Egypt. J. Chem. **Vol. 65,** No. 10 pp. 523 - 529 (2022)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Polymer Resin Modelling for Chemical and Biomedical Purposes

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Abstract

Thermoset polymers were widely utilized in different chemical and biomedical applications. The mechanism of monomer reactions and heat of reaction plays an essential role in using these polymers in bones and implants. Modelling of homogeneous and catalytic reactions of thermoset polymer reactions have been studied by many researchers to identify the type of reactions. Chain-growth polymerization reactions tend to increase polymer viscosity faster compared to step-growth reactions. Simulation is an effective method for predicting the mechanism of the polymerization reaction. For non-catalytic processes, the catalyst introduces a chain-growth reaction mechanism as opposed to a step-growth mechanism polymerization. The viscosity increases lead to faster attaining to the gel point. In this study, a modelling program was written to distinguish and identify the types of homogenous and catalytic reactions of polyurethane gel reactions. Experimental results of polyurethane reactions prove the results from a modelling program. Reaction temperature and viscosity profile show good agreement with the simulation results when using different amounts of catalyst reagents. his simulation provides a powerful tool for better selecting and improving polymers in bones and implants.

Keywords: polymerization; reactions; polyurethane; modeling; biomedical; implant.

1. Introduction

Owing to its diverse application, the global market for polyurethane (PU) expands annually. With more than 12 million tons of its primary material worldwide, the estimated annual growth rates exceed 5%. Polyurethane applications vary from furniture, rigid insulation in houses and coolers to elastomeric tires and wheels [1]. Polyurethane gel is typically generated from the alcohols and isocyanates active group reactions with catalysts applied to boost the reactions[2]. Many scientists have been interested in the kinetic variables and mechanisms of reaction of urethane and studied utilizing chromatography, fluorescence, NMR, and modelling, all of them providing a durable characterization of the complicated polymerization. The urethane reactions are as follows [3, 4]:

$$RNCO+R'CH_2\,OH \rightarrow RNHCOOCH_2R' \qquad (1)$$

In the early stages of the reaction of a multi functional polyol and isocyanate, the effective groups in monomers react to produce polymers[5-7]. The active groups regulate late reactions in polymers that interfere with other active groups of the same polymer. With these reactions, polymer chains are complemented and linked in large three-dimensional lattices. Via a growing molecular weight of chains entering a gel level, the viscosity of the resin raises[8-10].

Researchers have proposed a new way of catalyzing base catalyzed reactions of isocyanates with hydrogen-acidic components. The first step of the

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Receive Date: 23 January 2022, Revise Date: 23 February 2022, Accept Date: 25 February 2022
DOI: 10.21608/EJCHEM.2022.117967.5314

urethane/carbamate formation is protonation and proton transfer. A team from the University of Bristol has identified three possible paths for the initial step's progression, including three different routes[11, 12]. The current work agrees with theses modelling steps.

Sultan et al. [13] synthesized linear and crosslinked polyurethane (LPUR) & crosslinked Polyurethanes (CLPUR) for methylene blue reduction. They discovered a 100% reduction in 16 and 28 minutes, respectively, although the decrease rate was much lower in the lack of these components.

Electrospinning, silver ion immobilization, and in situ decreases were applied by Liu et al.[14] to create silver nanoparticles loaded polyurethane/keratin nanofibrous mats (PU/Keratin/AgNPs). Changing the silver ion concentration in the solution controlled the size and loading amount of AgNPs.

The goal of Choi et al.'s[15] investigation was to achieve a dual-curing reaction that included radical and urethane reactions at low temperatures. $Mn(Acac)_3$, $Zn(Acetylac)_2$, $Co(Accec)_3$ and Co_2 were employed as metal acetylacetonates (Mt(acac)x). Although at modest curing temperatures, the surface properties of these metals are maintained after exposure to 100 degrees Celsius, according to the investigators.

The structures and morphologies were revealed, and thermogravimetric analysis revealed that adding two wt percent NiO enhanced the residual yield of RPUF (Rigid polyurethane foam) nano composites by 63.8 percent due to the catalytic coupling influence. Metal oxides and bimetallic oxides have been employed by Yuin et al.[16] to reduce smoke toxicity.

The gel step at the molecular stage relates to crosslinking to the degree that the more significant fraction of the mixture is crosslinked to construct a large three-dimensional molecule[17-20]. In this circumstance, the mixture passes through a transition from liquid to solid[21, 22].

