

# Exploring Formulation Variables: A Comprehensive Analysis of the Impact on 32 kg/m<sup>3</sup> Flexible Polyurethane Foam

## ABSTRACT-

This study investigates the effect of various formulation variables on flexible polyurethane foam (FPU) of a density of 32 kg/m<sup>3</sup>. A detailed observatory analysis is performed to figure out the impacts of toluene di-isocyanate (TDI), water, surfactant, stannous octoate, and amine on unfilled 32-density FPU foam. The concentration of each component was manipulated to study its influence on the conduct and quality of the PU foam. For comparative purposes, an ideal foam with the correct amount of chemicals was developed. Comparative findings indicated that amine influences the porous nature of the resultant material, silicone plays a crucial role in delivering strength and stability to the cells and cell struts, stannous octoate provides the foam the strength required to sustain its structural integrity, and TDI has a significant impact on the hardness of the foam. Water additionally functions as blowing agent which is essential to initiate the foam to rise from liquid components to a compressible solid. Each ingredient has a considerable impact on the chemistry, foaming procedure, and physical characteristics of the finished material. This paper delivers an insightful comprehensive description to the novices in PU field, researchers and industrial professionals about the correlations between the FPU's structure, physical characteristics, formulation compositions, and chemical mechanisms.

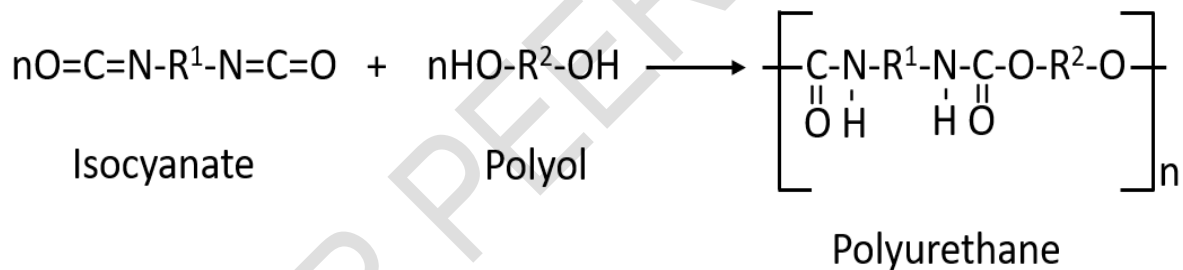
**Keywords-** Polyurethane foam, surfactant, TDI, gelling catalyst, blowing catalyst

## 1. INTRODUCTION

Polyurethane is a complex mixture of several substances, including polyurea, biurets, allophanates, and others, formed via the reaction of isocyanates with one another or with other reactive hydrogen-containing reactants such as amine and water. Polyurethane (PU), also known as carbamate, is an ester of unstable carbamic acid [1-2]. The polyurethane (PU) market has been divided into adhesives, coatings and sealants, elastomers, rigid foam, and flexible foam based on product type. The flexible polyurethane foam (FPU) sector dominates the market due to its widespread use as a cushioning material for furniture, bedding, mattresses, seating, and other soft products [1-2]. According to a March 2023 Business Research insights analysis, the global market for polyurethane foam mattresses was predicted to be worth 782.97 billion in 2021 and is projected to rise at a compound annual growth rate (CAGR) of 4.1% over the course of the forecast period, reaching at 1040.46 billion by 2028.

Polyurethanes (PU) are polymeric materials containing urethane linkages [NH-C(O)-O] formed by the chemical reaction of polyols with hydroxyl (-OH) groups and isocyanates (N=C=O) [3-4]. The addition polymerization reaction between isocyanate and polyol that

results in the synthesis of polyurethanes is displayed in figure:1. The production of polyurethane foams primarily involves two key reactions: The initial process, called the gelling isocyanate-polyol reaction, creates the urethane group's backbone [4-7] Urethane linkages make up a large fraction of polyurethanes. Through the assistance of organometallic catalysts that encourages the polymerization or gelation process between an isocyanate and a polyol, a cross-linked polymer is produced as a result of this process. A significant withdrawing effect is caused by the high electronegativities of N and O towards C, which turns C partially positive. Isocyanates are hence susceptible to nucleophilic attacks[4]. This clarifies the reason behind isocyanates reactive nature towards hydroxyls, amines, phenols, and other substances. The usage of TDI is made possible by its aromatic rings, which are known to impart rigidity to the structure[4]. Due to the fact that PU foam's affordability and readily accessibility, it is used as a comfort layer in mattresses because of its softness[7]. The second reaction is the isocyanate-water blowing reaction, which results in the unstable carbamic acid that subsequently decomposes to form an amine and carbon dioxide gas bubbles[5-8]. Toluene diisocyanate (TDI) is the most often utilised isocyanate in flexible foams. The two most significant TDI isomers are 2,4 and 2,6 toluene diisocyanate. Reactivity is higher in the 2,4 isomer compared to the 2,6 TDI isomer[9]. The three stages of the foaming or expansion process are: generating small discontinuities or cells in a fluid or plastic phase; allowing these cells to enlarge to the desired volume; and stabilizing the cellular structure by chemical or physical means[10].



*Fig. 1: Addition polymerization reaction of isocyanate and polyol into formation of polyurethanes.*

Catalysts play a significant part in polyurethane synthesis because they balance the reaction of the isocyanate and polyol. Its primary function is to leverage the diverse reactions in order to create an end result with the necessary characteristics[5,7,9]. A greater quantity of blowing yields collapsed foams, whereas a greater amount of gelation generates a closed-cell structure and shrinkage[5-8][11]. Not only are catalysts vital in regulating and balancing the gelling and blowing mechanisms, but they also optimize the curing speed and foam characteristics during the foam synthesis step[5]. It has been noted that stannous octoate has a higher catalytic impact on the gelling reaction in comparison to the blowing reaction[6]. Metal complex catalysts have an advantage over amine-based catalysts due to their lower volatility. The metal complex catalysis mechanism involves the creation of complex bonds between the metal centre and oxygen-rich species, which may arise from either the hydroxyl or isocyanate groups[4]. These connections further lower energy levels and encourage the formation of the urethane linkage[4]. A proper expansion is obtained through the balance between the

polymerization (gelling) and the gas generation (blowing)[7]. In that sense, the adjustment of catalyst type and quantity dramatically influence the expansion.

Organometallic catalysts promote the polymer-forming or gelation reaction between an isocyanate and a polyol. Tin compounds are the most extensively utilized metal among the several that are available[9]. Due to their extreme selectivity towards the isocyanate-polyol reaction, organometallic compounds are employed as polyurethane catalysts. These chemicals function as Lewis acids and are thought to interact with basic sites in the isocyanate and polyol compounds[5]. The most popular catalysts for producing polyurethane foams are tertiary amines and tin octoate[5]. The recommended gelling catalyst for flexible slabstock foam is stannous octoate (tin II 2-ethyl hexoate). The chemical is easily hydrolysed and oxidized in the presence of water and tertiary amines, necessitating cautious handling. Amine's catalytic activity is caused by the existence of a free electron pair on the nitrogen atom. The primary determinants of the relative catalytic activity of different amines are steric hindrance about the nitrogen atom and the electronic effects of the substituent groups. The isocyanate group's nitrogen atom is triggered by the development of an amine complex that readily interacts with nearby hydrogen atoms of sources such as polyol or water [4,9]. This mechanism, first put forth by Baker and Holdsworth in 1947, suggests that the amine mount a reversible nucleophilic attack on the carbon atom in order to form an activated complex[4,9]. Aromatic isocyanates have moderate electron-withdrawing effects on both the aromatic and carbonyl groups[9]. A variety of process criteria, including cream times, rise profiles, gel times, and even the curing of the outer layer of skin, can be met by selecting the type and concentration of amine catalysts. The amine used may also change foam characteristics like as airflow and load bearing by impacting on primary and secondary foam reactions. The addition of more volatile amines may reduce odour in the finished product, but it may also shorten cure time due to quick catalyst degradation. High volatility frequently leads to high vapor pressures, low flash points, and attendant handling difficulties[9].

Nowadays, polysiloxane-polyoxyalkylene copolymers from the category of surfactants, are commonly employed in the production of most flexible foams. Conceptually, these materials are typically represented by their various head/tail configurations. The part of the surfactant that is composed of polyoxyalkylene polymer (or polyol), contributes to the overall emulsification effect and enables the surfactant to dissolve into the bulk polyol. The bulk surface tension gets reduced by the silicone end of the molecule[9]. To satisfy the needs of various foam systems, the surfactant structure can be modified by varying the length and composition of the polydimethylsiloxane backbone, as well as the number, length, and composition of the pendant polyether chains. There is an ideal ratio between the surfactant's silicone and glycol moieties for each type of slabstock foam. Enhancement in foam porosity can be achieved by blending silicone surfactants with blends of polyoxyethylene/polyoxypropylene block copolymers[9]. Although isocyanates and polyols react swiftly, the reaction's constituent parts are usually not effectively mixed. Thus, surfactants are utilized in both foaming and nonfoaming procedures to ensure homogenous reaction medium. Typically, silicon-based oils or copolymers like polyether polysiloxane are used for this purpose. Surfactants are crucial because they improve mixability between the polyol and isocyanate, resulting in a homogeneous foaming process [4,10]. Surfactants based on silicone that are nonionic are utilized in the production of all flexible polyurethane foams.

