Effect of Polyol/Di-Isocyanates Concentration and Temperature on the Synthesis of Polyurethane Foam

S. Abdehamid Ahmed*

Department of Chemistry, Science and Art College, King Abdulaziz University, Rabigh Campus, 21911, Saudi Arabia

***Abstract*— A number of polyurethanes (PUs) from renewable resource e were synthesized by reacting castor oil with polymeric 4,4`diphenylmethane diisocynate (PMDI). Different NCO/OH ratios such as 1.2, 1.5, 1.8 and 2 was applied. Preparation of polyurethane werecarried out at 17, 30, 40, 50, 65 and 72 oC for each NCO/OH ratio. Milled fiber glass with average size 200 µm was dispersed in the pre-polymer with weight fractions 5 up to 50% by intense mixing (1000 rpm) in open and isothermal systems in order to study the effect of the filler contents on the gel time. The results showed that both of the temperature and the NCO/OH ratio have a significant effect on the gel time. Filler loading showed no significant effect on the gel time of the isothermal system. Predictable gel time model which is function in the temperature and NCO/OH ratio was achieved. This model can play an important role to estimate the safe conversion for reactor operation and the cycle time during the polyurethane production.**

***Keywords*— Castor oil, PMDI, Polyurethane, Fiber glass, Gel time, EDS, SEM**

I. INTRODUCTION

Gel point can be theoretically defined as the time required forming the essential infinitely large polymer networks in the reaction mixtures, while practically it can be determined when the polymerizing mixture suddenly loses fluidity or becomes a continuous mass [1]. Gel time has a great importance during synthesis and polymer processing. Deduction of the time required for the process of production, conversion of the reactants and controlling the conditions of the reaction can be achieved if the gel time is obtained.

In this work polyurethane based on renewable resources (castor oil) was selected to be the matrix. During the past few decades, castor oil with low cost and natural resources has been used to replace most polyol from petroleum derivatives in industrial production of cross-linked polyurethanes. Conditions of the synthesis were investigated extensively such as the effect of diisocynate (NCO) to polyol (OH) ratios, temperature of the medium and the filler loading on the gel time. NCO/OH ratio plays a great role in the degree of polyurethane rigidity that can be achieved. Theories of the influence of the NCO/OH ratio on the polyurethane rigidity have been extensively published in the literature and supported by experimental data however the studying of gel time versus NCO/OH is still limited.

Temperature of the medium always has a great effect on the rate of reaction. Both of the production rate and the heating system should be adjusted and compromised to get a high economical value. It's supposed that gel time can be used to estimate the proper temperature of synthesis.

Fillers are added to the polymer for diverse purposes such as polymer toughening, reinforcement, wear resistance, flame retardants and environmental stability [2]. Content analyses of scientist's account of their experiences with contrary data revealed their views of the relation between the filler loading versus gel time. Anil Srivastava and P. Singh [3], they worked with (polyurethane–Al powder) system, it's suggested that filler loading has caused a constant delay in the gelation process because it's supposed that at high viscosity molecular motion ceases and the presence of fine particles may be hindrance to establishing intimate contact between the pre-polymer and the unreacted reactants additionally the formation of fine powder agglomerate in the viscous zone might have trapped the reactants and distributed the interfacial tension, resulting in lower conversion of reactants, however Arvind Shukla and R.M.V.G.K.Rao [2] worked with (polyester-$CaCO_3$, $CaSiO_3$, and glass powder) as well as (epoxy-$CaCO_3$, $CaSiO_3$, and glass powder) systems, they stated that the gel time decreases as the percent filler loading is increased and they attributed it to the increased surface area made available for the curing mass with the progressive addition of the filler which is similar to that reported by Rao and Pourassamy [4]. In the present work, Isothermal system was applied to study the effect of milled fiber glass loading on the gel time individually. EDS analysis was applied to analyze the recycled milled fiber glass. Scanning electron microscopy (SEM) was used to investigate dispersion of the fiber glass.

2. EXPERIMENTAL

2.1. Materials

Castor oil (hydroxyl number 156, functionality 2.59) was obtained from A.S.O (Lab reagent, India). It was dried under vacuum at 105 oC for 4 h before using in the experiments.

