Effect of NCO/OH on the Mechanical properties of Polyurethane Elastomers

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Absract

The present work is concerned with the preparation of polyurethane elastomers.

Polyurethane elastomer was prepared by the bulk polymerization via one-shot method of 4,4'diphenyl methane diisocyanate (MDI) with polypropylene glycol (PPG) and 1,4 butandiol using stannous octeate as a catalyst.
The operating conditions of the polymerization were studied and their affects on the mechanical properties of the prepared elastomer.

100 grams of polypropylene glycol with 0.1 ratio of catalyst was used with 4,4'diphenyl methane diisocyanate to equivalent of polypropylene glycol (NCO/OH) (1.5-3), and curing temperature of about 110 °C.

Under these conditions, the mechanical properties of polyurethane elastomers were:
- The tensile strength (16 MPa).
- Hardness, shore A (86).
- Elongation % (274).
- Modulus of elasticity 100% (9 MPa).

Kinetic of the reaction also was studied using adiabatic temperature rise method. The overall order of reaction was 1.5, the activation energy of the reaction was (40 KJ/mole), and frequency coefficient of reaction (4.857×10^4 (mole/g mixture)$^{-0.5}$ S^{-1}) .

Introduction

Polyurethane elastomer is one of the most successful materials for solid tires that are used for military and industrial applications. This was one of the first large-scale applications for polyurethane elastomer. Many important advantages of polyurethane tires can offer over natural and reclaim rubber such as higher mechanical properties, ease of production, and have higher load bearing in addition to the long lifetime and reducing the overall cost.

Polyurethanes (PU) are the polymers containing significant number of urethane groups (–NH-CO-O-) in the molecular chain. The most common method of preparing polyurethane is condensation reaction of a diisocyanate and a polyol. Unlike conventional polycondensation, this polymerisation reaction does not produce any by-product [1].
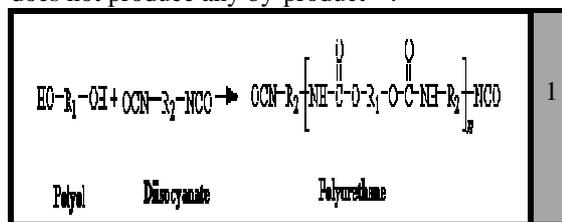
The structure of polyurethane is a complex and diverse containing "hard and soft" segment, which contribute to the balance between rigid and elastomeric properties [2].

Generally, The polyurethane elastomers can be classified into: castable, millable, thermoplastic, and cellular polyurethane elastomers and from these types the castable polyurethane elastomers of approximately 75 to 80 shore A hardness is used for this application (Figure (1)) [3].

Castable Polyurethanes are synthesized by two methods namely, prepolymer method and one-shot method. In prepolymer method, the isocyanate and polyol are reacted to form an intermediate polymer called "prepolymer". It is then converted into final high molecular weight polymer by further reaction with diol or diamine chain extender. In the "one-shot" method, the polymer formation is carried out by simultaneous reaction of polyol, isocyanate and chain extender [4].

**Fig.(1) Hardness range of polyurethane elastomers [3].**
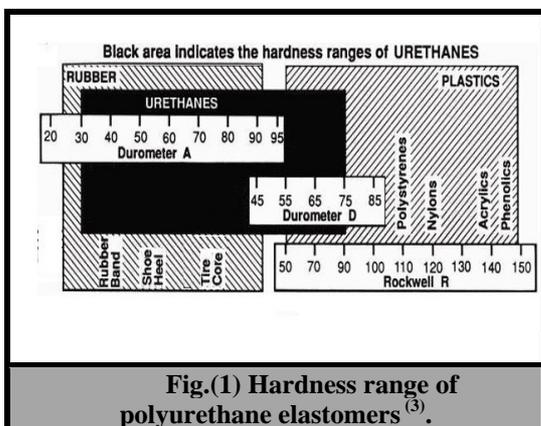
In addition to elastomers, polyurethane can also be produced as foams (rigid and flexible), adhesives, binders, coatings, and paints. Because of their unique properties, polyurethane has found a wide variety of applications in the tires industries, propellant, refrigerator insulation, exterior panels, sealants, housing for electric equipment, furniture, and construction.

