

THE ROLE OF AMINE CATALYST ON THE MECHANICAL PROPERTIES AND MORPHOLOGY OF POLYURETHANE FOAM MORTAR MIXES

A. A. Mahmoud¹, A. A. ma'moun¹, E. A. Nasr² and E. A. Soliman³

¹ Department of physics and Mathematics, Faculty of Engineering, Ain Shams University.

² Department of structural engineering, Faculty of Engineering, Ain Shams University.

ABSTRACT

Rigid Polyurethane foam are found virtually everywhere in our modern world and are used in sound and thermal insulation applications such as refrigerators, insulated buildings, thermosets. Amine catalysts are used to control and/or balance both the gelling reaction and the gas-forming or foaming reaction responsible for foam formation. Although several organometallic compounds or salts may be used as catalysts in the production of polyurethanes, many polyurethane manufacturers use either tertiary aliphatic amines or alkanolamines. Amine catalysts are typically 0.1 to 5.0 percent of a polyurethane formulation. In this work the effect of amine catalyst on the mechanical properties and morphology of polyurethane foam were investigated. Also the thermal conductivity and sound absorption coefficient for polyurethane foam mortar formulations were determined. The morphology of polyurethane foam contains different percentages of amine was investigated using scanning electron microscope. It was clear from the results that polyurethane foam has good thermal and sound insulation capabilities.

KEY WORDS: Polyurethane Foam, Amine Catalyst, Compressive Strength, Thermal Conductivity, Sound Absorption Coefficient.

1. INTRODUCTION:

Polyurethanes (PUs) are versatile engineering materials which find a wide range of applications because their properties can be readily tailored by the type and composition of their components. Catalysis plays a fundamental role in industrial chemical transformations. More than 85% of industrial chemicals are made through catalytic processes since catalysts provide more energetically favorable reactions in comparison to non-catalytic ones, thus allowing the use of milder reaction conditions [1]. Catalysts have significant influence on the polymerization reaction mechanism e.g. Free-radical, cationic, anionic and insertion polymerization [2]. The right choice of the catalyst has a significant effect on polymer formation and on the time required for polymerization. Moreover, the catalyst determines the properties of obtained polymers such as polyurethanes which are manufactured by polyaddition reaction between di- or poly-isocyanates and two- or multi-functional polyols. Flexible foams are low-density cellular polyurethane materials, with limited and reversible resistance to compression. Among them, the most widely used are water-blown slabstock and molded flexible foams. Proper selection of catalyst formulation in the preparation of polyurethane foams influences the properties which are required for a number of applications in bedding, furniture and automotive industry [3]. The polyurethane market accounts for around 7% of the global polymer market [4]. Generally, polyurethanes can be classified into flexible foams (Figure 1.a) (50%; furniture, mattresses, automotive seats), rigid foams (Figure 1.b) (30%; insulation and structural materials), as well as coatings, adhesives, sealants and elastomers (20%; paints,

binders, lacquers and elastomeric materials) [5, 6]. From the chemical point of view, polyurethanes are obtained from a range of different reactions, including reaction between isocyanate (-NCO) and polyol (-OH) which gives 'urethane' groups (-NHCOO). Polyurethane foam formation essentially consists of two reactions (Figure 2). The first one is isocyanate-polyol reaction, known as the gelling one which forms the backbone urethane group. This reaction leads to the formation of a cross-linked polymer, since polyols with several hydroxyl groups are used. The secondary reaction of a urethane group with an isocyanate group to form an allophanate group is another possible way to further cross-link the polymer [7].

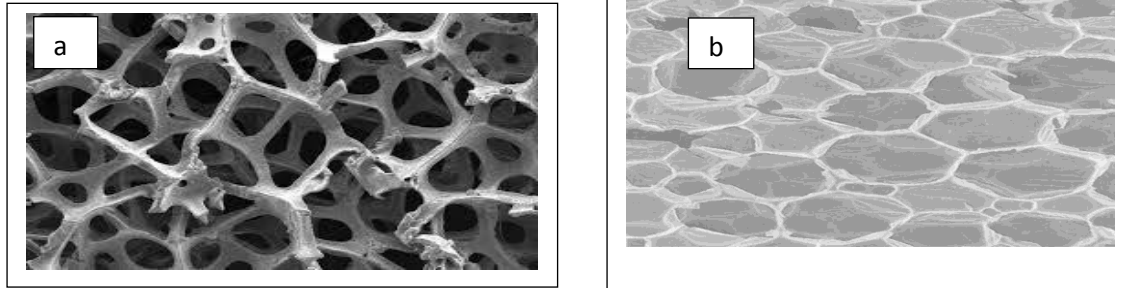


Figure 1: (a) Open cell structure of PUF.

(b) Closed cell structure of PUF [8].

The second one is isocyanate-water reaction, known as the blowing one which forms the carbamic acid which decomposes to give an amine and carbon dioxide gas in the form of bubbles. Next, the formed amine group reacts with another isocyanate group to give a disubstituted urea. The second part of the blowing reaction contributes to chain extend the aromatic groups of the isocyanate molecules to form linear hard segments. Another secondary reaction involves the formation of biuret and allophanate linkages which could lead to the formation of covalent cross-linking (Figure 2). The correct balance between these reactions is required since it controls the foam stability and allows to achieve foams with tailored physical properties. The catalysts used in the synthesis of polyurethane foams help to precisely control the relative reaction rates of the isocyanate with both polyol and water. The imbalance between them can cause the foam collapse or formation of inappropriate cells that can be closed or opened prematurely [3, 5, 7, 9].