Surfactants, in general, serve a number of purposes. The stability of the cell walls is certainly the most crucial of these roles. Moreover, surfactants also aids in regulating the precise timing and degree of cell opening. In order to provide the polyhedral framework enough time to develop a strong enough covalent network to withstand collapse, silicone surfactants play an important role in moderating the cell-opening effects of urea precipitation[9]. The impact of various formulation parameters on FPU foam is studied in this work. An extensive observational study is conducted to examine the effects of TDI, amine as a blowing catalyst, silicone as a surfactant, water as a blowing agent, stannous octoate as a gelling catalyst on the 32-density flexible polyurethane foam. Understanding the principles of foam and the ways to modify and extend its properties serves a few of the objectives.

## 2. MATERIALS AND METHODS

**2.1. Materials-**In the production of 32 density PU flexible foams ingredients used are conventional Polyether polyol (Voranol) (DOW Chemical International Pvt. Ltd.) of 56 mg KOH/g Hydroxyl number and Dynamic Viscosity (at 25°C) between 550 to 650 millipascal-seconds (mPas), Toluene diisocyanate (Lupranate-T80) is an isomers mixture of toluene diisocyanate (80%-20% mixture of the 2,4 and 2,6 TDI) from BASF, Stannous octoate (tin) (D-19) as a gelling agent and amine which is a combination of Bis(2-dimethylaminoethyl) ether (< 60% w/w) and Dimethylaminoethoxyethanol (> 40% w/w) (B-11) as a blowing catalyst from Momentive, Polyethyleneoxidemethylsiloxane copolymer (L-618) as a silicone surfactant from Sistersville plant, Colours from Milliken and Distilled water as blowing agent.

**2.2. Preparation and formulation of foams-** A standard foam (N) was synthesized with the amount of each chemical component chosen to achieve a target density of  $(32 \pm 2)$  kg/m<sup>3</sup> at a temperature of  $(25 \pm 1)$ °C and a relative humidity within the range of (37-40) %. The chemical temperatures of the TDI and Polyol were constantly maintained within the range of  $(24 \pm 1)$ °C to minimise their influence on potential foaming variations. The hydroxyl content of the polyether polyol and the parts of water utilised in the traditional foam formulation were taken into account to calculate the appropriate quantity of isocyanate. Equations:1&2 were used to compute the parts of TDI and water. Parts per hundred parts (pph) of polyol were used to quantify each of these compounds. To ensure an accurate stoichiometric reaction, stannous octoate, silicone, amine, and water were measured with syringes. A series with varying formulation parameters of each chemical were prepared and compared to the standard  $(32 \pm 2)$  density foam with optimal chemical concentrations. To study the role of each formulation ingredient in the final manufactured foam, series: T,A&S were developed with ( $\pm 50\%$ ,  $\pm 100\%$ ) varying parts of tin, amine and silicone, while series:I&W were developed with ( $\pm 25\%$ ,  $\pm 50\%$ ) varying TDI and water concentrations. Table:1 lists the different ingredients and the proportionate quantities that were utilised to make the foam samples.

*Table:1 Formulations of standard flexible polyurethane foam and foams at varying concentrations of formulation parameters*

Chemicals	Polyol	Color	TDI	Water	Tin	Amine	Silicone
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FOAMS ↓							
<b>Standard (N)</b>	100	0 (White)	39.5	2.81	0.125	0.04	1
<b>I-1</b>	100	0.1 (Violet)	19.75	2.81	0.125	0.04	1
<b>I-2</b>	100	0.1 (Violet)	29.62	2.81	0.125	0.04	1
<b>I-3</b>	100	0.1 (Violet)	49.375	2.81	0.125	0.04	1
<b>I-4</b>	100	0.1 (Violet)	59.25	2.81	0.125	0.04	1
<b>W-1</b>	100	0.1 (Blue)	39.5	1.41	0.125	0.04	1
<b>W-2</b>	100	0.1 (Blue)	39.5	2.11	0.125	0.04	1
<b>W-3</b>	100	0.1 (Blue)	39.5	3.52	0.125	0.04	1
<b>W-4</b>	100	0.1 (Blue)	39.5	4.22	0.125	0.04	1
<b>T-1</b>	100	0.1 (Yellow)	39.5	2.81	0	0.04	1
<b>T-2</b>	100	0.1 (Yellow)	39.5	2.81	0.063	0.04	1
<b>T-3</b>	100	0.1 (Yellow)	39.5	2.81	0.188	0.04	1
<b>T-4</b>	100	0.1 (Yellow)	39.5	2.81	0.25	0.04	1
<b>A-1</b>	100	0.1 (Red)	39.5	2.81	0.125	0	1
<b>A-2</b>	100	0.1 (Red)	39.5	2.81	0.125	0.02	1
<b>A-3</b>	100	0.1 (Red)	39.5	2.81	0.125	0.06	1
<b>A-4</b>	100	0.1 (Red)	39.5	2.81	0.125	0.08	1
<b>S-1</b>	100	0.1 (Green)	39.5	2.81	0.125	0.04	0
<b>S-2</b>	100	0.1 (Green)	39.5	2.81	0.125	0.04	0.5
<b>S-3</b>	100	0.1 (Green)	39.5	2.81	0.125	0.04	1.5
<b>S-4</b>	100	0.1 (Green)	39.5	2.81	0.125	0.04	2

$$\text{Parts of TDI} = \{9.67 \times \text{Parts of water} + [0.155 \times \text{OH no.}]\} \times \frac{\text{TDI Index}}{100} \times \frac{\text{Polyol \%}}{100} \text{---[1]}$$

where,  $9.67 = \frac{\text{Equivalent wt. of TDI}}{\text{Equivalent wt. of H}_2\text{O}}$

$0.155 = \frac{\text{Parts of polyol} \times \text{Equivalent wt. of TDI}}{\text{Molecular mass of KOH in 1kg of polyol}}$

TDI Index = 110

$$\text{Parts of H}_2\text{O} = \frac{90}{D} \text{ [2]}$$

where,  $D = \text{Required Density of the foam}$

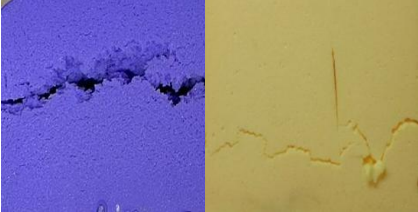
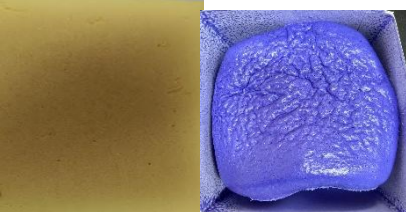


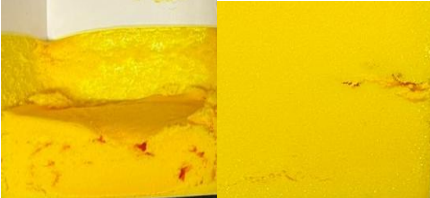

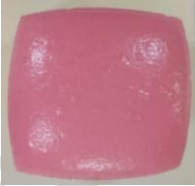



**NOTE:** Equation-2 is only applicable for flexible polyurethane foams for density of  $18 \text{ kg/m}^3$  and above.

Flexible polyurethane foams with varying chemical concentrations were manufactured by using the discontinuous batch foaming method. An electronic balance was used to weigh toluene diisocyanate (TDI) and polyether polyol in two separate beakers. The polyol and other reagents (Component A) were carefully mixed by a direct-drive foaming stirrer set at  $(2500 \pm 10)$  rpm. The mixture was thoroughly stirred for two to three minutes until the foam solution appeared homogenous. TDI (Component B) was promptly added to the foam mixture and continuously stirred for 10 to 15 seconds. After that, the rising foam mixture was poured into the mould and allowed to cure for 72-hour. The foam was sliced with the foaming mould after the duration of the curing process was over in order to examine the finished foam product.