Polyurethane elastomers are high-polymeric materials having urethan groups (−NHCOO−) in the backbone of the polymer. The groups are present in the polymer as a result of reaction of an isocyanate (−NCO) at the end of the monomers (NCO−R−NCO) with hydroxyl (−OH−) groups present at the ends of other monomer (OH−R−OH) [6]. They are used for variety of unique application that is inappropriate for other polymer. Their advantageous properties include high hardness for a given modulus, high abrasion and chemical resistance, excellent mechanical and elastic properties [1].

THEORY

The most important reaction is the reaction of isocyanate with compound contains OH group to form a urethane at temperature of about (25-50°C), which is considered the basis of all methods for polyurethane formation. The reactivity of the hydroxyl group decreases in the order of primary, secondary, tertiary alcohol, which is very unstable. The urethane group can be dissociated to isocyanate at elevated temperature therefore, the reaction is reversible: [5]

$$R-N=C=O \ + \ HO-R'$$
$$O$$
$$\|$$
$$R-NH-C-OR' \qquad 2$$
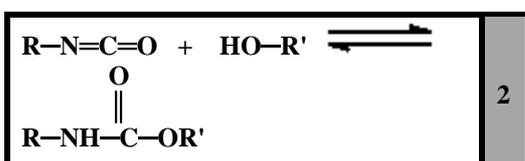
When the compound contain (NH_2) group, urea linkage is formed [6].

$$R-N=C=O \ + \ NH_2-R'$$
$$O$$
$$\|$$
$$R-NH-C-NHR' \qquad 3$$
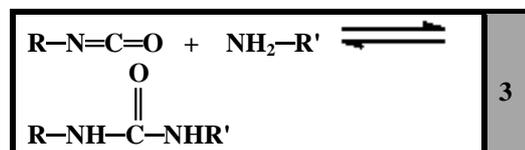
The reaction between isocyanate and water is a special case of an alcohol − isocyanate reaction [7]. This reaction of isocyanate with H_2O is generally undesirable for castable elastomers because the CO_2 released as a by-product can cause bubble formation in the resulting elastomer and weaken its physical property. Therefore, the removal of water from the castable system is of utmost importance.

$$R-N=C=O \ + \ HO-H$$
$$O$$
$$\|$$
$$[R-NH-C-OH] \qquad 4$$

$$O$$
$$\|$$
$$[R-NH-C-OH] \longrightarrow R-NH_2 \qquad 5$$
$$+ \ CO_2$$
$$(5)$$

$$R-NH_2 \ + \ R-N=C=O$$
$$O$$
$$\|$$
$$R-NH-C-NHR \qquad 6$$
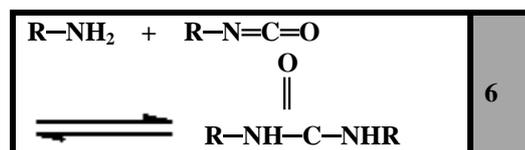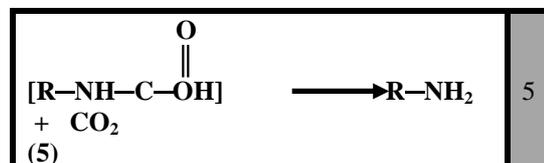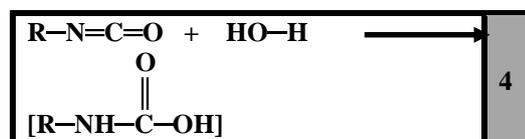
The organometallic compounds are extremely catalysts for the isocyanate-hyroxyl reaction. They include stannous octeate, stannous oleate, dibutyl tin dilurate, and dibutyl tin di-2-ethylhexaoate.In certain applications where very fast reaction rates are desired e.g. (RIM). Occasionally lead salts such as lead octeate or naphthanate are also employed [8].

Rausch et al. [9] studied the effect of various organometallic catalysts on properties of MDI-diamine rubbers and the results shown that tin compounds especially stannous octeate and dibutyl tin dilurate are the best to obtain elastomer with high physical properties compare with lead compounds.

Axelrood et al. [10] have been studied the variation of stannous octeate concentration on the properties of (TDI, polypropylene glycol and MOCA as achain extender) system. They found that a lower catalyst level leads to improved tensile strength but higher compression set.

Two of the most important aromatic isocyanate is TDI and MDI, and modifications of these products, especially "crude" TDI and MDI. TDI consists of a mixture of the 2,4- and

2,6- toluene diisocyanate isomers. The commercially available TDI is a mixture of these two isomers with various ratios. On the other hand, the MDI is available as isomers (4,4'- and 2,4'- diphenyl methane diisocyanate), although the pure MDI is also available commercially. This product is of low volatility as comparable with TDI, so that at normal temperature hazardous concentrations of vapour do not occur.