Polymeric 4,4'-diphenyl methane diisocynate (PMDI) was imported from DOW. It was used without any extra treatment with NCO contents 31% and functionality 2.7.

Waste light bulbs were collected, milled and then sieved to give grain size less than 200 µm. Drying process were applied at 110 ^{o}C to avoid water-Isocynate reaction which yields CO_2 gas causing bubbles defects in the produced elastomer.

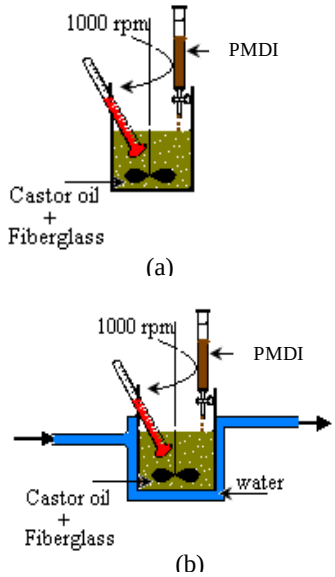

Figure 1 Synthesis of castor oil based polyurethane (a) open system and (b) Isothermal system.

2.2. Polyurethane synthesis

PMDI was added to the castor oil to maintain NCO/OH ratios 1.2, 1.5, 1.8 and 2. The reaction (one-shot polymerization) took place at room temperature; Open and Isothermal systems were applied as shown in fig. 1.a and b respectively. Synthesis of polyurethane was carried out at system at 17, 30, 40, 50, 65 and 72 oC. Water was used for both of cooling and heating system. Time of mixing was 20 min. with 1000 rpm speed. Complete addition of PMDI was taken as zero time.

2.3. Fillers

Waste milled fiber glass was dried at 110 ^{o}C for two hours to get rid off any humidity which cause bubbles in the elastomer. The milled fiber glass was sieved to maintain particle size less than 200µm. Its weight fraction was varied between 5 to 50 % w/w.

2.4. Scanning electron microscopy (SEM)

The dispersion of the fiber glass was analyzed using scanning electron microscopy. Samples were fractured in liquid nitrogen and then sputtered with gold to make them conductive. Fiber glass-Polyurethane interfacial face was examined under a scanning electron microscope (SEM), JEOL model JXA 840A (ADS+OM-Japan).

2.5. Energy dispersive X –ray analysis (EDX)

The energy dispersive X-ray analysis was employed for quantitative elemental analysis of the waste fiber glass in polyurethane composites. This was determined using JEOL model JXA 840A (ADS+OM-Japan). Scanning electron microscope coupled parallel to an energy dispersive X-ray spectrometer by Oxford instruments was applied.

3. RESULTS AND DISCUSSION

3.1. Scanning electron microscopy

Fig.2 shows a typical cross–section SEM picture of the polyurethane with the untreated milled fiber glass 30%. It is seen that surfaces were smooth and still large gaps between the fiber glass and the matrix. It is possible to see the existence of voids due to fiber pull-out during fracture.

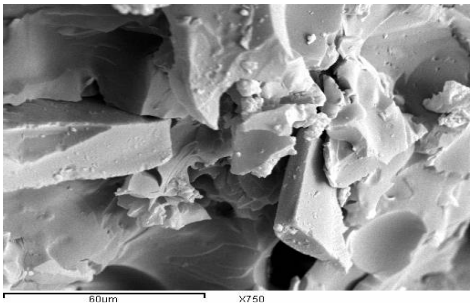

Figure 2 Typical cross–section SEM of milled fiber glass-polyurethane composite

3.2. EDS

The energy dispersive X- ray spectrum is shown in Fig. 3. The relative percentage of the light bulb waste fiber glass shows that the chemical composition of waste milled fiber glass in the fiber glass-polyurethane composite was mainly Si and Ca oxides. Silicon oxide represented around 89.83% while calcium oxide was 10.17% of light bulb waste fiber glass.