### 3. RESULTS AND INTERPRETATION-

PU foam is one of the most comfortable, easily accessible, and affordable mattress materials. The initial polyol structure opted can have a significant impact on the processing and final foam's qualities. Hydroxyl reactive groups are offered from the polyol. If a polyether alcohol is employed as the primary hydroxyl-containing group, the resulting foam is frequently referred to as polyether polyurethane foam[12]. Nowadays, polyether type polyols are the raw material utilised in the production of 90% of total flexible foams[9]. Several properties of PUFs can be controlled by varying the functionality of the polyol. As an example, a modest rise in foam hardness and a slight decrease in tensile strength, tear strength, and elongation result from increasing the polyol functionality without altering the molecular weight. Thus, while retaining a polyol's functionality, and raising its equivalent weight (molecular weight divided by functionality) results in an increase in elongation and tensile strength of the foam. The soft segments are generated by the polyol [7]. All proposed formulations utilised the same polyol but other formulation parameters were altered in order to gain an improved comprehension of the intended application of each component in 32- density flexible polyurethane foam. The soft segments of PU foams are formed by polyol, whilst the hard segments are linked to the urethane and urea moieties[4]. Table:2 provides an informative look into the problems that arise in PU foams because of different chemicals at their varying concentration levels.

*Table:2 Virtual representations of problematic resultant foams at different formulation parameter concentrations.*

Scanty conc. of chemicals	Chemicals	Excessive conc. of Chemicals
 <p data-bbox="193 591 612 622">No strength in foam , split foam</p>	<p data-bbox="687 367 852 472"><b>Toluene diisocyanate (TDI)</b></p>	 <p data-bbox="887 591 1390 696">Discoloration in foam due to excessive heat generated (scorching), shrunken foam</p>
 <p data-bbox="193 958 384 990">Shrunked foam</p>	<p data-bbox="711 734 828 893"><b>Distilled water (Blowing agent)</b></p>	 <p data-bbox="887 958 1390 1028">Large pores is generated in foam (pinholes), split foam</p>
 <p data-bbox="193 1279 660 1348">Collapsed foam, internal splits in foam</p>	<p data-bbox="687 1066 852 1225"><b>Stannous octoate (tin) (Gelling catalyst)</b></p>	 <p data-bbox="887 1285 1390 1355">Shrunked foam, extremely closed (blind/dead) foam</p>
 <p data-bbox="264 1592 584 1624">Closed non-porous foam</p>	<p data-bbox="711 1397 828 1503"><b>Amine (Blowing catalyst)</b></p>	 <p data-bbox="983 1592 1291 1624">Extremely porous foam</p>
 <p data-bbox="193 1906 660 1975">Boiling effect, extremely coarser cells in foam</p>	<p data-bbox="695 1662 847 1731"><b>Silicone (Surfactant)</b></p>	 <p data-bbox="887 1899 1390 1968">Very finer cells with exteme strength, increase in production cost</p>

The nature of the isocyanate is just as significant as the impact of the polyol type used[7]. Each formulation used an isomeric blend of toluene diisocyanate (80%-20% mixture of 2,4 and 2,6 TDI), and variations in TDI concentrations was done in I-series foams. The isocyanate acts as a source of NCO groups, that react with functional groups from the polyol, water, and cross-linkers in the formulation [9]. Variation in the TDI in a foam has a noticeable impact on the final foam's hardness. Equation:1 calculates the necessary amount of isocyanate essential to react with the polyol and any other reactive additives.

The gelling of the cellular structure is also caused by the reaction between isocyanate and polyol, which subsequently creates polyurethanes[6]. Isocyanate reacts with polyol to produce urethane groups as shown in figure:2a ; it additionally reacts with water to yield CO<sub>2</sub> and urea groups which is illustrated in figure:2b [7]. The diisocyanate and polyether polyol reaction results in an exothermic reaction that generates the polyurethane foam. A small amount of water reacts with a part of the diisocyanate during the polymerization phase to produce an unstable intermediate carbamic acid, which then degrades into amine and carbon dioxide, which is responsible for the blowing in PU foam, enabling the solution to foam and expand in volume. Within minutes, the polymer transforms from a liquid structure into a compressible solid structure because of the high degree of crosslinking caused by the multifunctionality of the reactants. Theoretically, the consumption of isocyanate by water and polyol can be computed using equations 3 and 4.

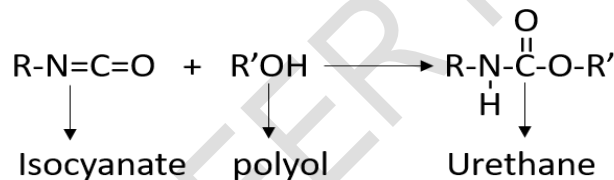


Fig. 2a: Reaction of isocyanate and polyol to form urethane linkages in flexible polyurethane foams.

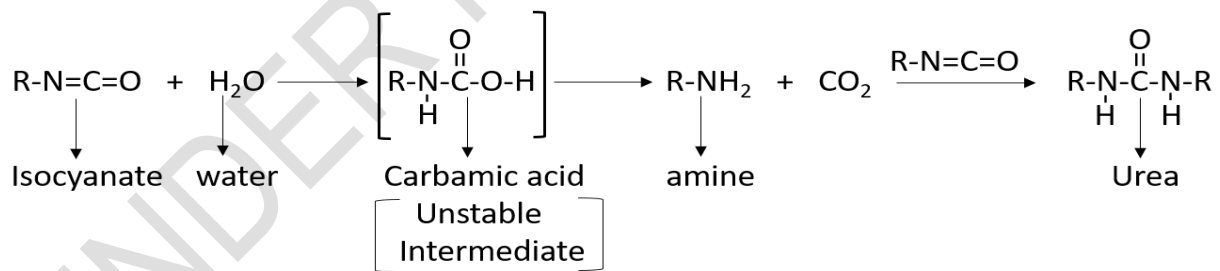


Fig. 2b: Reaction of isocyanate and water to yield CO<sub>2</sub> and urea.

$$\text{Consumption of TDI by H}_2\text{O (in grams)} = \frac{\text{Amount of H}_2\text{O (in grams)} \times \text{Equivalent wt. of TDI}}{\text{Equivalent wt. of H}_2\text{O}} \text{---[3]}$$

$$\text{where, Equivalent wt. of TDI} = \frac{\text{Molecular wt. of TDI}}{\text{Functionality}}$$

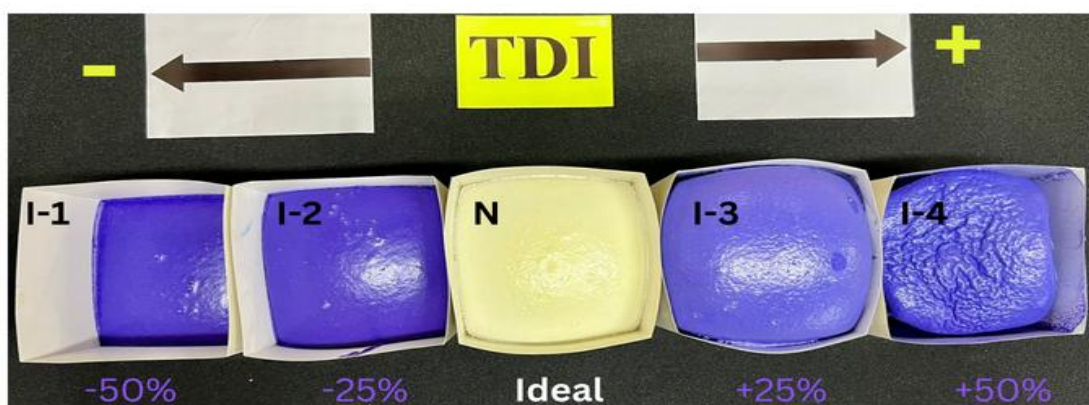
$$\text{Equivalent wt. of H}_2\text{O} = \frac{\text{Molecular wt. of water}}{\text{Functionality}}$$

$$\text{Consumption of TDI by Polyol (in grams)} = \frac{100 \times \text{OH value of polyol} \times \text{Equivalent wt. of TDI}}{\text{Molecular mass of KOH in 1kg of polyol}} \quad [4]$$

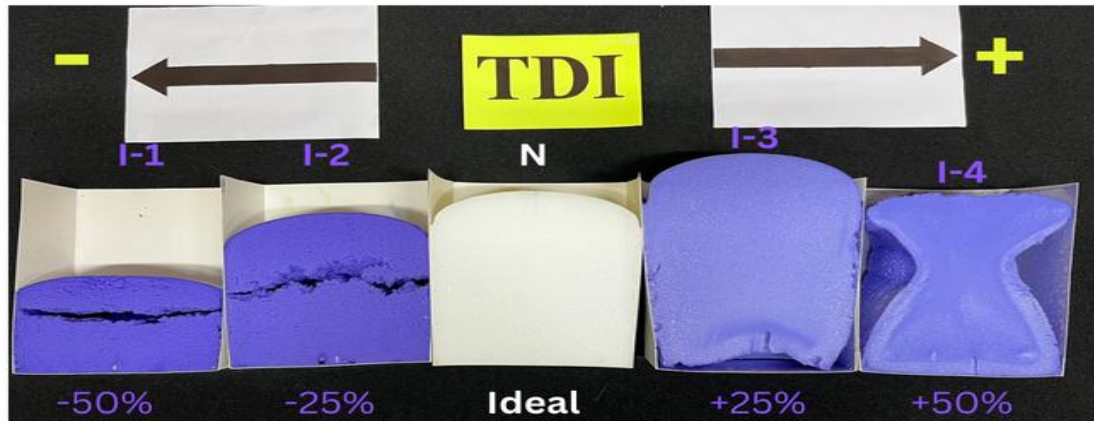
where, OH value of Polyol = 56mg KOH/g

The polymerization reaction between polyol and TDI was reduced because Foam I-1 had 50% less TDI content than the ideal amount of TDI. As a result, the I-1 foam development was incomplete, and no strength in foam was detected due to lack of polymerization and urethane formation during foaming process. Foam I-2, which had a TDI content that was 25% lower than the ideal amount, demonstrated the isocyanate and polyol reaction in order to produce urethanes in FPU foam. Since, an adequate amount of TDI was not delivered, the resulting foam lacked appropriate stability and gelation, limiting the foam's rise height and leading to formation of a ruptured foam. Foam-N with the proper concentration of TDI demonstrated the optimal foam height and strength as a proper reaction was established during foam the production process.