The MDI based elastomer is preferred over TDI for two reasons [11]:

a. The MDI elastomer has faster recovery or resilience.
b. The quicker recovery is also accompanied by less heat generation and this property is considered essential to prepare solid tires with low heat build up.

Chain–Extenders, or curing agents, are chemical compounds that can react with functional groups in reactants mixture and bring necessary polymerization to completion. Without a chain–extender, polyurethane formed by directly reacting diisocyanate and polyol generally has very poor physical properties and often does not exhibit microphase separation. In the preparation of the castable urethane elastomer the chain–extender extended the polymer to convert from low M.wt to higher M.wt and also the chain-extender acts as curative (curing agent) to obtain the product, as shown in Equation(7) [1]:

$$
\begin{array}{c}
\textbf{Low} \quad \textbf{(Chain-Extender)} \quad \textbf{High} \\
\textbf{M.wt polymer} \xrightarrow{\hspace{2cm}} \textbf{M.wt polymer} \\
\textbf{Curatives} \\
\xrightarrow{\hspace{1.5cm}} \textbf{Product} \\
\textbf{(Chain-Extender)}
\end{array} \qquad 7
$$
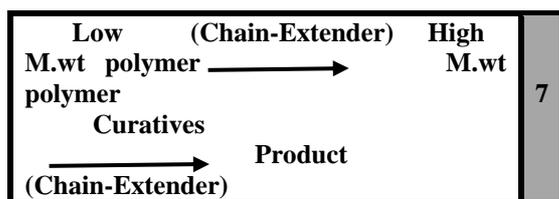
Polyurethane chain extender can be categorized into two classes: aromatic diol and diamine, and the corresponding aliphatic diol and diamine. The two most frequently used curatives are 4.4'–ethylene bis (2- chloro aniline) or MOCA, and 1.4 butanediol.

The NCO/OH ratio, which called isocyanate index, is a term commonly used in the preparation of polyurethane elastomers. It refers to the equivalents ratio of the reacting isocyanate compound to the polyol.

The polyurethane molecule is composed of long, low-melting, flexible polyol joined to high-melting, rigid, concentrated urethane area. Increasing the NCO/OH ratio will increase the concentration of high-melting, rigid area of the chain, and thereby affects the physical properties of elastomer. The popular NCO/OH index is 2/1 [31].

Generally, Experiments should be run to determine the best isocyanate index to produce the most satisfactory end product.

Many studies [12, 13] have been carried out to study the effect of NCO/OH ratio on properties of polyurethane. Some of these studies show the improvement in elastomeric properties when the NCO/OH ratio increases, but the other studies found, further increasing the NCO/OH ratio has decreased the mechanical properties considerably as the materials became very brittle, and the decrease in elongation at break is particularly marked.

kinetics of polyurethane polymerization

An overall nth order reaction kinetic expression was chosen to describe the reaction rate.

$$
\begin{array}{c}
2(-N=C=O) + 2(-O-H) \rightarrow \text{urethane} \\
\quad (A) \qquad\qquad (B)
\end{array} \qquad 8
$$
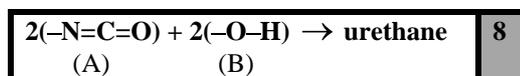
$R_A = K\, C_A{}^a\, C_B{}^b$
$R_A = K\, C_A{}^{a+b}$ (When NCO and OH groups are present in their stoichiometric ratio)

$$
\therefore \quad R_A = K\, C_A{}^n \qquad 9
$$

And assume an Arrhenius temperature dependence

$$
K = A\, Exp\, (E/RT) \qquad 10
$$

With the above mentioned assumptions, the balance of energy per unit mass becomes:

$$
C_{pm}\, \frac{dT}{dt} = \Delta H\, R_A \qquad 11
$$

With the complete derivation in (Ref.14):

$$
ln\frac{dT}{dt} = lnF - E/RT + n\, ln\left(\frac{Tad - T}{Tad - T_O}\right) \qquad 12
$$

Where $F = A \times \Delta Tad \times CA_0{}^{n-1}$

EXPERIMENTAL WORK

Raw Materials
[4, 4' Methylene Diphenyl Diisocyanate]
Acronym: MDI, Supplier: Bayer, Molecular Formula: C15H10N2O2, Melting Point:

30°C/760 torr, Boiling Point: 150°C/ 0.2 torr, Chemical Structure:

^{3}CN—⬡—CH$_2$—⬡—NCO
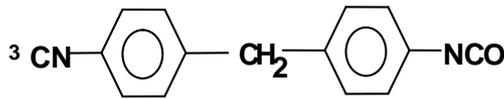
[Polypropylene Glycol]
Acronym: PPG, Supplier: BASF, Molecular Formula: (C3H6O)n, Molecular Weight: 1500 g/mole, Chemical Structure;

OH–(–CH$_2$CHO–)$_n$–H

CH$_3$
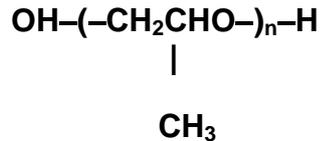
[Stannous bis(ethylhexanoate)]

Acronym: Stannous Octoate, Supplier: Sigma Chemical, Molecular Weight: 405 g/mole, Chemical Structure:

CH$_3$CH$_2$ ... HC–C–O–Sn–O–C–CH ... CH$_2$CH$_3$
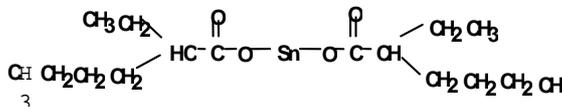
polymerization of the monomers

The polymerization was carried out in a 1000 ml jacketed stainless-steel reactor (Figure(2)), which was heated to the required temperature 60°C by circulation hot water in the jacket of the reactor. This polymerization reactor was equipped with variable speed stirrer vacuum outlet, vacuum gauge pressure.

The premix of PPG and 1,4 BD was added to the polymerization reactor after purification and continually heated to a temperature of about 60°C. The catalyst was added and then the stoichiometric amount of MDI was added plus 5% excess to compensate for any allophanate formation and the wastage of diisocyanate remain behind in the container. The diisocyanate (MDI) was quickly added in (5-10 sec.) with stirring and when its addition was completed the reaction mixture was degassed under vacuum to remove any trapped gas, which might lead to bubbles in the final cast polyurethane. After 3 to 5 minutes of degassing, during which time the temperature rose to (80-85°C), and at this temperature the agitation was stopped, the vacuum was released by dry nitrogen and the liquid polyurethane obtained casting into a mould, which had previously coated with a release agent (silicone oil).

Curing and Post curing of the Liquid polyurethane

These are very important stages to determine the final physical properties of the polyurethane. The curing can be processed by placed the filled mold in the oven at the range of (70-140°C) for 24 hours. Each elastomers was then post-cured for not less than 7 days at room temperature before testing for any properties.

mechanical testing
Stress-Strain Properties

Uniaxial stress-strain properties were measured at room temperature according to BS 903: part A2: 1971, in a tensometer machine using the following conditions:

Crosshead speed = 500 mm/min, Stress range= 10-20 MPa,Strain range= 1000%

Test specimens were BS dumbbell, and the thickness was 2-4 mm. Three specimens were used for each sample and the reported data were the average of the three tests. The properties determined by this measurement are:

a. Ultimate Tensile Strength

This is the maximum tensile strength reached in stretching the test piece to breaking point. The UTS (MPa) is calculated as follows:

$$UTS = \frac{Force\ at\ break\ (N\ )}{Initial\ cross-sectional\ area\ (mm^2)}$$

b. Modulus at a given tensile strain (100% or 300%)

This is the tensile stress in the test length when subjected to a given strain. It is calculated in MPa as follows:

$$Modulus\ at\ 100\%\ or\ 300\% = \frac{Force\ at\ a\ given\ strain\ (N)}{Initial\ cross-sectional\ area\ (mm^2)}$$

c. Elongation at break

This is the tensile strain in the test length at breaking point. It was found by counting the number of centimeters and expressing the result as a percentage of the initial distance. For BS dumbbell, the initial distance is 25 mm.

Hardness

The hardness of all the polyurethane elastomers prepared was determined according to ASTM D-2240, using a Durometer microhardess tester (Shore A). One measurement is made at each of three or more

different points distributed over the test piece, and the average of the result is then taken.

adiabatic temperature rise measurement

The adiabatic reactions were carried out in jacketed stainless-steel reactor which was already used to polymerize the polyurethane after it is covered with an insulated lid. Reactants (isocyanate, polyol, chain extender using catalyst ratio 0.1) were introduced at stoichiometric. Thermocouple wire was threaded through the reactor shell and the polymerization started at a temperature of about 60°C. Temperatures versus time are recorded through the polymerization and when the reaction shows any temperature decreasing the recording of temperature should be stopped. Thus, the reaction can be assumed adiabatic.