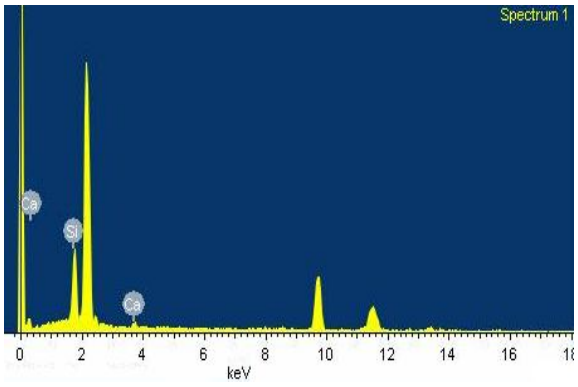

Figure 3 Energy dispersive X-ray spectrum of light bulb milled

3.3 Effect of NCO/OH ratio on gel time

Castor oil is naturally has free secondary hydroxyl groups, around 90% represents ricinoleic acid while the

remaining 10 % is oleic and linoleic acids [9]. 77% of the ricinoleic acid is utilized in the glyceride molecule for forming trihydroxy glyceride and glyceryl tricinoleate, while 23% is used to form the dihydroxyl glyceride, glyceryl diricinoleate monooleate or monolinoleate [9]. It is considered that castor oil is composed from three and two functional components and castor oil is a derivative of the ricinoleic of molecular weight M= 930 g.mol-1, the number average functionality could be calculated based on equation 1.

$$\bar{f}_{nOH} = \frac{(M_{Castor\,oil} \times OH\#)}{(56100)}$$

$$\bar{f}_{nOH} = \frac{932 \times 156}{56100} \approx 2.59 \qquad (1)$$

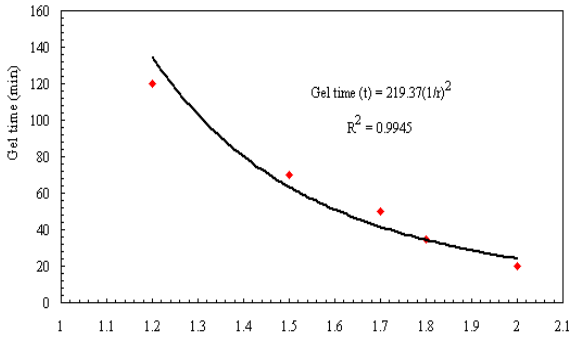

Figure 4 Effect of NCO/OH molar ratios on the gel time at 40 °C.

Weight average functionality can be calculated by Stockmayer's rule as shown in equation 2 [6]:

$$\bar{f}_{wOH} = \frac{\sum n_{iOH} f^{2}_{iOH}}{\sum n_{iOH} f_{iOH}} \qquad (2)$$

Where:
niOH: Mole fraction of the functionality; fiOH: The functionality
n3OH ≈ 0.77(Triol)*0.9 (ricinoleic acid) = 0.693; n2OH ≈ 0.23 (Diol)*0.9 (ricinoleic) = 0.207
f3OH=3; f2OH=2
So, the weight average functionality=2.83

M.Ilavský [5] stated that the gelation process can be achieved when the NCO/OH ratio r beyond the range indicated in equation 3:

$$((f_{wOH} - 1)(f_{wNCO} - 1)) > r > \frac{1}{(f_{wOH} - 1)(f_{wNCO} - 1)} \qquad (3)$$

fwNCO=2.7. So, in our case gelation does not take place if (r) is greater than 3.1 and less than 0.321.

The effect of NCO/OH molar ratio on the gel time was studied in the range 1.2-2. at 40 °C. The plotted data (fig. 4) shows the inverse relationship between gel time and NCO/OH molar ratio (r).

It can be postulated a simple empirical equation for gel time estimation at different NCO/OH ratios and 40 °C. As depicted in equation 4.

$$t = \frac{219.37}{r^{2}} \qquad (4)$$

Table 1 General formula describes the relationship between gel time (t) and temperature (T) at different NCO/OH molar ratio.