The excess isocyanate that is typically added to I-3 and I-4 foam formulations will further react with the urea and urethane groups, consolidating the structure through the production of crosslinks. A 25% increase in TDI concentration in I-3 foam resulted in an elevated foam height compared to foam:N, which reduced the foam's density. The exothermic reaction during foaming is enhanced by excess TDI in the I-3 foam formulation, which in turn speeds up the foam's reaction and shortens its full rise time. Small splits and detected dead/temporary hardness in the foam are prompted by the abrupt surge in foam. It is demonstrated that the increased covalent cross-linking that is caused by the presence of excess isocyanate groups is directly responsible for this increase in hardness which is because of complete consumption of isocyanate reactive sites. As a result, higher isocyanate concentrations enable harder PUFs by offering more hard segments [7]. This means that an increase in TDI content reduces the viscoelastic strength of polyurethane foam, which results in a decrease in the switch-off factor and permanent pressure. It was found that it resulted in an increase in shrinkage rate [13]. Foam I-4 produced surplus polyurea due to the presence of 50% more TDI concentration than the recommended quantity. Excess polyurea is deposited on struts, preventing appropriate cell growth and resulting in the production of a shrunk foam. Figure:3a articulates the final products obtained with different TDI concentrations, and Figure:3b reflects the quality of the resultant foams.



**Fig. 3a:** A pictorial representation precisely demonstrating the influence of quantity of TDI on the final finished flexible polyurethane foams obtained at different concentrations of TDI.



**Fig. 3b:** A visual illustration of the impact of varying TDI concentrations on the quality of eventual flexible polyurethane foams.

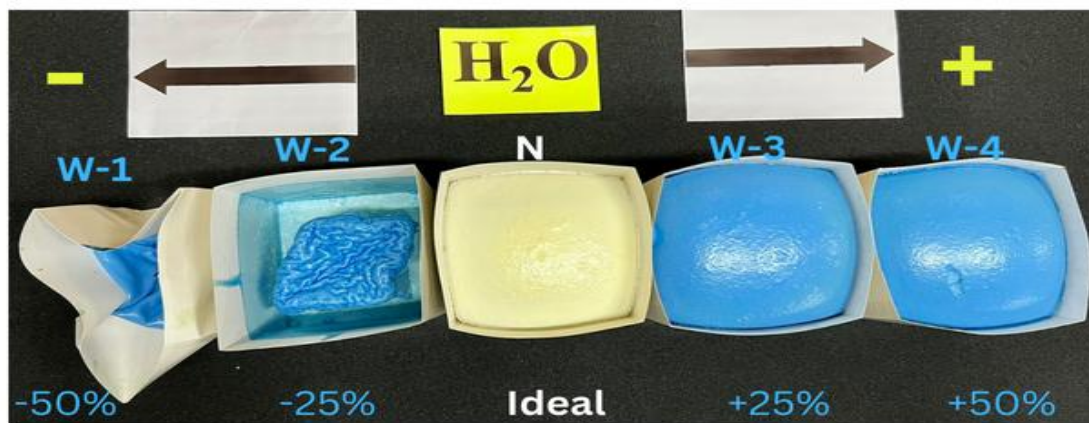
**Note:** (I-1) = Foam with approximately 50% lesser TDI conc. than optimum TDI conc., (I-2) = Foam with approx. 25% lesser TDI conc. than optimum TDI conc., (N) = Foam with optimum conc. of TDI, (I-3) = Foam with approx. 25% higher TDI conc. than optimum TDI conc., (I-4) = Foam with approx. 50% higher TDI conc. than optimum TDI conc.

Distilled water is used as a blowing agent. Water is a source of active hydrogens. Only demineralized water should be used for foam production [9]. One practical method for creating a gas that can be used for blowing the polymer into a foam structure is the reaction of polyisocyanates with water. Isocyanate reacts with water to yield polyurea molecules and carbon dioxide gas. The gas leads to the expansion of foam by diffusing into the nucleated bubbles and pores are formed in the mixture. The final polymer's characteristics are influenced by the invasion of polyurea molecules [6,9]. The initial viscosity is attained through the production of polyureas. The amount employed will help foster the gelling reaction in addition to delivering a more influential blowing reaction [6]. PU foams are manufactured by blowing agents which plays a crucial role in defining the morphology, cell structure, and physical characteristics of PU foams [4]. The blowing agent plays a significant role in determining porosity of the foam as it is directly related to the generation of bubbles. An ideal quantity of blowing agent ought to produce homogeneous, evenly distributed pores. Thus, it's critical to regulate the blowing agent's quantity. All W-series foams were created with varying distilled water concentrations to investigate its impact on PU foam.

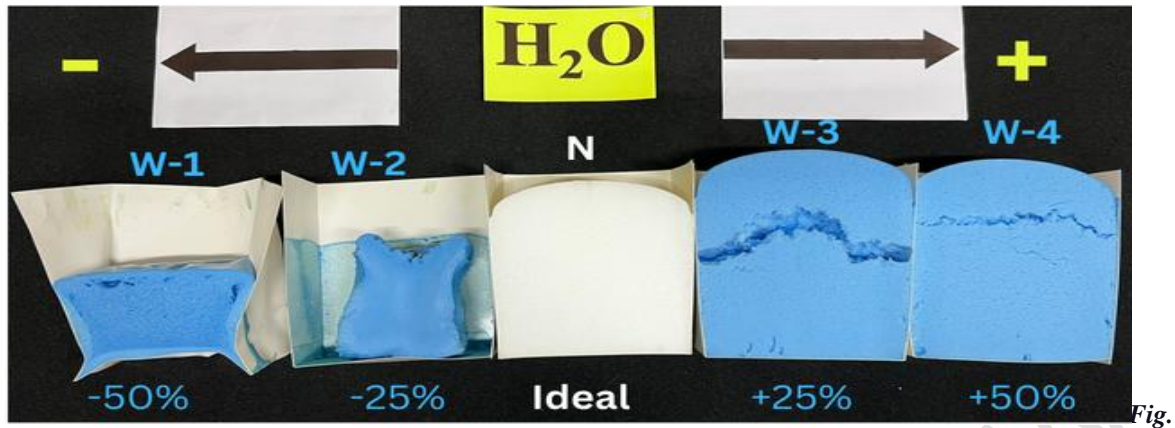
Foam W-1 had 50% less water concentration than the required dosage of water which resulted in inappropriate production of polyurea molecules and insufficient expansion of PU foam as lesser amount of  $\text{CO}_2$  was generated. As a result, Foam W-1 did not expand properly, which caused the foam matrix to compress and produce a shrunken foam. Although foam W-2 with 25% less water showed rise and expansion, the foam shrank during the curing period because the cell membranes in the foam were unable to break down by the escape of  $\text{CO}_2$  gas, resulting in an erratically porous foam. This happened mainly because the water content was too low for a blowing reaction to occur in the foam and the amount of  $\text{CO}_2$  gas produced in the foam was insufficient to rupture the foam's cell membranes. Foam N with the optimum amount of water demonstrated proper production of polyurea molecules and adequate cell expansion, yielding an acceptable porous material.

The foam's exothermic temperature rises with increasing water level in the formulation [10]. When the concentration of water increases, the overall exotherm that these formulations produce displays a more reactive system. The foam generates higher maximum temperatures and takes a shorter period to attain its final growth with a linear progression of the gelling reaction [6]. Higher water levels might raise the chance of scorching, which could lead to a fire. Consequently, this means that the blow index which is a measurement of the water and secondary blowing agent level is the primary factor influencing the foam density. As the amount of water increases, the foam's density and cell count inevitably drop [10].