RESULTS AND DISCUSSIO

The effect of NCO/OH ratio upon the mechanical properties (hardness, tensile strength, modulus 100%, and elongation) are shown in figures (3), (4), (5), and (6) respectively.

From Figure (3), it is shown that the hardness increases rapidly with increase in NCO/OH ratio up to 2.4, after this ratio (above 2.4) can be shown that a reduction in the rate of increasing of hardness is obtained.

It is clear from Figures (4), and (5) that the tensile strength and modulus increase with NCO/OH up to 2.4 and the polyurethane produced by using (NCO/OH=2.4) have higher tensile strength and modulus. But when increasing the NCO/OH ratio above 2.4, a marked decrease in tensile strength and modulus occurs.

Figure (6) shows that the elongation of polyurethane elastomers decrease with increasing NCO/OH ratio very slowly up to 1.86 which represented the peak value, after which further increasing of NCO/OH ratio, decrease the elongation rapidly.

As mentioned earlier that the polyurethane elastomers consist of a hard segment which responsible on (hardness, tensile strength, and modulus 100%) and a soft segment, which provide (flexibility). Now from this fact the hardness, tensile strength, and modulus increase by increasing the NCO/OH ratio up to 2.4 and this effect is attributed to the increasing the content of the hard segment in polyurethane structure. But increasing the NCO/OH ratio above 2.4 caused decreasing in all the mechanical properties,

except the hardness changes from 84.5 to 87.6, and this behavior results from the higher hard segment content over the soft segment and this bad combination between hard and soft segments will made the polyurethanes very brittle and then decreased in all mechanical properties.

The elongation is effected by the soft segment content; therefore, it is shown in Figure (6) the elongation decreases with increasing NCO/OH ratio above about 1.86 and ratio 1.86 considers the optimum balance between the soft segment and the hard segment for elongation.

Finally, it can be conclude that the 2.4 ratio gives polyurethane elastomers have a good combination of all mechanical properties (hardness, tensile strength, modulus 100%, and elongation).

kinetics of Polyurethane Polymerization

The kinetic parameters (n, E, and A) of catalyzed reaction of MDI with polypropylene glycol and 1,4 butandiol can be determine from adiabatic polymerization of these monomers at conditions (reaction temperature = 60°C, NCO/OH ratio=2.4. and catalyst ratio=0.1) which considered the optimum operation conditions.

Figure (7) shows the experimental data of temperature rise in the adiabatic reactor. From this figure, the maximum temperature rise gives value of Tad and also dT/dt can be evaluated. Thus, the variables in dT/dt, 1/T, and $(Tad-T)/(Tad-T_0)$ are known in equation (12). So by using a quasi-Newton method, equation (12) can be solved and obtain the order of reaction n, the activation energy E, and the constant F, as the follows:

Now from the above figure we can evaluated $(Tad-T)/(Tad-T_0)$, and
dT/dt by draw tangents to the cuvre at different points.

An excellent regression (R=0.99) was obtained for n=1.5 by using quasi-Newton method and the kinetic parameters took the following values:

E= 39.937 KJ/mole, lnF=12.0787

$\therefore F = A \ \Delta Tad \ CA_0^{n-1}$ (given from chapter two)

$$A = \frac{F}{\Delta Tad \times CA_0^{n-1}} =$$

$$\frac{1.76 \times 10^5}{78 \times 0.04647} = 4.857 \times 10^4$$

$$\frac{g^{0.5}}{mol^{0.5}.S}$$

Where $CA_0 = 0.002156$

$$\frac{mole.\ NCO}{g.\ mixture}$$

Both the reaction order and the activation energy are in good agreement with the results reported for thermosetting formulations by Broyer and Macosko [15].