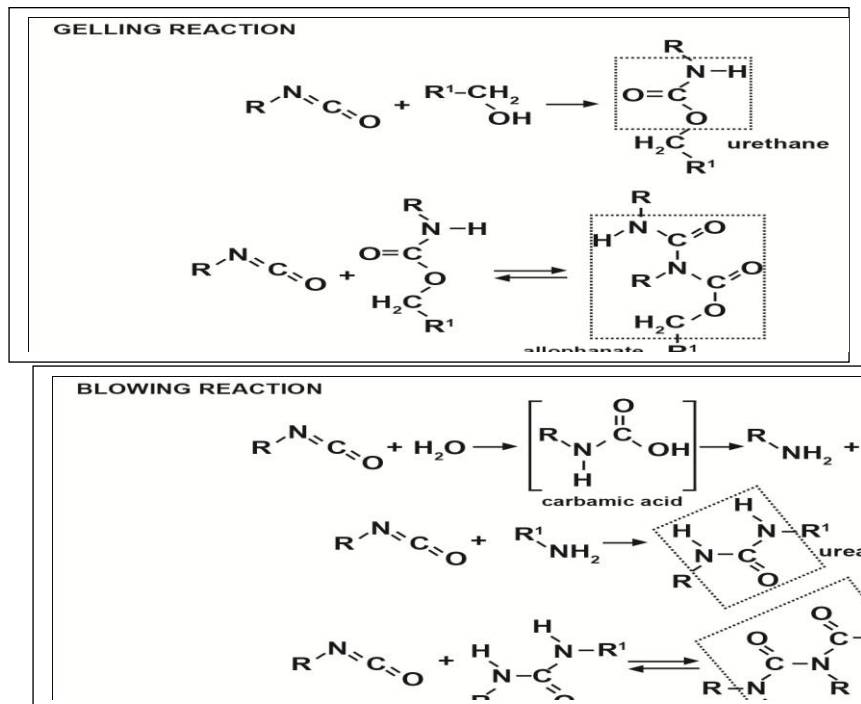


Fig. 2: Scheme of gelling and blowing reactions in the preparation of polyurethane foam [7].

There are organometallic catalysts used in polyurethane technology, i.e. amine catalysts and organometallics generally catalyze the isocyanate-water reaction better than the amine catalysts, while organometallics are considered as gel catalysts although they catalyze blowing reactions [3,5]. The amine catalysts, especially tertiary amines, are the most common and effective basic catalysts in the synthesis of polyurethanes. One of the most common amine catalysts is 1,4-diazobicyclo[2,2,2]octane (DABCO) Figure 3 [10].



One of the most common amine catalysts is 1,4-diazobicyclo[2,2,2]octane (DABCO) Figure 3 [10].

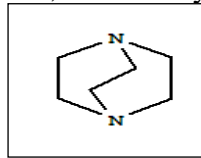
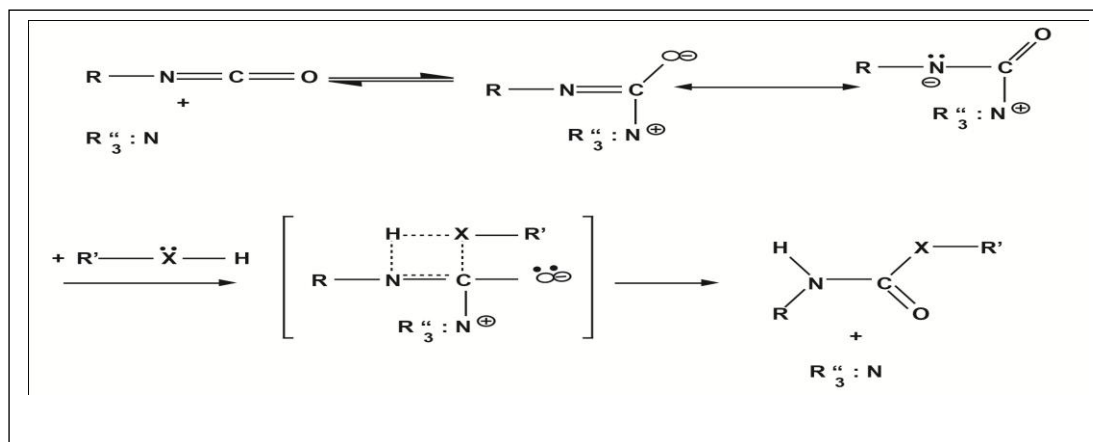


Figure 3: Structure of 1,4-diazobicyclo [2, 2, 2] octane [10].

It catalyzes both isocyanate-polyol and isocyanate-water reactions. One of the drawbacks of using tertiary amines is their offensive fish like odor and high volatility. Increasing environmental concerns toward decreasing emissions of volatile organic compounds (VOC) have contributed to the development of nonvolatile catalysts. Two mechanisms have been proposed to describe the amine catalyzed urethane formation (Figure 4). The first mechanism proposed by Baker assumes formation of a complex consisting of a tertiary amine catalyst and an isocyanate, which is followed by the attack of nucleophile. On the contrary Farka postulated formation of urethane through protonation of the catalyst by interaction of the amine with a proton source (such as polyol, water or amine) to form a complex, which subsequently reacts with the isocyanate [3, 11]. The type and concentration of amine catalyst can be selected to satisfy process requirements such as cream times, rise profiles, gel times and even cure of the outer surface skin [12].