The increased dosage of blowing agents results in less dense PU foams that have inferior mechanical attributes. The resulting polymer could display low compressive strength or become fragile when subjected to a load [4]. The W-3 foam attained a higher height than the ideal foam because its composition had 25% more water, which increased the amount of CO<sub>2</sub> gas released. Due to insufficient gelation to balance the blowing or gas evolution process, the excess gas generated resulted in split foam. A physical separation (a split) took place when the motive force of the expanding gas bubbles eventually exceeded the polymer matrix's tensile strength. Due to the formation of extra polyurea molecules during the foaming process, Foam W-4 with a 50% higher water concentration demonstrated inferior foam strength. Additionally, the height acquired was comparable to W-3 foam and the foam displayed several splits, which have been triggered by an excess of CO<sub>2</sub> gas generation. Figure 4a illustrates the finished products obtained at varying concentrations of H<sub>2</sub>O, whereas Figure 4b illustrates the caliber of the resulting foams. In order to achieve the ideal characteristics like a regular cellular structure, a desirable density, and robust mechanical qualities, the right amount has to be chosen [4].



*4a: A pictorial representation precisely demonstrating the influence of quantity of water on the final finished flexible polyurethane foams obtained at different concentrations of water.*



**4b:** A visual illustration of the impact of varying water concentrations on the quality of eventual flexible polyurethane foams. **Note:** (W-1) = Foam with approximately 50% lesser H<sub>2</sub>O conc. than optimum H<sub>2</sub>O conc., (W-2) = Foam with approx. 25% lesser H<sub>2</sub>O conc. than optimum H<sub>2</sub>O conc., (N) = Foam with optimum conc. of H<sub>2</sub>O, (W-3) = Foam with approx. 25% higher H<sub>2</sub>O conc. than optimum H<sub>2</sub>O conc., (W-4) = Foam with approx. 50% higher H<sub>2</sub>O conc. than optimum H<sub>2</sub>O conc.

Research has shown that the most effective catalysts are amines and organometallics. Various combinations of catalysts are utilized in order to establish a proper balance between the chain propagation (isocyanate with hydroxyl) reaction and the blowing reaction (isocyanate with water). The polymer and gas formation rates must be balanced in order to ensure the gas is efficiently entrapped in the gelling polymer and the cell walls achieve enough strength to sustain their structure without collapsing or shrinking. The completion of the reaction, or "cure," in the final foam is yet another reason why catalysts are crucial [9]. The concentration of stannous octoate (tin) was adjusted while producing the T-series foams to study its effect on PU foam. Foam T-1 was produced without tin, resulting in collapsed foam due to insufficient strength for sustaining the structure. Therefore, the foam rose to a point where urethane linkage could be seen, but then it abruptly collapsed because the foam's cell walls/struts lacked the strength needed to hold the foam's structure.

After then, a slight increase in the concentration of stannous octoate will result in a fine open foam with some relaxation or "sigh back." Foam T-2 had tin to hold the structure together, but not enough to sustain an ideal quality of the foam. Foam T-2 exhibited internal splits as well as a setback in foam, since it had 50% less tin content than the optimal amount. If the struts have not reached an adequate mechanical strength at the moment of cell-window rupture, film rupture will propagate. The resultant defect is referred to as a split if the rupture stops within a few inches [9]. Foam splits occur when there is insufficient gelation to balance the blowing or gas evolution reaction and after some point when the motive force of the expanding gas bubbles exceeds the tensile strength of the polymer matrix and a physical separation (a split) occurs [9]. Each foam formulation requires experimental determination of the specific concentration levels and it is possible to control the degree of cell openness practically by modifying the catalyst package [9]. Foam gradually becomes more tightly packed at ideal tin catalyst concentration, which eventually stopped relaxation in Foam N. The appropriate concentration of tin in Foam N demonstrated an ideal foam quality, urethane linkages, and strut strength for sustaining the PU foam structure. It is ideal to have a high

population of cell windows that are ruptured naturally through the gelling and blowing reactions in the manufacturing of flexible polyurethane foams. A sufficient number of open windows will reduce the pneumatic character of the foam, resulting in it being a better choice for applications demanding comfort cushioning. Additionally, it has been reported that a foam with greater open-cell will function better under fatigue [9].

The chemical events that take place up until the moment of polymer gelation culminate in the ultimate stability of the cells in a foam. At the gelation stage, all film movement and expansion of cells ceases except for the disruption caused by external physical forces which result in anisotropy [9]. Higher quantities of tin cause the foam to gel more quickly, resulting in mild to severe shrinkage and stronger, harder-to-break cell windows. A more compact cell structure of polyurethane foam is generated by increasing the amount of tin catalyst in polyurethane foam, which additionally enhanced the gelling reaction at the expense of the blowing reaction [5]. This refers to samples with high cross-linking polymers with excellent mechanical properties. Due to the existence of more closed cells, foam T-3 with a 50% extra tin concentration displayed characteristics of a dead foam with a minor setback. Increasing the proportion of tin catalyst increases the compressive strength of polyurethane foam because tin catalyst promotes the gelling process between polyether polyol and polyisocyanate [5]. Although the compressive strength of the foam improved, its ability to bounce back deteriorated, thus reducing the foam's resilience. Foam has to be compressed with more pressure; nevertheless, it will not return to its initial state once the pressure is released. As the amount of tin catalyst increases, so does the maximum temperature attained by the foam. Additionally, a shorter full rise time is required for attaining the maxima. Stability times decrease with increasing tin because it stabilizes foam more quickly and causes a slight rise in temperature [6]. Foam T-3 height was higher than optimal foam N due to the maximum temperature attained by the foam contributed to an increase in foam height, and additional tin provided more stability to the foam to hold the elevated structure.

When there is a significant number of foam cells with intact windows at the end of the foam manufacturing process, and these cells are filled with hot, pressurized carbon dioxide gas, the flexible foam shrinks [9]. When the foam cools, two things happen: the internal gas pressure decreases, and carbon dioxide diffuses out of the cells around fifteen times quicker than air does into the cells. The overall consequence is a partial vacuum in the cell, which, when applied to a population of closed cells, causes the foam to shrink and lose its physical dimensions [9]. Foam T-4 with twice as much tin as what was required, which caused the simultaneous gelling and blowing reactions to become unbalanced and leading the foam to shrink. The correct proliferation of cells in the PU matrix was hampered by the gelling reaction, which happened significantly earlier than the blowing reaction. Thus, these findings lend credence to the theory that stannous octoate functions primarily as a gelling catalyst. The blowing and gelling stages respective contributions to the total exotherm can be used to determine their relative relevance [6]. This necessitates careful consideration of the tin concentration and processing in the foam formulation in order to achieve a better end product with more open cells and adequate foam strength to restore to its former state after stress or load. The final products obtained at ranged concentrations of stannous octoate (tin) are displayed in Figure 5a, while the quality of the ensuing foams at different tin levels is demonstrated in Figure 5b.

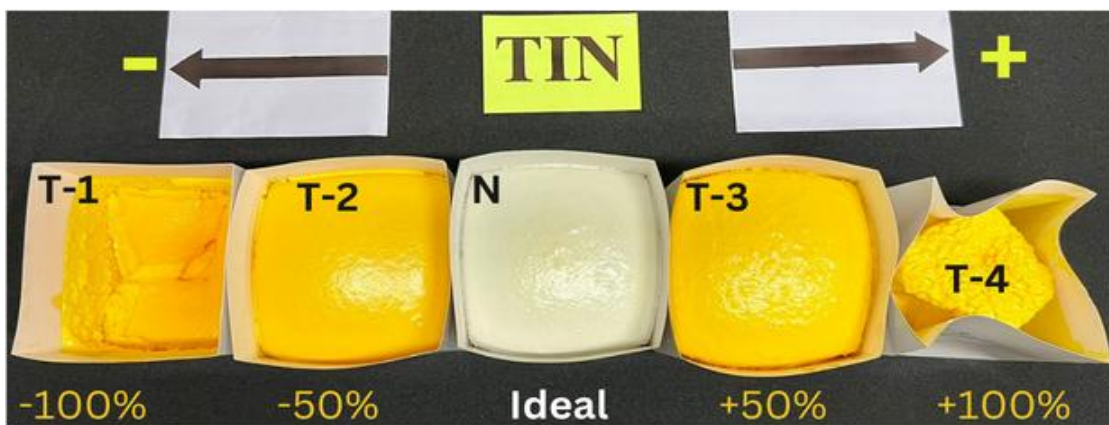


Fig. 5a: final finished flexible polyurethane foams obtained at different concentrations of tin.

