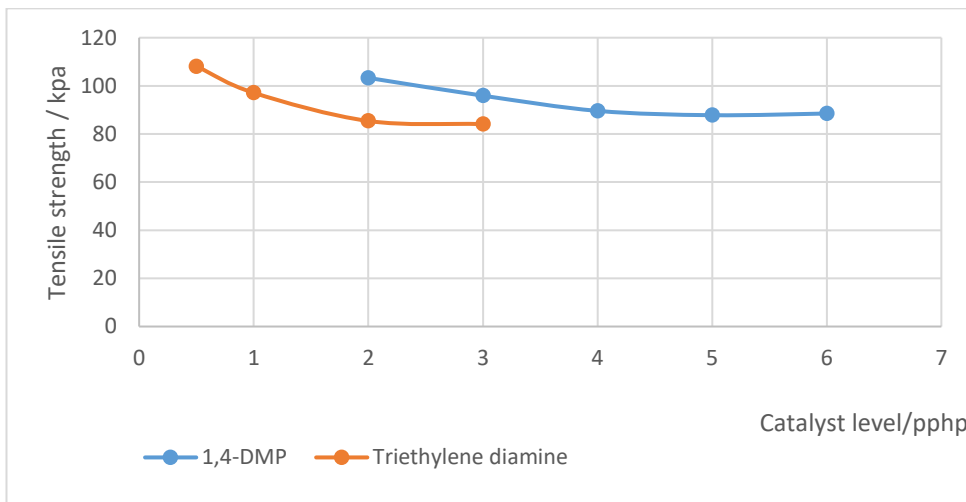


Figure 4.18: Effect of varying catalyst content on Tensile strength of the polyurethane sample

Breaking strength is the point where foam start to break when the force is applied during the Tensile test. Breaking strength has been reduced with additive content due to the reduction in hardness of the resulting foam (Figure 4.16). The foam stretches to its highest modulus and breaks at the elongation limit. This increase of length due to the force applied is measured as elongation %. When the catalyst content increases, the resulting foam become weaker and hence it tends to stretch more resulting an increase in elongation % (Figure 4.17).

Tensile strength is the amount of energy bearing within the polymer at its maximum modulus. This strength is directly proportional to the maximum capacity of the foam. Tensile strength has been reduced with the catalyst content due to the weakness of the foam at higher catalyst level. When the performance of the test catalyst (1,4 -DMP) is compared with control (Tegoamine 33), the test catalyst tends to stay in less performance side compared to the control. However comparative performance has shown at high dosage. (Figure 4.18)

4.8 Scanning Electron Microscope (SEM) image analysis

Micro cellular structures of the resulting foams were analysed using Scanning Electron Microscope. This was carried out for the comparable levels of control catalyst and test catalyst identified by above experiments which as 1 pphp level for control catalyst and 4 pphp level for test catalyst. These SEM images are shown in following figures.

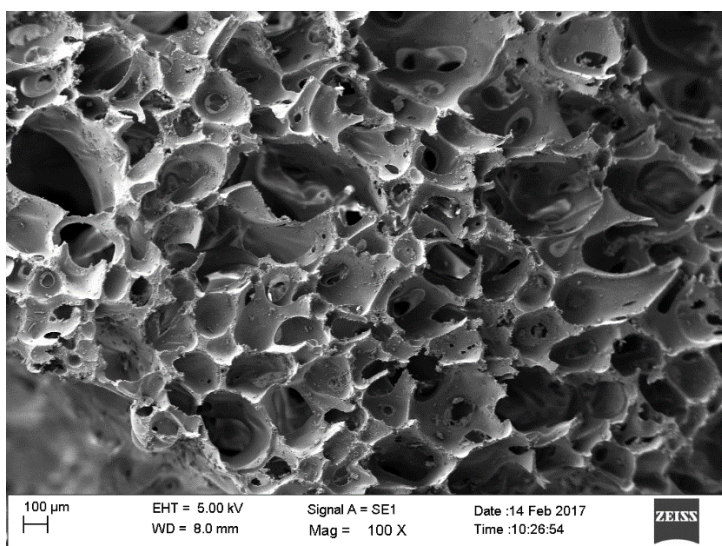


Figure 4.19 SEM of micrograph of foam made using 1pphp of Triethylene diamine at mag 100X