The novelty of the work is to write a simple but powerful simuaiton program for the polyurethane thermosetting reaction. The simulation agrees with the hypotheses when the molecular weight of the polymer becomes zero at the end of the reaction. Although the gel point is terminal for the handling of thermosets, this functional method is of particular importance [23, 24]. Homogeneous urethane reactions tend vaguely to be a mechanism for development, with multiple urethane catalysts, specific mechanisms are conceivable, and have many chemical and biochemical uses [23-36]. In order to ensure higher active sites which, react at a higher rate, catalyst proteins get associated with the alcohol or the isocyanate groups. Catalytic and non-catalytic interactions are replicated in tandem to provide the most accurate modelling [25, 26].

Table 1 Lists the probable homogenous reactions of active groups of multifunctional alcoholics and isocyanates.

Table 1. Homogeneous polymerization reactions (step-growth)[4]

Reactions	Rate of Reaction
$Polyol_M + Isocyanate_M \rightarrow Polymer$	$Rate\#1= K_1\ Act._{Polyol}\ C_A\ Act._{Isocyanate}\ C_B$
$Polyol_M + Isocyanate_P \rightarrow Polymer$	$Rate\#2= K_2\ Act._{Polyol}\ C_A\ Act._{IsocyanateP}$
$Isocyanate_M + Polyol_P \rightarrow Polymer$	$Rate\#3= K_3\ Act._{PolyolP}\ Act._{Isocyanate}\ C_B$
$Polyol_P + Isocyanate_P \rightarrow Polymer$	$Rate\#4= K_4\ Act._{PolyolP}\ Act._{IsocyanateP}$

Where:

$Polyol_M$ and $Isocyanate_M$: Isocyanate and polyol monomers

$Act._{Polyol}$ and $Act._{Isocyanate}$: Functionalities

C_A, and C_B: Concentrations

$Act._{PolyolP}$, and $Act._{IsocyanateP}$: Active groups in polymer

$K_1 – K_2$: Rate of reactions

Rate#1- Rate#4: Reaction rate expression.

A MatLab modelling was undertaken with a catalytic reaction chain-growth mechanism vs a non-catalytic homogeneous polymerization [27-29]. Figure 1 provides a schematic image of the pathways for polymerization of phase development relative to chain production. At the same conversion chain development generates less polymers of greater molecular weight [30-33].

The innovation of the new modelling is to use a written MatLab computer program to estimate the gelling degree in multi-function monomers and allow intramolecular reactions for improved gelling point estimation. Confirmation of adiabatic reactions, intramolecular reactions, and chain mechanisms achieves a level of precision that experimental techniques cannot match.

For the control of reaction levels and element rate phrases in the system, the below heuristics were adopted:

- The driving factor for reactions instead of the concentration of the molecules is involved in group concentrations.
- Concentration profiles and time of the gelling should be produced, at least, by means of the resolving of ordinary differential equations explaining their rate of change, with concentration profile of active groups, monomer and polymer.
- Catalyst-constructed materials are treated separately and independently from non-compliant materials.
- Polymers have been lumped into a group for either step-widening or chain-widening. Every lumped group has a measured mean concentration.
- Just one catalyst can be linked on a monomer to an active group.
- The heat capacity is measured as the total sum of the thermal components.
- Reactions are shown as first-order reactions.

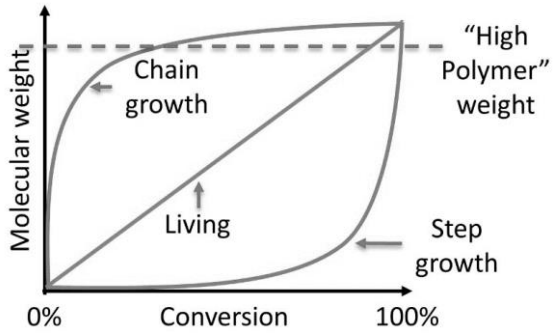

Figure 1. Stepgrowth and chaingrowth polymerization (Adapted from [34])

2. Materials and Methods

Dow Chemicals ' Pluracol 1016 and Huntsman's PMDI have been implemented in this analysis in the form of polyol and isocyanate. For the research and simulation of mechanisms for various kinds of catalysts, future studies were planned. The surfactant used was Momenteve L8900, and the fire retardant is TCPPI. The catalyst of amines (Cata8) was used as a catalyst for gelling. In the current article, the mechanism of the catalyst was examined, but a distinct mechanism can be produced by various kinds of catalysts (tin or bismuth). This article concentrates only on the analysis of the amine catalyst process. This research does not use a blowing agent. The surfactant and fire-retardant quantities were maintained at 0.1wt%. Table 2 shows the properties of Pluracol 1016. Table 3 shows the recipes of the materials. Figure 2 shows the experimental setup.