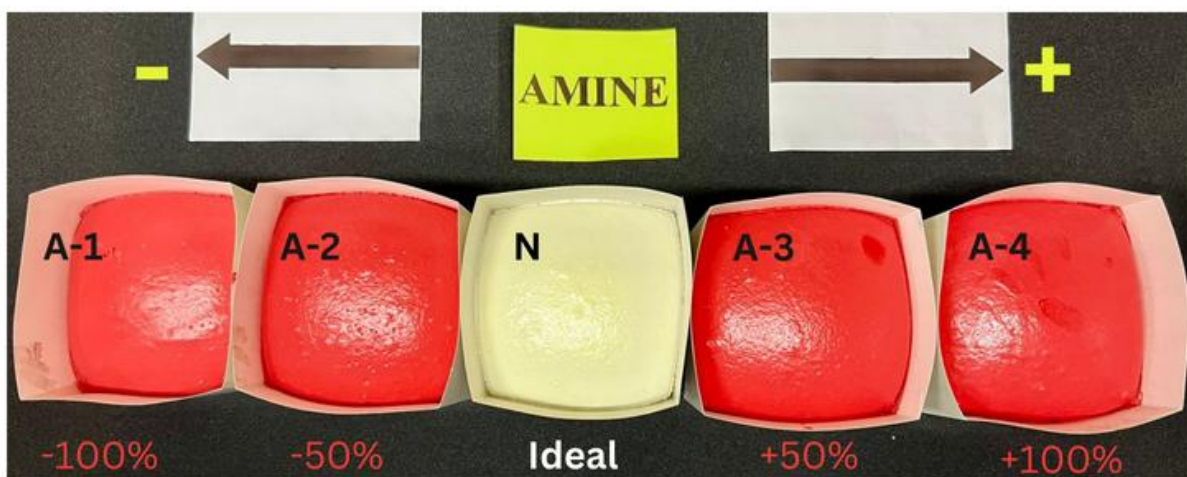


Fig. 5b: A visual illustration of the impact of varying stannous octoate (tin) concentrations on the quality of eventual flexible polyurethane foams

*Note:* (T-1) = Foam without tin, (T-2) = Foam with 50% lesser tin conc. than optimum tin conc., (N) = Foam with optimum conc. of tin, (T-3) = Foam with 50% higher tin conc. than optimum tin conc., (T-4) = Foam with 100% higher tin conc. than optimum tin conc.

Metal complexes and amine-based catalysts are the two main categories of catalysts utilized in the PU synthesis process [4,7]. Catalysts are employed to enhance the interaction between isocyanates and polyols and isocyanates and water [7]. Proper expansion is achieved by establishing a balance between the processes of polymerization (gelling) and gas generation (blowing) [5,7]. The blowing gas which is carbon dioxide, permeate into these tiny air bubbles and cause them to expand in size. The bubbles enlarge and the foam starts to rise as more blowing is produced. More blown gas emergence results in the enhancement in the diameter of the initiated bubble, whereas the number of initiated bubbles often remains constant [10]. Tertiary amines make up the majority of amine-based catalysts for flexible polyurethane foam, and their molecular structure and basicity are linked to their activity [4,9]. Reduced steric hindrance on the N atom and higher basicity in the catalyst can lead to enhanced catalytic activity. By donating the pair of electrons from the tertiary amine to the partly positive C in the isocyanate group, these catalysts form a complex bond with the isocyanate [4].

In order to investigate the effect of amine on polyurethane foam, the optimal quantity of amine was reduced and increased by 50% and 100% during the manufacturing process of A-series foams. Delay in the cream time in Foams A-1 and A-2 was noted, which will further prolong the full rise time or the total period of time taken for the production of PU foam. Catalysts are the agents that accelerate the rate of reaction. A key factor in industrial applications is the enhancement in reaction rate, as higher reaction rates translate into higher production rates [4]. Additionally, the absence of amine in foam A-1 resulted in reduced cell expansion and more closed cells, which increased the foam's density and decreased its overall height. Since a greater size of micropores tends to lower the density of the foam and can increase the overall flexibility of the material thus, controlling the morphology via blowing agents plays a crucial role in foam processing [4]. Despite having nearly the same height as foam N, foam A-2 with a 50% lower amine concentration had fewer open cells as a result of improper blowing. The perfect PU foam formation with adequate cell expansion was achieved by the right quantity of amine in Foam N, delivering an ideal porous matter. Foam A-3 had a shorter cream time than foams A-1, A-2, and N, whereas foam A-4 had the lowest cream time among all the foams in the A series. In consequence of the extreme blowing, internal and side cracks are observed in both foams. However, compared to foam A-4, foam A-3 showed fewer splits. Among the whole A series of foams, foam A-4 had the finest and smallest cells and was the most open foam. A greater amount of blowing causes collapsed foams, while a greater degree of gelation causes a closed-cell structure and shrinkage [5]. Further enhancement of amine concentration will lead to larger splits or even collapsed foam due to unbalanced gelling and blowing reactions, but increasing amine level to this extent resulted in just formation of finer cells. Figure 6a shows the end products obtained at various dosages of amines, and Figure 6b depicts the resultant foam's quality at different concentrations of amines. The A series foam results emphasize the role that amine plays in cell expansion and in the development of open foam. Accordingly, adjusting the type and quantity of catalysts has a significant impact on the expansion of the PU foam [7].



**Fig. 6a:** A pictorial representation precisely demonstrating the influence of quantity of amine on the final finished flexible polyurethane foams obtained at different concentrations of amine.



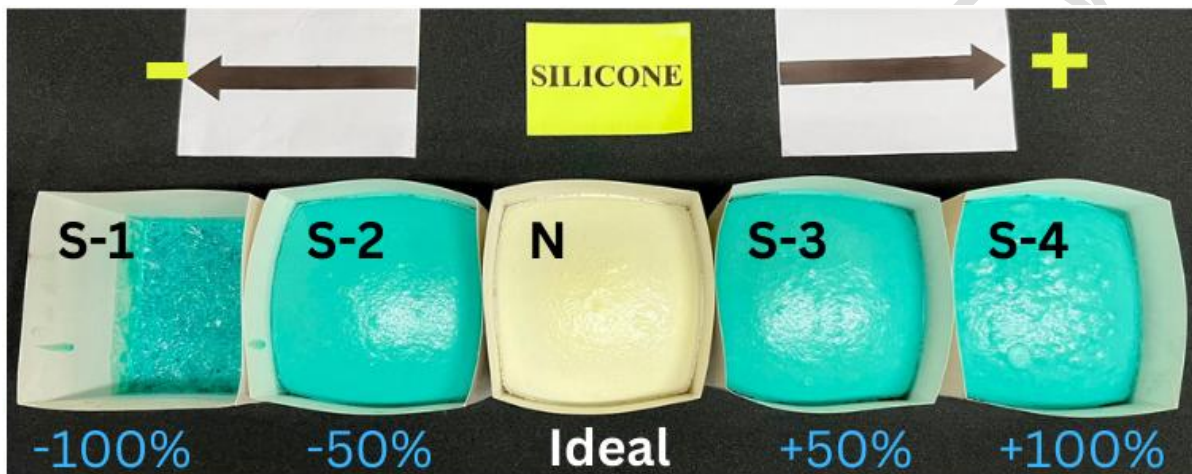
**Fig. 6b:** A visual illustration of the impact of varying amine concentrations on the quality of eventual flexible polyurethane foams.

**Note:** (A-1) = Foam without amine, (A-2) = Foam with 50% lesser amine conc. than optimum amine conc., (N) = Foam with optimum conc. of amine, (A-3) = Foam with 50% higher amine conc. than optimum amine conc., (A-4) = Foam with 100% higher amine conc. than optimum amine conc.

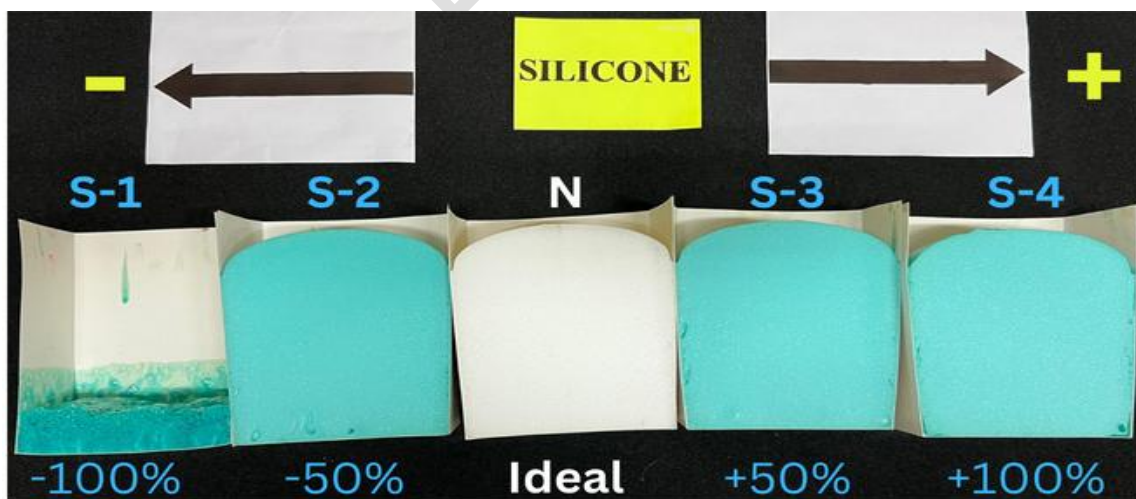
Silicone surfactants counteracts the defoaming effect of any solids added to or formed during the foam reaction, such as precipitated polyurea structures, lower surface tension, emulsify incompatible formulation ingredients, encourage the nucleation of bubbles during mixing, stabilize the rising foam by reducing stress concentrations in thinning cell-wall, and so on [9]. The silicone surfactant functions as an emulsifier and lowers the polyol's surface tension, which advances the mixing operation substantially. The silicone surfactant therefore helps to stabilize the foam thereby preventing it from collapsing [4,10]. Lowering the surface tension of a system by introducing a surfactant, reduces the work required to disperse a gas in the system and also promotes the development of smaller bubbles [9]. They also control the rate of window film thinning (by drainage into the struts) and prevent rupture by localised thinning until the cell-opening event occurs [7]. The surfactant prevents the coalescence of rapidly expanding cells until they have gained enough strength through polymerization to be self-sustaining. The absence of this action would result in complete foam collapse from ongoing cell coalescence [9]. The optimal quantity of silicone was decreased and raised by 50% and 100% during the production of S-series foams in order to examine the effect it had on polyurethane foam. Figure-7a displays the final products obtained at different silicone dosages, whereas Figure-7b illustrates the overall quality of the resultant foam at varied silicone concentrations.