NCO/OH molar ratio	General formula	a	b	Square value (R2)
1.2	$t = \frac{a}{T^b}$	10019	1.377	0.99
1.5		6287.5	1.45	0.98
1.8		6534	1.53	0.85
2		3899.2	1.74	0.95

3.4. Effect of temperature on gel time

In modern technology, it is often necessary to predict the behavior of a commercial system in relation to the ambient temperature, which may vary greatly in outdoor operations [7]. Thus during the gelation studies, the influence of temperature on the gelation process was investigated. Fig.5 shows the gel time at 17, 30, 40, 50, 65, and 72 ^{o}C for NCO/OH molar ration 1.2, 1.5, 1.8, and 2.

$$t = \frac{a}{T^b}$$

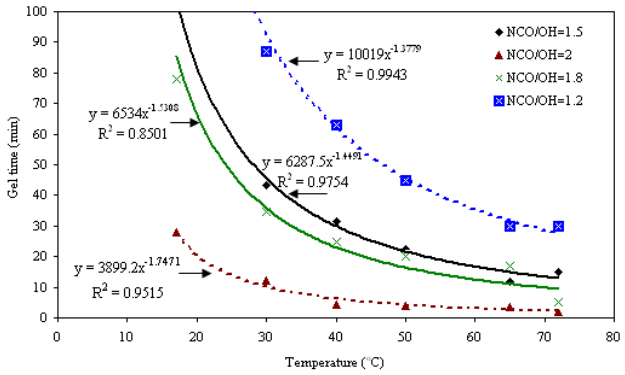

Figure 5 Effect of reaction temperature on the gel time

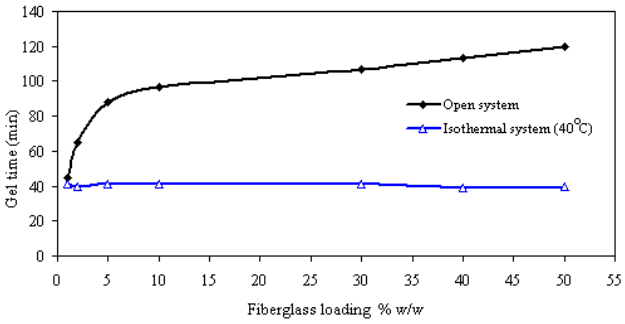

Figure 6 Effect of fiber glass loading on gel time using open and isothermal systems

The mathematical relation and the constants of each NCO/OH ratio can be deduced from the trend of graphs in fig.5, the results are listed in table 1. Accordingly, the empirical mathematical formula may be postulated as:

3.5. Effect of fiber glass loading on the gel time

Open and Isothermal systems were applied during addition of fiber glass to castor oil-PMDI reactants (fig.1) in order to evaluate the influence of fiber glass loading on the gel time. Fig. 6 shows that in the open system, increase of fiber glass loading caused decrease of gel time. In contrary, in isothermal system, fiber glass loading has no significant effect on the gel time. By studying the conditions and the results of the two systems, it can be concluded that the main reason behind decreasing in the rate of conversion and shift the gel time in the open system can be attributed to the heat released by fiber glass which accompanied with decrease in the temperature of the medium. Hindrance or cessation of fiber glass molecules to establish an intimate contact between the pre-polymer and the unreactants in the polyurethane-fiber glass system is almost neglected. This may because the fibreglass doesn't show any chemical reaction with the polyurethane in addition to the weak physical bond in the absence of coupling agents [8-12].

4. Conclusion

Research has been conducted to investigate the effect of NCO/OH molar ratio, temperature of the reaction media and the fiber glass loading on the gel time of castor oil based polyurethane system. Fiber glass is commonly used to reinforce polymer such as polyurethane [13-17] In addition to demonstrated of the microstructure and the composition of light bulb milled fiber glass in the polyurethane composite. The elastomer composite prepared using polymeric diphenylmethane diisocynate (PMDI) with fiber glass. The results showed that the NCO/OH molar ratio and the temperature of the medium have a great effect on the gel time while the fiber glass loading using isothermal system has no significant effect. Estimated empirical models were realized for both of NCO/OH ratio and medium temperature influences on the gel time.