Figure 2. Experimental setup.

Table 2. Properties of Pluracol 1016.

Properties	Value
Appearance	dark yellow liquid
OHvalue#, mg KOH/g	490 - 520
Water wt.% maximum	0.10
functionality	3
Nominal molecular weight	330
Density77°F, (lbs/gal)	8.8
Specific gravity @ 77ºF	1.06
@ 90ºF	1.05
@ 110ºF	1.04
Viscosity, cps @ 77ºF	291
@ 90ºF	180
@ 110ºF	90

Table 3. Components for polyurethane gel reaction.

Ingredients	Weight, g
Polyol Side	
Pluracol 1016	35
Cata8	0.24
Momenteve L8900	0.3
TCPPI	2.4
Isocyanate Side	
PAPI (1.1 index)	42

In a paper cup, the ingredients were blended together. The blade was used to blend the ingredients with 1800 rpm attached to a floor-model box press. The same blending period has been utilized to eliminate any variance in the calculation of viscosity profiles for each 10-second experiment. To calculate the temperature profile, a type-M thermocouple was connected to a data logger. The data logger reads the temperature of the reaction against the reaction time immediately. The viscosity pattern of the polymer was calculated utilizing a Cole-Parmer basic viscometer. To avoid variations in kinetics and polymer molecular

weight, all temperature of reaction and viscosity studies were performed at room temperature.

3. Results and Discussion

In comparison to experimental data, the non-catalytic modes of reactions were reported. Figure 3 and enables the correct match of the temperature and viscosity profiles to provide a method of moving development for non-catalytic urethane reactions.

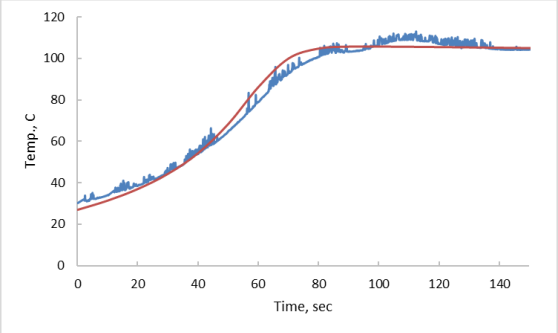

Figure 3. The homogeneous polymerization reaction temperature and resin viscosity profiles.

The simulation was enabled to simulate the experimental data of the viscosity profiles as illustrated in Figure 4. The simulation results show good agreement with the experimental data especially in prediction of the gel point.

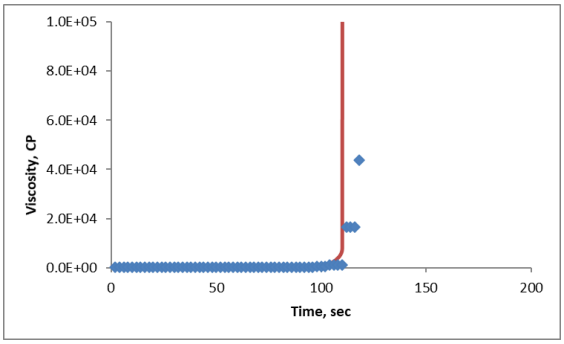

Figure 4. The viscosity profiles.

Figure 5 demonstrates how the viscosity of catalytic reactions at a high reaction temperature rises quicker. This is due to the catalytical reaction chain-growth mechanism. Assuming that the temperature rise is dependent on the size of the urethane reactions, greater viscosities at the same reaction site shall be ascribed to greater degree of polymerization formed by the chain mechanism.

The simulation results of the polyurethane viscosity profile is shown in Figure 6. The simulation results show good agreement with the experimental data.

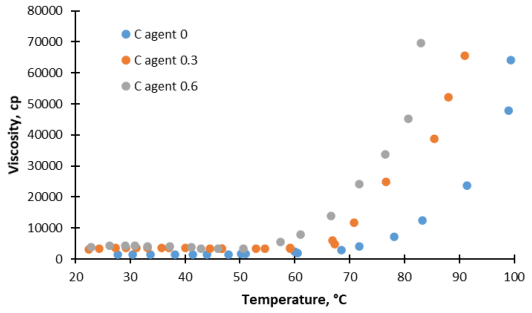

Figure 5. Polymer viscosity against temperature for non-homogeneous and heterogeneous reactions.