To generate commercially viable foam, each foam composition requires a minimum quantity of surfactant. A foaming system without a surfactant will typically undergo catastrophic coalescence and display the boiling event [9]. Bubbles resembling the boiling effect could be observed in Foam S-1 which had no surfactant at all. Foam S-2 system demonstrated greater stability and control over cell size than S-1 foam, which was not even developed, but had inferior quality than foam N since the surfactant concentration was 50% lower than the optimal concentration of silicone. Stable although imperfect foams are frequently generated by adding a little amount of surfactant. More stable open-cell foams can be developed at

optimal concentrations [9]. An excellent and reasonably priced market product was achieved by incorporating an appropriate quantity of silicone in Foam N, thereby allowing the formation of PU foam with acceptable cell expansion and strength. Higher dosages of surfactant in foam S-3 and S-4 caused the cell windows to become overstabilized, resulting in tighter foams with diminished physical characteristics. Foam S-4 demonstrated overstability much more than any other S-series foams. Although they are used in much smaller amounts than TDI and polyol, surfactants are an important raw ingredient in the manufacturing of flexible polyurethane foam and have a substantial financial impact [12]. This also highlights the fact that the cost of production will also increase for foam S-3 & S-4. Thus, surfactants play a significant role in regulated cell opening through their impacts on bubble nucleation and stability.



**Fig. 7a:** A pictorial representation precisely demonstrating the influence of quantity of silicone on the final finished flexible polyurethane foams obtained at different concentrations of silicone.



**Fig.**

**7b:** A visual illustration of the impact of varying amine concentrations on the quality of eventual flexible polyurethane foams.

**Note:** (S-1) = Foam without silicone, (S-2) = Foam with 50% lesser silicone conc. than optimum silicone conc., (N) = Foam with optimum conc. of silicone, (S-3) = Foam with 50% higher silicone conc. than optimum silicone conc., (S-4) = Foam with 100% higher silicone conc. than optimum silicone conc.

## CONCLUSION

This detailed observational analysis was conducted in order to evaluate the impacts of TDI, water, surfactant, stannous octoate, and amine on unfilled 32-density foam to study examine their effects on forming process, texture and quality of the resultant flexible polyurethane foam (FPU). A moderate amount of TDI produced a slitted foam, however increasing TDI concentration prompted hard segments in the foam matrix and exhibited a shrunk resulting foam. Considering that TDI reacts with water to produce urea molecules and polyol and TDI interact to form urethane linkages, rigid segments in foam are the outcome of these reactions. Excess TDI resulted in the development of excess urea and urethane linkages, which dropped the foam bounce effect (resilience) in foam, whereas moderate levels of TDI resulted in no foam strength due to the shortage of hard segments and split in foam was noted. Extreme water quantities promotes a strong blowing reaction during the foaming process, which reduces the density of the foam and causing it to split. Modest water concentrations cause the foam to shrink owing to the fact that a smaller amount of carbon dioxide gas is generated, which hinders the proper expansion from proceeding. A legitimate PU matrix failed to develop and a shrunked foam was obtained as a consequence of inappropriate cell expansion.

The manufacturing of foam with outstanding characteristics at a reasonable cost demands a balanced blowing and gelling reaction. Tin-free foam lacked the strength required to attain the structure, thus resulting in a collapsed debris whereas tin concentrations too high resulted in dead/ closed-cell and shrunken foams. Tin, as a gelling ingredient, is required in foam formulation to provide strength to the foam while preserving its structure. Foam without surfactant showed no cell growth and development, while foam with high surfactant demonstrated exceptionally stable and finer cells. This proves that surfactant is crucial for the proper stability of cells in foam. In order to achieve a final product that is acceptable and permeable, amine is required. In contrast to foam with an adequate quantity of amine, foam without amine displayed a higher number of closed cells, whereas foam with double the quantity of amine exhibited more open cells. Comparative analysis indicated that amine regulates the finished material's porosity, silicone is essential for offering stability to cells and cell struts, stannous octoate delivers sturdiness required to maintain its structural integrity of the foam, TDI substantially impacts the foam's the degree of hardness and water serves as a blowing agent, which is necessary for initiating the foam's transition from liquid components to a compressible solid. Every component significantly affects the final material's chemistry, foaming process, and physical properties. Therefore, it is of the utmost importance to incorporate an optimum quantity of chemicals during the foaming process with the intention to yield an end-product foam with the superior physical attributes at an affordable price.

This study delivers solutions for foaming challenges encountered by novices, researchers, and industry professionals functioning in the PU foam sector by merely observing and monitoring the physical texture of the resulting PU foam, the reason for the problem can be easily detected, assessed and rectified. Achieving the finest quality foam is the primary objective of this study of foam principles, that is designed to demonstrate, regulate and improvise the

boundaries of foam characteristics. This work presents an informative and in-depth perspective of the relationships between the FPU's structure, physical attributes, formulation components as well, and chemical mechanisms.

## REFERENCES

1. Chris-Okafor, P. U., Uchechukwu, A. R. M., Nwokoye, J. N., & Ukpai, E. U. (2017). Effects of coconut husk and corn cob as fillers in flexible polyurethane foam. *American Journal of Polymer Science and Technology*, 3(4), 64-69. doi: 10.11648/j.ajpst.20170304.12
2. Souza, D. A. D., Araujo, D. M. D., Carvalho, C. D. F., & Yoshida, M. I. (2008). Physico-chemical analysis of flexible polyurethane foams containing commercial calcium carbonate. *Materials research*, 11, 433-438. <https://doi.org/10.1590/S1516-14392008000400009>
3. Suleman, S., Khan, S. M., Gull, N., Aleem, W., Shafiq, M., & Jamil, T. (2014). A comprehensive short review on polyurethane foam. *Int. J. Innov. Sci. Res*, 12(1), 165-169.
4. de Souza, F. M., Sulaiman, M. R., & Gupta, R. K. (2021). Materials and chemistry of polyurethanes. In *Materials and Chemistry of Flame-Retardant Polyurethanes Volume 1: A Fundamental Approach* (pp. 1-36). American Chemical Society. DOI: 10.1021/bk-2021-1399.ch001
5. Mahmoud, A. A., Nasr, E. A. A., & Maamoun, A. A. H. (2017). The influence of polyurethane foam on the insulation characteristics of mortar pastes. *Journal of Minerals and Materials Characterization and Engineering*, 5(2), 49-61. <https://doi.org/10.4236/jmmce.2017.52005>
6. Van Gheluwe, P., & Leroux, J. (1983). Sequential nature of the exothermic reactions leading to the formation of flexible polyurethane foams. *Journal of Applied Polymer Science*, 28(6), 2053-2067. <https://doi.org/10.1002/app.1983.070280618>
7. Gama, N. V., Ferreira, A., & Barros-Timmons, A. (2018). Polyurethane foams: Past, present, and future. *Materials*, 11(10), 1841. <https://doi.org/10.3390/ma11101841>
8. Bailey Jr, F. E., & Critchfield, F. E. (1981). Chemical reaction sequence in the formation of water-blown, urethane foam. *Journal of Cellular Plastics*, 17(6), 333-339. <https://doi.org/10.1177/0021955X8101700604>
9. Dow Polyurethanes Flexible foams. (1997). The DOW Chemical company <https://www.scribd.com/document/551466732/DowPolyurethanesFlexibleFoams>
10. Ilaboya, R., Umukoro, L., Omofuma, F. E., & Atikpo, E. (2011). Effects of Formulation Parameters on the Properties of Flexible Polyurethane Foam (FPF). *World Applied Sciences Journal*, 14(1), 167-174.
11. Burkhart, G., Kollmeier, H. J., & Schloens, H. H. (1984). The Importance of Catalysts for the Formation of Flexible Polyurethane Foams. *Journal of Cellular Plastics*, 20(1), 37-41. <https://doi.org/10.1177/0021955X8402000103>