References

1- J. Brandrup and E. H. Immergut and Wiley, Polymer Handbook, 3rd. ed., 1989

2- Arvind Shukla and R. M. V. G. K. RAO, Curing Studies on Modified Epoxy and Unsaturated Polyester Resins Journal of Applied Polymer Science, **29**, pp. 1553-1558 (1984).

3- Anil Srivastava and P. Singh, Gel point prediction of Metal-filled Castor Oil- based Polyurethanes system, polym. Adv.Technol. **13**, pp. 1055- 1066 (2002).

4- Rao, R.M.V.G.K. and Pourassamy, Studies on the curing of a loaded unsaturated polyester binder. Polymer, 17. pp. 611-612 (1976).

5- Zoran S. Petrović, Wei Zhang, Alisa Zlatanć, Charlene C.Lava, and Michal Ilavský, Effect of OH/NCO molar ratio on properties of Soy-based polyurethane networks, Polymer and Environment, **10**, pp. 5-12 (2002).

6- L.Matějka and K.Dušek, Formation of polyurethane networks studied by the gel point method, 7th IUPAC discussion conference " polymer network", polymer Bulletin **3**, pp. 489-595 (1980).

7- P. S. Tukums, U.K. Stirna,U. K. Silis, V. A. Yakushin, and I. V. Sevast'yanova, Possibility of describing process of formation of polyurethane foams by the use of foaming parameters, Mekhanika Kompozitnykh Materialov, **4**, pp. 703–707 (1985).

8- Huibo Zhang, W. Li, Xujie Yang, Yongchun Zhang and Yadong Chen, Micro structural characterizations and mechanical behavior of polyurethane elastomers strengthened with milled fiber glass, Materials processing technology **190,** pp. 96-101 (2007).

9- Hamdi Yeganeh and Mohammad Reza Mehdizadeh, Synthesis and properties of isocynate curable mllable polyurethane elastomers based on castor oil as a renewable resources polyol, European polymer, **40**, pp. 1233-1238 (2004).

10- M. Bassyouni , Sayed A., Sherif , M.A., Sadek and F.H., Ashour, Synthesis and characterization of Polyurethane – treated waste milled light bulbs composites, Composites Part B: Engineering, Volume 43, Issue 3, April 2012, PP1439–1444

11- M. Bassyouni and Saud. A. Gutub, Materials Selection strategy and surface treatment of polymer composites for wind turbine blades fabrication, Polymer & Polymer composites journal, Polymer & polymer composites journal, Vol.21, No. 7, 2013.

12- Nadeem Iqbal, Sadia Sagar, Mohammad Bilal Khan, Mohamed Bassyouni, Zaffar M. Khan, Aluminum silicate fibers impregnated acrylonitrile butadiene rubber composites: Ablation, thermal transport/stability, and mechanical inspection, Volume 130, Issue 6, pages 4392–4400, 2013.

13- M. Bassyouni, S. Gutub and Shereen M.S Abdel-hamid. Dissolved solids adsorption of freshwater using synthesized bio-foam composite, Life Sci J 2013;10(2):464-471.

14- M. Sh. Zoromba, M. Bassyouni and A. Dahshan, Preparation and Mechanico-Optical properties of UV-Curable Transparent Polyurethane Elastomer Nanocomposites, Journal Nanotechnology in Engineering and Medicine, February 2012, Vol. 3 / 011008-1

15- M. Bassyouni, I. Taha, Shereen M.-S. Abdel-hamid and L. Steuernagel "Physico-Mechanical Properties of Chemically Treated Polypropylene Rice Straw bio-Composites". Journal of Reinforced Plastics and Composites, March 2012 31: 303-312, 2012 doi: 10.1177/0731684411436024.

16- Sayed A.Sherif, M.A.Sadek, F.H.Ashour, M. Bassyouni, 2009. Effects of surface treatment of ground rice husk on the polyurethane based on castor oil. Polymer & Polymer composites, 17 (8), pp 467-471

17- R.Sakthivel , D.Rajendran. "Experimental Investigation and Analysis a Mechanical Properties of Hybrid Polymer Composite Plates", International Journal of Engineering Trends and Technology (IJETT), V9(8),407-414 March 2014. ISSN:2231-5381

.