The manufacturing of flexible polyurethane foams requires precise kinetic control over the above mentioned competing gelling and blowing reactions. If the blowing reaction is much faster than the gelling one, the cells will open too early, before reaching adequate viscosity. This will inhibit the formation of strong foam struts and foam will collapse. On the other hand, if the gelling reaction is faster than the blowing one, the formed polyurethane network will entrap the gas and suppress formation of bubbles, thus resulting in foam with closed cells. Therefore, it is important to find a kinetic balance point for the foaming process [13].

Baker's mechanism:



Farka's mechanism:

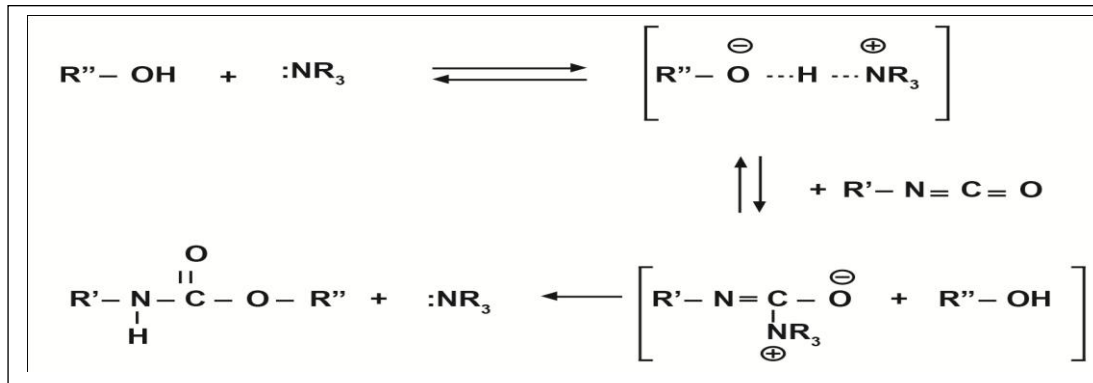


Figure 4: Mechanisms of urethane formation catalyzed by amine [12]

The basis for sustainable economic growth is the need of environmental protection. Production of flexible polyurethane foams requires a variety of chemicals and additives. At present, great importance in polyurethane industry is related to the application of vegetable oil-based polyols instead of petrochemical equivalents [14,15], as well as to the usage of non-volatile, reactive catalysts, since unreacted traditional amine catalysts create toxic vapors [16].

Experimental program:

2. Materials

2.1 polyurethane foam materials:

The foam formulations were prepared using:

- VORANOL 230-056 having hydroxyl value equal to 56 mg KOH/g, molecular weight of 3000 g/mole and viscosity at 25⁰C equal to 235 mpa.s (Polyether polyol),
- Cosmonate M-200 PMDI (Polymeric methylene diphenyl diisocyanate, kumho mitsui chemicals),
- Dabco 33-LV catalyst (Triethylene diamine, Air Products Company),
- Dabco T-99 catalyst (Stannous octoate, Air Products Company),
- Dabco SI3504 (Silicon surfactant, Air products company) and
- Clean tap water.

2.2 polyurethane foam mortar materials:

Polyurethane foam mortar is produced by a combination of Portland cement, sand, potable water and appropriate polyurethane foaming.

Table 1: Physical properties of cement:

Property	Fineness (Cm ² /gm)	Initial setting time	Final setting time	Expansion(lechatilier test)mm
Test results	2790	2hrs and 10 minutes	6hrs and 20 minutes	1.00

Table 2: Physical properties of sand:

Property	Specific gravity	Bulk density (t/m3)	Fineness modulus	Clay, silt and fine dust%(by volume)	T.D.S.
Test results	2.5	1.585	2.3	2.8	0.06%

Table 3: Chemical analysis of water:

Component	PH Value	Total dissolved salts	calcium	magnesium	sodium	potassium	chloride	Sulphates	iron
Test results	7.25	610p.p.m	75p.p.m	125p.p.m	18p.p.m	15p.p.m	180p.p.m	170p.p.m	0.1p.p.m

2.3 preparations of Polyurethane foams:

Rigid polyurethane foam (PUF) were synthesized by two-shot method. At first, polyol mixture, catalysts and surfactant were put into a reactor and mixed for 15 sec using brushless type stirrer at the rotating speed of 2,500 rpm. After premixing, blowing agent was added to the mixture of reactants and mixed for 10 sec using brushless type stirrer at 3,000 rpm. Finally PMDI then was added to the reactants and all the reactants were mixed for 7 sec using brushless type stirrer at 5,000 rpm. Finally, the reactants were poured into the open stainless steel mold (20 Cm × 20 Cm × 15 Cm) (length × width × thickness) to produce free-rise foams and cured for 1 week at room temperature. In order to avoid the change of thermal conductivity and mechanical strength, the curing was done at room temperature.



Figure 5: Polyurethane foam samples

2.4 preparations of Polyurethane-mortar foam:

Polyol, catalysts and surfactant were put into a reactor and mixed for 15 sec using brushless type stirrer at the rotating speed of 2,500 rpm. After premixing, blowing agent was put into the mixture of reactants and mixed for 10 sec using brushless type stirrer at 3,000, then added to the cement and sand and mixed for 20 sec using brushless type stirrer at the rotating speed of 3,000 rpm. Finally PMDI was added into the reactants and all the mixes were stirred for 7 sec using brushless type stirrer at 5,000 rpm.