12. Ogunleye, O. O., Oyawale, F. A., & Suru, E. (2008). Effects of castor oil on the physical properties of polyether based Flexible Polyurethane foam. *Advances in Natural and Applied Sciences*, 2(1), 10-16.
13. Choi, H. J., Choe, H., Seo, W. J., & Kim, J. H. (2019). Physical properties of flexible polyurethane foams manufactured by varying toluene diisocyanate contents. *POLYMER-KOREA*, 43(4), 532-539.
14. Victor<sup>1</sup>, E. I., Louis, I. C., Alfred, N. O., & Ozioma<sup>4</sup>, U. N. (2019). Use of Chicken Eggshells as Fillers in Flexible Polyurethane Foam Production. *International Journal of Industrial Engineering*, 3(1), 1-6.
15. Burt, J. G., & Brizzolara, D. F. (1977). Auxiliary Blowing Agents for Flexible Polyurethane Foams. *Journal of Cellular Plastics*, 13(1), 57-61. <https://doi.org/10.1177/0021955X7701300106>
16. Jaiswal, H., Gopalamudram, M. N., & Maitra, J. (2024). Improvisation in wicking property of flexible polyurethane foams by adding bamboo and gelatin fillers. *Brazilian Journal of Development*, 10(1), 1143–1156. <https://doi.org/10.34117/bjdv10n1-075>
17. Szycher, M. (Ed.). (1999). *Szycher's handbook of polyurethanes*. CRC press.
18. Akindoyo, J. O., Beg, M., Ghazali, S., Islam, M. R., Jeyaratnam, N., & Yuvaraj, A. R. (2016). Polyurethane types, synthesis and applications—a review. *Rsc Advances*, 6(115), 114453-114482. <https://doi.org/10.1039/C6RA14525F>
19. Latinwo, G. K., Aribike, D. S., Susu, A. A., & Kareem, S. A. (2010). Effects of different filler treatments on the morphology and mechanical properties of flexible polyurethane foam composites. *Nature and Science*, 8(6), 23-31.
20. Das, A., & Mahanwar, P. (2020). A brief discussion on advances in polyurethane applications. *Advanced Industrial and Engineering Polymer Research*, 3(3), 93-101. <https://doi.org/10.1016/j.aiepr.2020.07.002>
21. Dutta, A. S. (2018). Polyurethane foam chemistry. In *Recycling of polyurethane foams* (pp. 17-27). William Andrew Publishing. <https://doi.org/10.1016/B978-0-323-51133-9.00002-4>
22. Saunders, J. H., & Frisch, K. C. (1962). *Polyurethanes: chemistry and technology* (Vol. 16). Interscience Publishers.
23. Rokicki, G., Parzuchowski, P. G., & Mazurek, M. (2015). Non-isocyanate polyurethanes: synthesis, properties, and applications. *Polymers for Advanced Technologies*, 26(7), 707-761. <https://doi.org/10.1002/pat.3522>
24. Suleman, S., Khan, S. M., Jameel, T., Aleem, W., & Shafiq, M. (2014). Synthesis and characterization of flexible and rigid polyurethane foam. *Asian Journal of Applied Sciences*, 2(5).
25. Modesti, M., Lorenzetti, A., & Dall'Acqua, C. (2005). Long-term performance of environmentally-friendly blown polyurethane foams. *Polymer Engineering & Science*, 45(3), 260-270. <https://doi.org/10.1002/pen.20272>
26. Wang, C. Q., Lv, H. N., Sun, J., & Cai, Z. S. (2014). Flame retardant and thermal decomposition properties of flexible polyurethane foams filled with several halogen-free flame retardants. *Polymer Engineering & Science*, 54(11), 2497-2507. <https://doi.org/10.1002/pen.23794>
27. Onwuka, C. O., Anekwe, O. J., Ogudo, M. C., & Chris-Okafor, P. U. (2021). Impact of Mixed Fillers on the Physico-mechanical Properties of Flexible Polyether Foam. *Organic Polymer Material Research*, 3(1), 17-23. <https://doi.org/10.30564/opmr.v3i1.3604>
28. Khemani, K. C. (1997). Polymeric foams: an overview. **DOI:** 10.1021/bk-1997-

29. Baysal, G., & Kasapbası, E. (2017). Polyurethanes and usage areas. *Global Journal of Science Frontier Research B: Chemistry*, 17(1), 29-35.
30. Ooi, T. L., Chuahl, C. H., Ahmadz, S., & Malaysia, K. L. (2007). Effect of Isocyanate Index on Physical Properties of Flexible Polyurethane Foams. *Malaysian Journal of Science*, 26(2), 91-98.
31. Ramesh, S., Tharanikkarasu, K., Mahesh, G. N., & Radhakrishnan, G. (1998). Synthesis, physicochemical characterization, and applications of polyurethane ionomers: A review. <https://doi.org/10.1080/15583729808546030>
32. Chen, L., Blizard, K., Straff, R., & Wang, X. (2002). Effect of filler size on cell nucleation during foaming process. *Journal of cellular plastics*, 38(2), 139-148. <https://doi.org/10.1177/0021955X02038002245>
33. Oyetunji, O. R., & Hamed, B. M. (2016). The effect of overall density on the mechanical properties of flexible polyurethane foam. *J Manag Inf Technol Eng*, 2(1), 19-32.
34. Usman, M. A., Adeosun, S. O., & Osifeso, G. O. (2012). Optimum calcium carbonate filler concentration for flexible polyurethane foam composite. *Journal of Minerals & Materials Characterization & Engineering*, 11(3), 311-320.
35. Aou, K., Meng, H., & Thiede, C. (2016). New Cell Structure Control Technology for Ultra-High Air Flow Viscoelastic Polyurethane Foam.
36. Javni, I., Song, K., Lin, J., & Petrovic, Z. S. (2011). Structure and properties of flexible polyurethane foams with nano-and micro-fillers. *Journal of cellular plastics*, 47(4), 357-372. <https://doi.org/10.1177/0021955X11398115>
37. Ofora, P. U., Eboatu, A. N., Arinze, R. U., & Nwokoye, J. N. (2014). Effects of Fillers of Animal Origin on the Physiomechanical Properties of Utility Polymer. *ISOR-Journal of Applied Chemistry (IOSR-JAC)*, 7(7), 19-23.
38. Wolska, A., Goździkiewicz, M., & Ryszkowska, J. (2012). Thermal and mechanical behaviour of flexible polyurethane foams modified with graphite and phosphorous fillers. *Journal of Materials Science*, 47, 5627-5634. DOI 10.1007/s10853-012-6433-z
39. Ogudo, M. C., & Chris-Okafor, P. U. (2021). IMPACT OF MIXED AGRO WASTE AS HYBRID FILLERS ON THE MECHANICAL, MORPHOLOGICAL, WATER ABSORPTION AND BIODEGRADATION PROPERTIES OF HIGH DENSITY POLYETHYLENE COMPOSITES. *Journal of Basic Physical Research*, 10(1), 39-48.
40. Wolska, A., Goździkiewicz, M., & Ryszkowska, J. (2012). Influence of graphite and wood-based fillers on the flammability of flexible polyurethane foams. *Journal of Materials Science*, 47, 5693-5700. DOI 10.1007/s10853-012-6394-2
41. Bryśkiewicz, A., Zieleniewska, M., Przyjemaska, K., Chojnacki, P., & Ryszkowska, J. (2016). Modification of flexible polyurethane foams by the addition of natural origin fillers. *Polymer Degradation and Stability*, 132, 32-40. <https://doi.org/10.1016/j.polymdegradstab.2016.05.002>
42. Onuegbu, T. U., Ejikeme, C., Obi, J. N., & Ekejiuba, I. O. C. (2010). The Use of Chicken Bone Powder as Filler in Flexible Polyether Foam. *Ultra Scientist*, 22(3), 613-618.
43. Onuegbu, T. U., Ejikeme, C., & Obi, J. N. (2011). The Effects of Animal Wastes on the Tensile Strength, Elongation-at-break and Hardness of Flexible Polyether Foam. *International Journal of Chemistry*, 21(2), 129-134.
44. Navarro, M. V., Vega- Baudrit, J. R., Sibaja, M. R., & Melero, F. J. (2012, December). Use of rice husk as filler in flexible polyurethane foams.

In *Macromolecular Symposia* (Vol. 321, No. 1, pp. 202-207). Weinheim: WILEY- VCH Verlag. <https://doi.org/10.1002/masy.201251136>

45. Onuegbu, T. U., Ugwu, L. E., & Ogunfeyitimi, O. (2013). Physio-mechanical Properties of Flexible Polyether Foam: Comparative effects of fillers. *Chemistry and material research*, 3(9), 48.

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