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Nomeclature

Symbol	Definition	Units
A	Frequency coefficient of reaction	$(\text{mole/ g mixture})^{1-n} \, s^{-1}$
C_{A0}	Initial concentration of isocyanate	mole.NCO/ g mixture
Cp_m	Mean heat capacity of reaction mixture	kJ/g mixture .K
E	Reaction rate activation energy	kJ/mole
K	Reaction rate constant	$(\text{mole/ g mixture})^{1-n} \, s^{-1}$
n	Overall reaction order	—
R	Gas constant (8.314)	J/g.mole.K
R_A	reaction rate according to isocyanate	mole.NCO/ g mixture. S
T	Temperature	^{o}C
T_0	Initial temperature	^{o}C
Tad	Maximum(adiabatic) temperature	^{o}C
ΔH	Heat of reaction	kJ/mole. NCO

Abbreviations

ASTM	American Standards for Test and Methods
B.S.	British Standard
mole. NCO	Equivalent of NCO (mole of isocyanate $\times$ functionality)
J	Joule

Fig. (2): Polymerization reactor[15].

Fig. (3): Effect of NCO/OH ratio on the hardness of polyurethane at catalyst ratio 0.1, and curing temperature 110°C
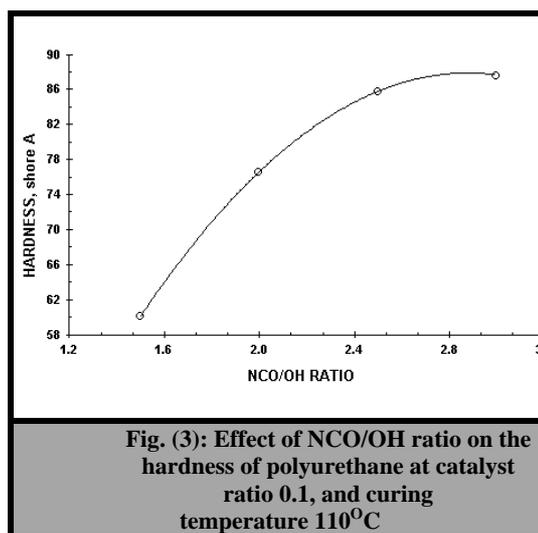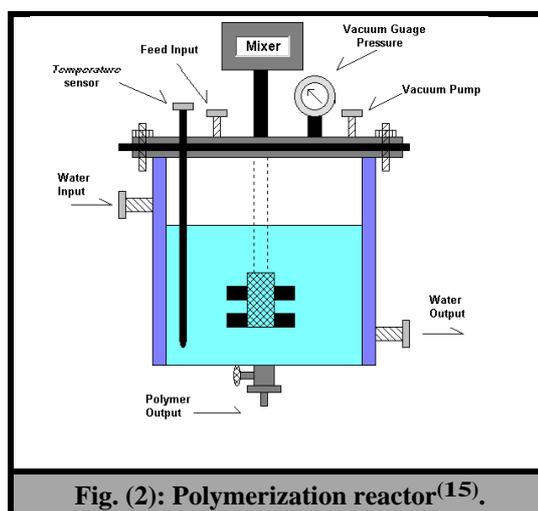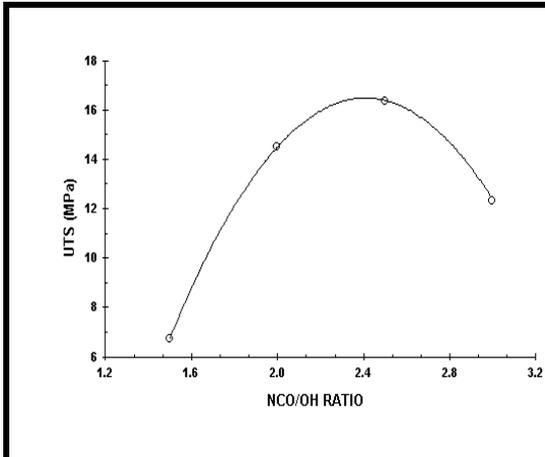
Fig. (4): Effect of NCO/OH ratio on the tensile strength (UTS) of polyurethane at catalyst ratio 0.1, and curing temperature 111 ^{O}C
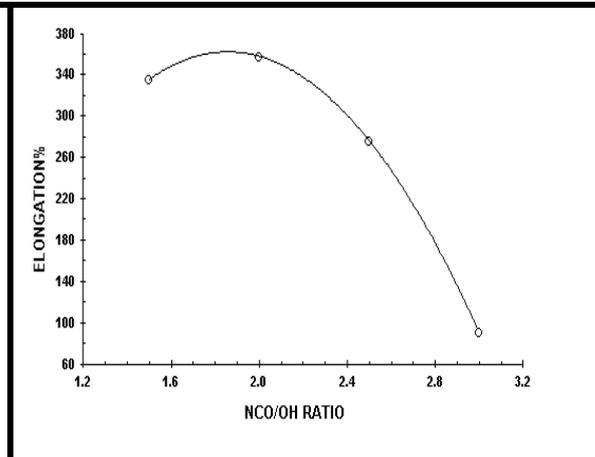
Fig. (6): Effect of NCO/OH ratio on the elongation of polyurethane at catalyst ratio 0.1, and curing temperature 110 ^{O}C
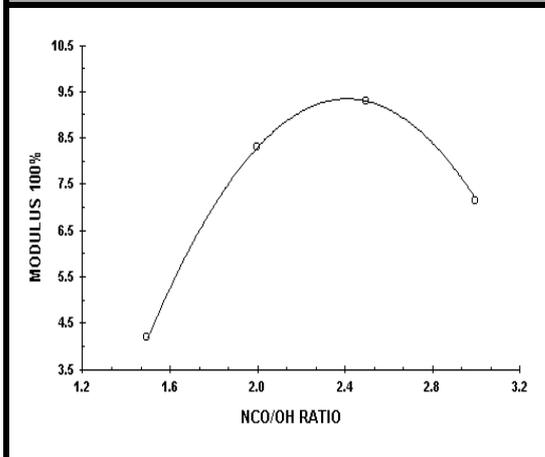
Fig. (5): Effect of NCO/OH ratio on the modulus 100% of polyurethane at catalyst ratio 0.1, and curing temperature 112.5 ^{O}C.
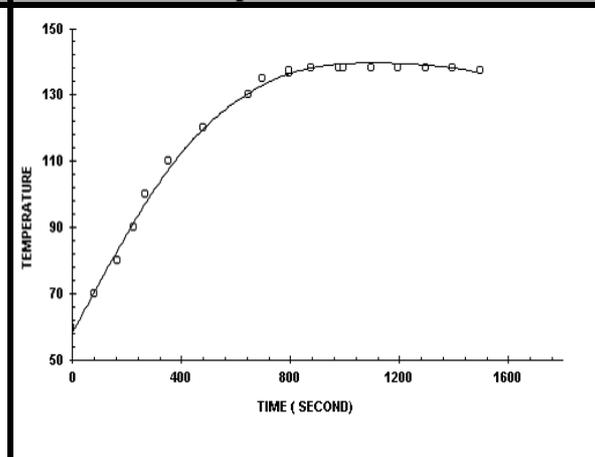
Fig.(7): The experimental data of temperature rise vs time.