Table 4: Properties of used materials

Component	Description	Company
cement	Ordinary Portland cement (CEM I – 52.5 N)	Suez company
sand	natural sand	
Polyol (Voranol™ 3137)	A 3100 Mw polyether polyol with functionality of 3, 87% propylene oxide and 13% ethylene oxide	Dow Chemical
Water	Clean tap water	
Isocyanate (COSMONATE M-200) (PMDI)	Polymeric methylene diphenyl diisocyanate	Kumho mitsui chemicals)
Silicone surfactants	Silicone-polyether copolymer	Air Products
Amine catalyst (Dabco@33LV)	33% triethylenediamine in 67% dipropylene glycol	Air Products
Tin catalyst T-9	Stannous octoate catalyst	Air Products

Table 5: Typical rigid Foam mortar Formulations

Chemicals *	PUF-1#	PUF-2#	PUF-3#	PUF-4#	PUF-5#	PUF-6#	PUF-7#
Cement (Gram)	250	250	250	250	250	250	250
Sand(Gram)	750	750	750	750	750	750	750
Polyol (Voranol™ 3137)	131.25	131.25	131.25	131.25	131.25	131.25	131.25
Water	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Isocyanate (COSMONATE M-200) (PMDI)	157.5	157.5	157.5	157.5	157.5	157.5	157.5
Silicone surfactants	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Amine catalyst (Dabco@33LV)	2.6	3.15	3.78	4.1	4.72	5.1	5.5
Tin catalyst (Dabco T-9)	0.65	0.65	0.65	0.65	0.65	0.65	0.65

*part per weight (p.p.wt)

2.5 Experimental tests

2.5.1 Polyurethane foam tests:

2.5.1.1 Compression test: Compressive strength of the cured polyurethane foam was measured according to (ASTM) standard D 1621 in parallel and perpendicular direction to the foam rise by Zwick Roell (Germany) device. Specimens' dimensions of 10Cmx10Cmx8Cm (length, width, thickness) were cut out from the top part of the foam buns. Compressive properties were determined in a 10 kN force range, 15 mm displacement till failure and record the reading.



Figure 6: Zwick Roell device (Germany), compressive strength determination

2.5.1.2 Scanning electron microscopy study: Polyurethane foams were investigated with a scanning electron microscope (SEM) FEI Inspect S, Czech Republic. The specimens were mounted on an aluminum stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination. The accelerating voltage was 30 kV and magnification was 70.



Figure 7: Scanning electron microscope measurement

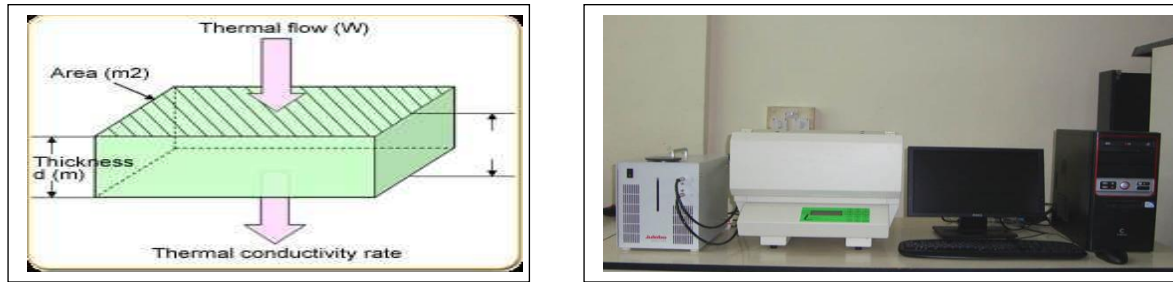


Figure 8: Thermal conductivity measurement by lasercomp Fox 314

2.5.2 Polyurethane foam-mortar tests:

2.5.2.1 Thermal conductivity: Thermal conductivity was measured using thermal conductivity analyzer (model TCA Point2, Anacon) according to ASTM C518. A sample was placed in the test section between two plates which are maintained at different temperatures during the test. Dimensions of the specimen were 30cm × 30cm × 3cm (width × length × thickness). The thermal conductivity of samples was measured.

2.5.2.2 Sound absorption measurements: The measurement and calculation procedures for the determination of the normal incidence sound absorption coefficient and related acoustic properties of a sample was carried out using a two-microphone impedance tube (Type 4206). It is based on ISO 10534-2 and ASTM E1050 and includes transfer function calibration to eliminate the effects of phase and amplitude mismatches between the two measurement channels. The large sample tube has an inner diameter of 100 mm. It is rated for a frequency range of 100 to 1600 Hz.