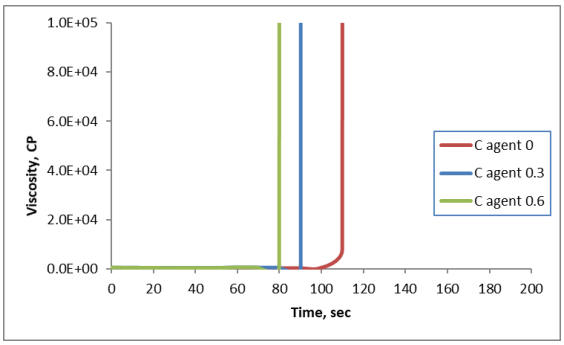

Figure 6. Simulation viscosity profile.

Figure 7 display the temperature of the reactions modelling and experimental findings while evaluating a method for phase development for the heterogeneous reactions. Temperature profiles seem to be useful when viscosity data are not consistent with the modelling. The rapid gelling of experimental data is attributable to the fewer polymer molecules produced by the chain growth mechanism and greater molecular weight. The results of the current research were compared with the results of other researchers[35-40] and good agreement were obtained.

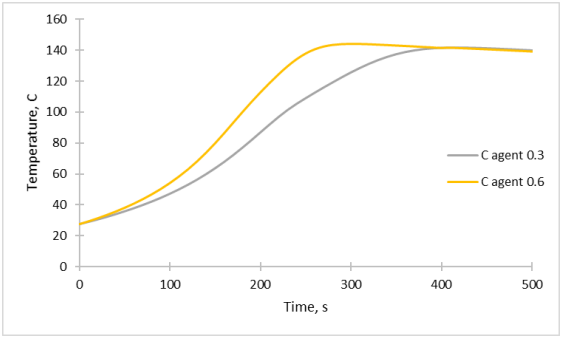

Figure 7. Temperature of reaction considering step growth mechanism.

The polyurethane simulation grabs the attention of many researchers in last centuries. Figure 5 show an

investigative study on the number of published articles on polyurethane simulation. The simulation programs was versatile. Matlab was adopted in the last two centurtes and C+, visual basic, gw basic, and many other programs were also adopted. Figure 8 shows the number of published papers per countries. China and the Unites States of America occupy the main publications as polyurethane has a very wide consumption, as shown in Figure 9.

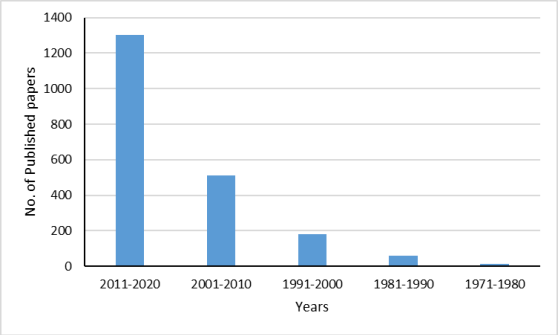

Figure 8. Number of published paper on polyurethane simulation.

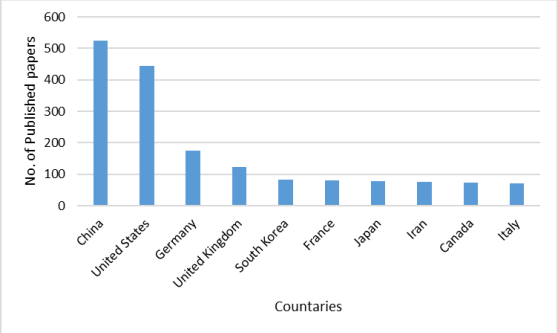

Figure 9. Number of published papers per country.

4. Conclusions

Thermoset polymers are used in bone and implants. In the optimal adiabatic reaction, the temperature increase is relative to the extent of the reaction. When variations were found in viscosity and temperature profiles with or without a catalyst, it has been assumed that reaction mechanisms were added.

The program has predicted how temperature and viscosity could be predicted by solving tens of normal chains-growth and step-growth formulas. Chain growth mechanism generates fewer polymers with greater molecular weights than mechanisms for step-grow in identical reaction levels. They found that chain growth led to higher viscosities even at low concentrations of large molecules. The researchers found that non-catalytical reactions appear to be quicker in the early stages of polymer polymerization accounting. In the first-hand account of polymer-polymerization accounting is vital to estimate gelling accurately.

5. Acknowledgments

The authors would like to thank Al-Esraa University College, Baghdad, Iraq, for its support in the current work. The authors also acknowledge the support of Mustansiriyah University, Baghdad-Iraq, University of technology, Al Rafidain University College, University of Birmingham, UK and University of the Free state, Bloemfontein, South Africa, for their valuable support.

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