الملخص

يهدف هذا البحث الى دراسة عملية أنتاج مطاط البولي يورثان. تم أنتاج مطاط البولي يورثان عن طريق بلمــرة الكتلة(باستخدام طريقة الدفعة الواحدة) لـ(٤,٤' داي فنيل ميثان داي أيزوسيانات (MDI) مع البولي بروبلين كلايكول(PPG) و ١,٤بيوتان داي أول) بوجود عامل مساعد ٢ـأثيل هيكسات القصدير والذي يسمى بـ(Stannous octeate).

تم دراسة الظروف التشغيلية لهذه البلمــرة وتاثيرها على الخواص الميكانيكية والتي هي نسبة وزن العامل المساعد الى وزن ١٠٠غم من البولي بروبلين كلايكول   (٠.١) والنسبة الوزنية المكافئة لمادة ٤,٤' داي فنيل ميثان داي أيزوسيانات الى مادة البولي بروبلين كلايكول ضمن المدى (١.5- ٣) وأخيراً درجة حرارة التقسية 110 ? م.

تحت هذه الظروف كانت الخواص الميكانيكية كالاتي:

- قوة الشــد (١٦ميكا باسكال).
- الصلادة نوع shore A (٨٦).
- الاســتطالة كنسبة مئوية (٢٧٤).
- قوة الشــد عند الاستطالة ١٠٠% (٩ميكا باسكال).

كـذلك تم دراسة حركية التفـاعل بأستخدام طريقة أرتفاع درجة الحرارة الاديباتية ووجــد ان المرتبة العـامة للتفاعــل هي (1.5). كما وجد ان طاقة التنشيط للتفاعل بحــدود(٤٠كيلوجول/مـول) ووجد أيضاً معامل تردد التفاعل تســاوي(S 4.857×10^4 (mole/g mixture)$^{-0.5}$