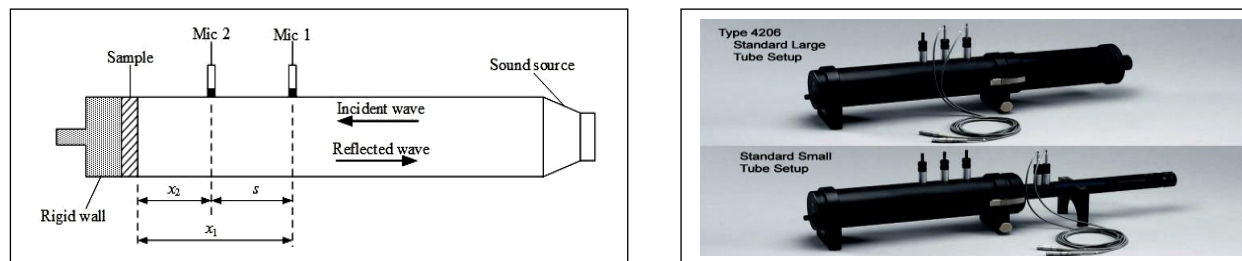


Figure 9: Sound absorption coefficient measurement.

3. RESULTS AND DISCUSSION

Polyurethane foam continue to grow at a rapid pace throughout the world, because of their light weight, excellent strength to weight ratio, superior thermal and acoustic insulating capabilities, energy absorption ability and their good cushioning and comfort features. In addition, foams can have the ability to absorb an enormous energy, which makes them more useful in cushioning and packaging applications compared to the solid polymer. Another advantage of polymeric foams is the small amount of polymer mass needed to obtain high volume, because of cellular structure with entrapped gas.

3.1 compression strength

Table 6: Compressive strength results of polyurethane foam.

Sample	PUF-1#	PUF-2#	PUF-3#	PUF-4#	PUF-5#	PUF-6#	PUF-7#
Compression strength(N/mm ²)	0.10161	0.12671	0.14424	0.13533	0.10587	0.0727	0.06724

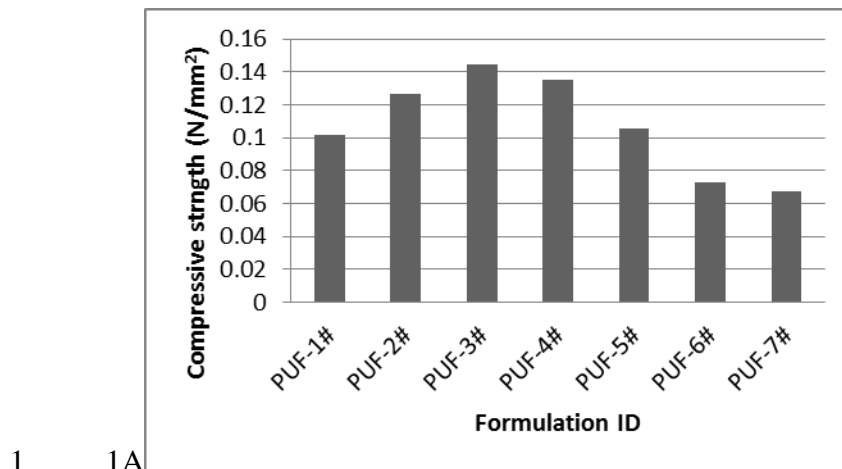


Figure 10: Shows the relation between different percentages of amine catalyst and compressive strength of polyurethane foam

Analysis of data in (Table 6) show that compressive strength increased by increasing amine catalyst from PUF-1# to PUF-3#, in contrast compressive strength decreased by decreasing amine catalyst from PUF-4# to PUF-7# as shown in (Figure10). This could be due to amine catalyst used as gelling and blowing catalyst at the same time. At the low percentages of amine catalyst, gelling reaction improved lead to high compressive strength. While at high percentage of amine catalyst, blowing enhanced at the expense of gelling reaction which lead to decrease in compressive strength.