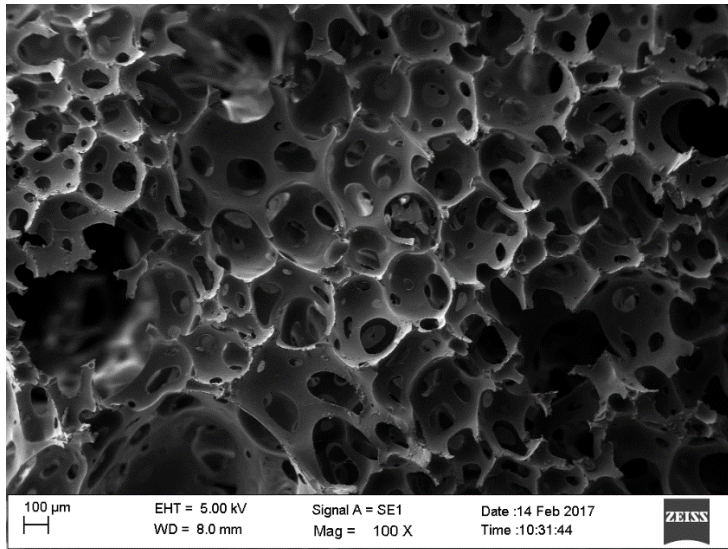


Figure 4.20 SEM of micrograph of foam made using 4 pphp of 1,4 -DMP at Mag 100x

According to the above SEM images, there is no significant deviation of the cellular structure of polyurethane foam made from Triethylene diamine compared to the cellular structure of polyurethane foam made using 1,4 Dimethylpiperazine. The comparability was carried out using factors such as nature of cells, nature of cell walls, number of cells in a unit area, number of open cells, number of close cells, etc. If the cellular structure is not comparable we would expect to observe many larger collapsed areas and areas with different cell sizes. The detailed level analysis needed to be carried out to identify any minor variations. But at this level the resultant polyurethane microstructure made using 1,4-DMP is comparable.

CHAPTER 5 CONCLUSIONS

According to the results of this investigation, following conclusions can be made;

1. Performance of 1,4 dimethyl piperazine (test catalyst) is comparatively low in all the aspects such as foam density, foam hardness, kinetic data (gel time, rise time, curing time), physical properties (Breaking strength, elongation % and the tensile strength) when compared with Tegoamine 33 (control catalyst). According to the data obtained the reactivity is approximately 4 times low compared to the reactivity of control catalyst.
2. Even though the reactivity is low in 1,4-dimethyl piperazine, comparable performance can be achieved at a certain level. Hence this low reactivity could be utilized to develop delayed gelling and blowing action catalyst on polyurethane foam formation.
3. As the reaction is controlled itself by the delayed action catalyst, the flowability inside the mold increases would be helpful to achieve complex, intricate designs out of polyurethane foams.

CHAPTER 6 RECOMMENDATIONS FOR FUTURE WORK

According to the study carry out following recommendations can be made.

1. 1,4 dimethyl piperazine can be developed into a delayed action catalyst after modifying it by combining with a weak acid such as acetic acid which would lower the reactivity profile for molded foams.
2. Polyurethane system with lower reactivity profile would be more suitable for better mold flowability and faster cure times.
3. By combining with a weak acid this can be converted it to its conjugated salt which can then be developed in to a commercial scale catalyst by dissolving in a proper glycol (such as ethylene glycol, propylene glycol, etc) in suitable ratio.
4. Dissolved modified catalyst could be used with standard polyol system to generate series of data related to all the kinetic and physical properties of the foam.

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