3.2 Effect of amine catalyst on cell morphology:

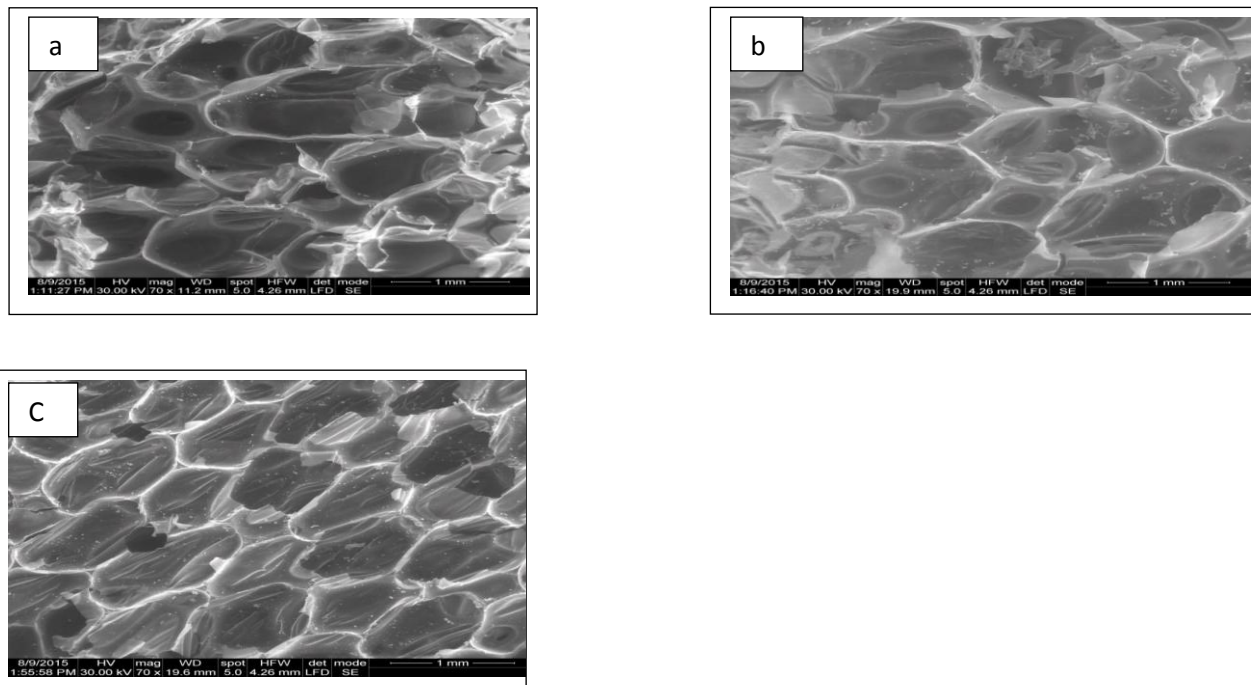


Fig. 11: SEM micrographs for PUF-1# (a), PUF-2# (b), PUF-3# (c) showing the effect of increasing Amine catalyst on the cellular structure of polyurethane foam.

Amine catalyst has a great influence on the morphological structure of polyurethane foam. The cell morphology is an important factor that affects the physico-mechanical properties of cellular structure of polyurethane foam. (Figure 11) shows the morphologies of different samples from polyurethane foam containing different dosages from amine catalyst with the same magnification. Comparing with PUF-1#, PUF-2# and PUF-3# it can be seen that the cell shapes are approximately spherical, polyhedral and symmetrical. Microscopic examination of the resulting internal structure reveals that all samples contain open and closed cells. The latter accounting for the greater portion in PUF-1#, PUF-2# and PUF-3# this is due to formation of biuret linkage which lead to more rigid cell structure.

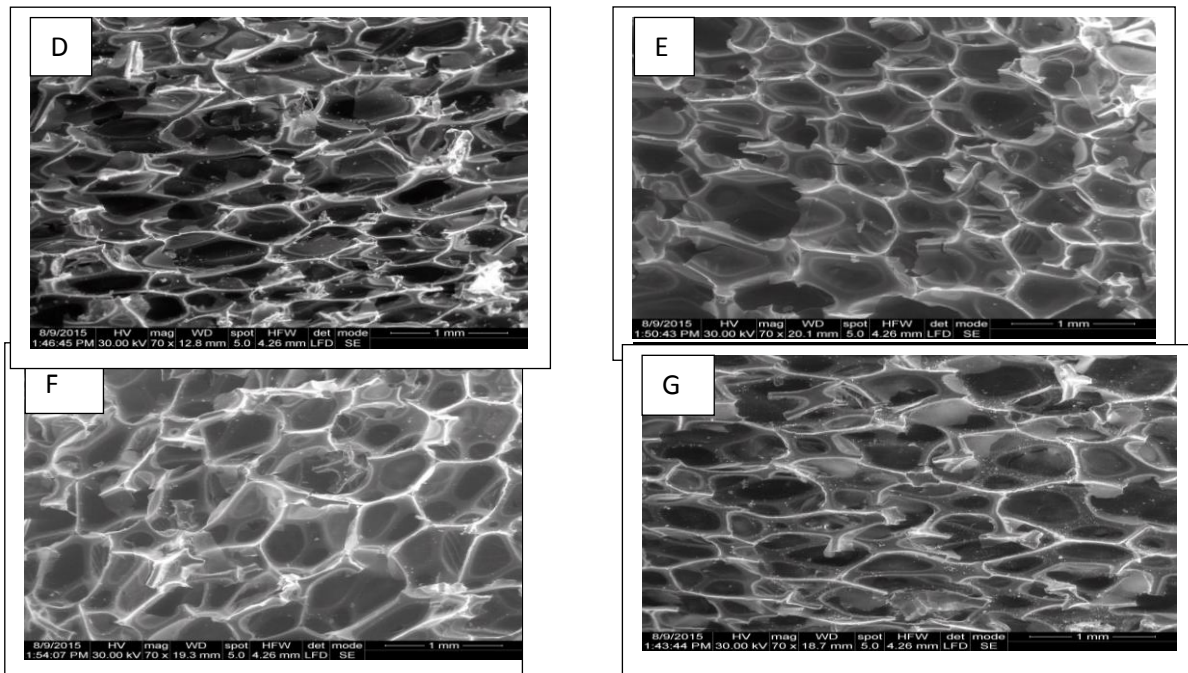


Fig. 12: SEM micrographs for PUF-4# (d), PUF-5# (e), PUF-6# (f), PUF-7# (g) showing the effect of increasing Amin catalyst on the cellular structure of polyurethane foam.

Also increasing amount of amine catalyst in polyurethane mixes enhanced blowing reaction at the expense of gelling reaction which leads to increase pores in cell structure of polyurethane foam as shown in (Figure 12) PUF-4#, PUF-5#, PUF-6# and PUF-7 #

3.3 sound absorption of polyurethane mortar mixes:

The sound absorption coefficient measured at different frequencies (from 100Hz to 1600Hz) for each formulation (Figure 13) which indicate the higher ability of polyurethane polymer to absorb sound waves than sample containing no polymer (blank).

Analysis of the data in (Table 7) shows that polyurethane foam has good acoustic characteristic, due to large amount of pores in the cellular structure of polyurethane foam which absorbs sound waves and convert to other forms of energy, usually heat this can be shown in (Figure 14).

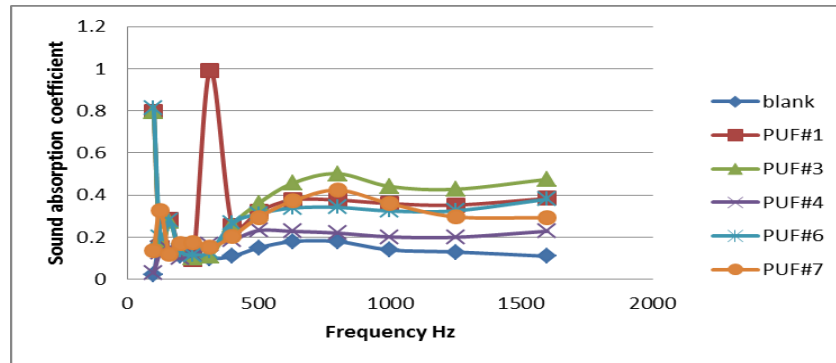


Fig. 13: Sound absorption coefficient vs. frequency of the different samples of polyurethane foam containing various dosages of amine catalyst.

Table 7: Sound absorption coefficient for selected mixes of polyurethane mortar.

Sample	blank	PUF-1#	PUF-3#	PUF-4#	PUF-6#	PUF-7#
Sound absorption coefficient	0.14	0.375	0.345	0.322	0.3	0.256

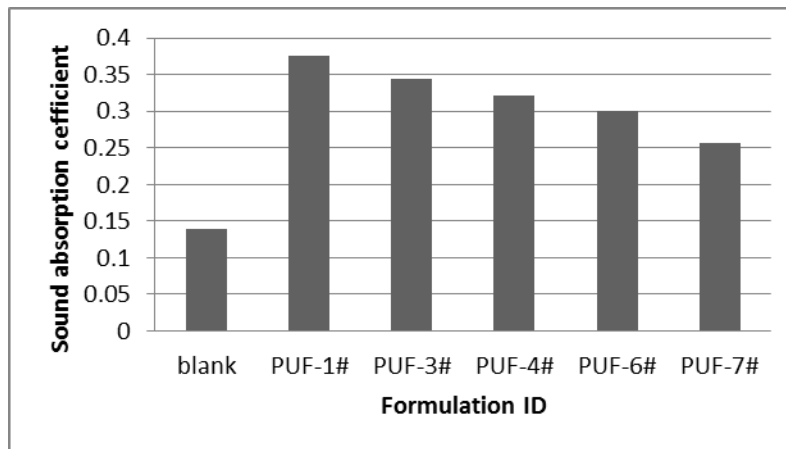


Fig. 14: Relation between sound absorption coefficient and different formulations from polyurethane foam contains dissimilar dosages from amine catalyst.

3.4 Thermal conductivity for polyurethane mortar mixes

Analysis of data in (Table 8) indicates that foam has low thermal conductivity comparing with limestone, concrete, sand and rubber. This could be due to cellular structure of foam material as shown in (Figure 15). The total thermal conductivity is the sum of the conductivities of both the gas and solid phases in polyurethane foam. It is clear from the results in (Table 9) that the thermal conductivity is very low for polymeric foam comparing with sample containing no polymer (Blank) as shown in (Figure 16) because the amount of solid in the foam is very small (on the order of 3%-10% of the total volume) and volume of gas is very high. The gas phase contributes the most to heat transfer. The thermal conductivity of a gas decreases with an increase in molecular weight, so a heavy gas is more desirable as a blowing agent. After usage and time the gas phase in the foam is replaced by air which has just slightly higher thermal conductivity than some heavier blowing agent like CO₂. The large molecular weight compounds also diffuse much slower through the polymer matrix, and the replacement of air into the foam goes much slower, keeping the thermal conductivity as low as possible.

Table 8: Thermal conductivity values for different materials [17].

Materials	Limestone	concrete	sand	rubber	foam	cotton	Still air
thermal conductivity	1	0.8	0.33	0.2	0.122	0.06	0.0262

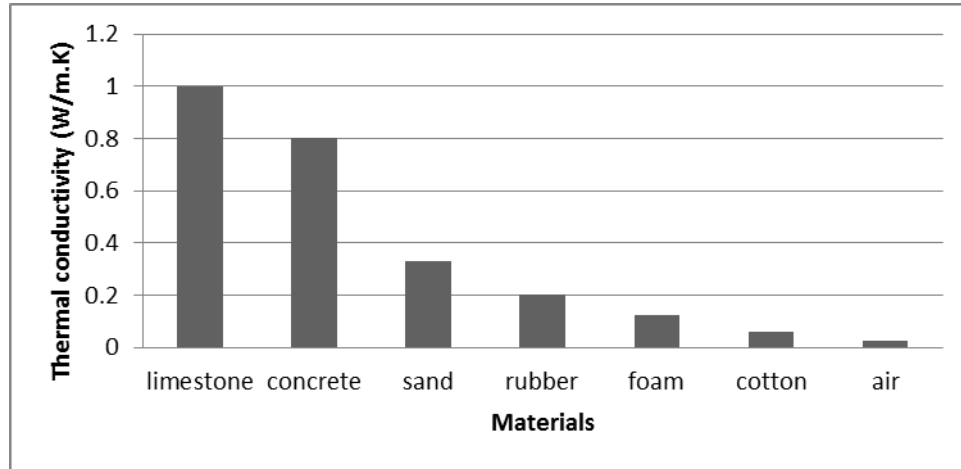


Fig. 15: Comparison between thermal conductivity of different materials.

Table 9: Thermal conductivity for selected mixes of polyurethane mortar.

Sample	blank	PUF-1#	PUF-3#	PUF-4#
Thermal conductivity (W/m.K)	0.335	0.167	0.128	0.122

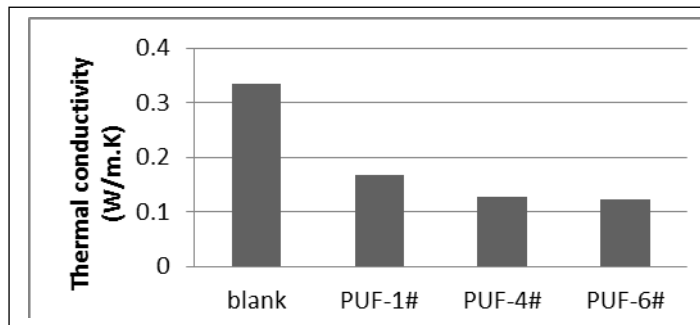


Fig. 16: Relation between thermal conductivity and different formulations from polyurethane foam contains dissimilar dosages from amine catalyst

4. CONCLUSIONS:

The following conclusions could be drawn from this study:

- The chemistry of PU makes use of the poly-addition reactions of organic isocyanates with compounds containing at least two active hydrogen atoms. An isocyanate group reacts with the hydroxyl group of a polyol/diol to form the repeating urethane linkages. The polymer is usually formed into the final article during this polymerization reaction.
- There is a wide variety of PUs with quite different compositions and correspondingly with different properties. Rigid polyurethane foams (PUFs) are microcellular three dimensional cross-linked thermosetting plastics and have mainly closed cell structure.

- Thermal conductivity measurement indicates that rigid polyurethane foam insulation materials display excellent insulation characteristics. They have extremely low thermal conductivity values and can achieve optimal energy savings.
- The excellent mechanical strength values and exceptional durability of rigid polyurethane foam fulfill all the requirements made of insulating materials used in the building industry.
- Polyurethane foam has good acoustic characteristics due to large amount of pores inside the cellular structure of rigid polyurethane foam.

Acknowledgments

This research was supported by chemistry and material Labs at Faculty of engineering Ain Shams University. Tests in this research were performed by National Institute for Standards (NIS) and Housing & Building National Research Center (HBRC).

REFERENCES

- [1] Chorkendorff and J.W. Niemantsverdriet, "Concepts of Modern Catalysis and Kinetics", WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003.
- [2] P.J. Lutz, P. Rempp and E.W. Merrill, "Polymer Synthesis", 3rd ed., Wiley-VCH, New York, 2004.
- [3] D. Randall and S. Lee, "The Polyurethanes" Book, Wiley Ltd., New York, 2002.
- [4] Szycher M.: Szycher's handbook of polyurethanes. CRC Press, New York (1999).
- [5] G. Woods, "Flexible Polyurethane Foams", Applied Science Publishers, London, 1982.
- [6] Z. Wirpsza, "Polyurethanes Chemistry, Technology and Applications", Ellis Horwood Ltd., New York, 1994.
- [7] Sylwia Dworakowska, Dariusz Bogdał, Federica Zaccheria and Nicoletta Ravasio, "The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials", Catalysis today, Vol.233, PP.148-156,(2014).
- [8] S.T.lee and N.S.Ramesh, "Polymeric foams : mechanisms and materials", Technology and engineering, 2004.
- [9] Strachota A., Strachotová B., Špírková M. and Ribot F. "Polyurethane networks with inorganic nano-building" blocks. 9th Annual Conference of the Yugoslav Materials Research Society 'YUCOMAT', Herceg Novi 10.-14.9. 2007
- [10] Uppuluri V. Mallavadhani, Nicolas Fleury-Bregeot. "1,4-Diazabicyclo [2.2.2]octane". In Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons, Ltd., 2010.
- [11] L. Silva and J. C. Bordado, "Recent developments in polyurethane catalysis", Catalytic mechanisms review, Cat. Rev., Vol. 46(1), pp. 31-51, (2004)
- [12] Christian Brandl, Jobst Grimminger and James Paul, "Advances in additives for polyisocyanurate foams", Air products and chemicals Inc., 2015.
- [13] Z. Wirpsza, "Polyurethanes Chemistry, Technology and Applications", Ellis Horwood Ltd., New York, 1994.
- [14] Chattopadhyay DK and Webster DC. "Thermal stability and flame retardancy of polyurethanes". Prog Polym Sci, Vol. 34(10), pp.1068–1133, (2009)
- [15] Kim SH, Lee MC, Kim HD, Park HC, Jeong HM, Yoon KS, et al. "Nanoclay reinforced rigid polyurethane foams", J Appl Polym Sci, Vol.117(4), PP. 1593-1605 (2001).
- [16] Singh H., Sharma T. P. and Jain A. K.: "Reactivity of the raw materials and their effects on the structure and properties of rigid polyurethane foams", Journal of Applied Polymer Science, Vol 106, PP.1014–1023, (2007).
- [17] D.D.L.Chung, "Materials for thermal conduction", Applied thermal engineering, Vol. 21, PP.1593-1605,(2001).