

# Cure Behaviour of a Fast Reacting Green Polyurethane Adhesive System

Norazwani Muhammad Zain<sup>1, a</sup>, Sahrim Ahmad<sup>2, b</sup>, Ernie Suzana Ali<sup>3, c</sup>

<sup>1</sup>*Fabrication & Joining Section, Universiti Kuala Lumpur Malaysia France Institute,*

*Jalan Teras Jernang, Bandar Baru Bangi, Selangor, MALAYSIA.*

<sup>2</sup>*School of Applied Physics, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, MALAYSIA.*

<sup>3</sup>*Faculty of Science & Technology, Universiti Sains Islam Malaysia, 71800 Bandar Baru Nilai, Negeri Sembilan, MALAYSIA.*

<sup>a</sup>[norazwani@unikl.edu.my](mailto:norazwani@unikl.edu.my) (corresponding author), <sup>b</sup>[sahrim@ukm.my](mailto:sahrim@ukm.my), <sup>c</sup>[ernie@usim.edu.my](mailto:ernie@usim.edu.my)

**Abstract**— Cure behaviour analysis of a fast reacting thermosetting system is critical in the manufacturing process of laminated composites. This study focuses on the investigation of the cure kinetics of polyurethane (PU) adhesive based on green polycaprolactone (PCL) polyol for aluminum laminated composites. Four different formulations of polyurethane adhesive by varying the NCO: OH ratio (1.3, 1.5, 1.7, 2.0) which were prepared from PCL polyol with a blend of aromatic and cycloaliphatic diisocyanate. The cure kinetics study was conducted by Differential Scanning Calorimetric (DSC) and evaluated by Star-e Mettler Toledo analytical software as a function of curing temperature and the ratio of isocyanate to a hydroxyl (NCO: OH). The results from dynamic calorimetric measurements clearly indicated that the increase of NCO: OH ratio effectively reduced the exothermic peak and temperature of the curing reaction. Isothermal calorimetric measurements suggested that the curing reaction time reduced as the isotherm temperature increased. This effectually increased the curing reaction rate and contributed to the reduction in the gelation time as well as working life of PU.

**Keywords**— polyurethane adhesive, cure behaviour, DSC, working life

## I. INTRODUCTION

Thermoset polymers are an important class of materials with many superior properties as compared with thermoplastic materials [1]. Because of their easy processing [2] and superior properties, this class of polymers are used in wide range of applications; from home appliances and furniture to the engineering applications including structural, automotive and aerospace [3]. Polyurethane is one of the thermoset polymers that possess excellent properties and can be tailor-made for various applications.

Thermosets systems consist of one or more resin and are cured using a different curing agents and catalysts [4]. Apparently, the curing process in thermosets involves the exothermic reaction, which means that heat is produced during the curing process. During the curing process, thermosets experience chemical reactions that initiate the growth of crosslink between the molecules and branching of the chains, thus increase the viscosity of the thermoset mixture. Numerous

chains are ultimately connected to a network formation of infinite molecular mass and, therefore, the mobility of individual polymer chains consequently diminishes [5, 6]. The materials turn into an insoluble and rigid infusible part once they are completely cross-linked.

The design of moulding process and optimization of process parameter are key factors in the production of thermosetting polymers, especially for fast reacting polyurethane. One of the prerequisites of the process parameter optimization is cure kinetics analysis. It has been revealed that the process of curing is the most crucial stage in the manufacturing of composite parts [7, 8]. Mijovic et al. [9] reported that a significant aspect of composite processing still in need of fundamental research relates to the development and implementation of in-situ sensors in aerospace industry.

The information related to internal process variables such as degree of cure of the fast reacting PU is very limited. Furthermore, problems occurred in the composite processing industry such as they cannot follow the recommendation provided by the manufacturers of thermoset resin regarding the cure cycle due to different component and mould geometry. Therefore, it is necessary to study the curing characterization of the fast reacting thermoset to control the exothermic reaction and predict the cure cycle of the materials.

The ratio of isocyanate to a hydroxyl (NCO: OH) is the most important parameter in the production of PU includes the production PU adhesive. This ratio can be varied in accordance with the PU application. This paper deals with the study of the influence of NCO: OH ratio (1.3, 1.5, 1.7 and 2.0) on the curing rate and degree of cure of PU adhesive based on green polycaprolactone (PCL) polyol by using Differential Scanning Calorimetric (DSC). This paper also highlights on the correlation between curing rate and the working life of PU adhesive. Working life of an adhesive is the period a resin or adhesive remain usable after the two components i.e. polyol resin and isocyanate were mixed.

## II. MATERIALS AND METHODS

### A. Materials

A PCL polyol based on PPKO ( OHV: 522 and molecular weight: 754 Daltons) was produced formerly using a method reported in the previous study [10]. 2,4-diphenyl methylene diisocyanate (MDI) with an NCO content of 31% was obtained from Maskimi Polyols Sdn. Bhd., bis(4-isocyanatocyclohexyl) methane (H<sub>12</sub>MDI) with an NCO content of 32%, propylene carbonate (PC), and ethanol were purchased from Sigma Aldrich.  $\gamma$ -Glycidoxypropyl- trimethoxysilane A 187 ( $\gamma$ -GPS) was supplied by Momentive Performance Materials Pte Ltd.

### B. Preparation of Polyurethane Adhesives

The PU samples were equipped with a clean, dry paper cup. Two types of isocyanate namely MDI and H<sub>12</sub>MDI with a ratio of 65:35 were mixed prior adding to the requisite amount of polyol resin. The ratio of NCO: OH was also varied from 1.3, 1.5, 1.7, to 2.0. The samples of PU were labelled PU1.3, PU1.5, PU1.7, and PU2.0, respectively. The mixture was mixed well using a mechanical stirrer at 1000 rpm for about 15 seconds, and then the adhesive mixture were ready to be applied or tested.

### C. Differential Scanning Calorimetric (DSC) Kinetics Study

The study of kinetics by using DSC comprises the quantification and measurement of heat released throughout curing to determine the extent of reaction [11]. Both calorimetric measurements i.e. dynamic and isothermal were performed by using a Mettler Toledo DSC823 thermal instrument. The PU samples were weighed in the range of 5 – 10 mg in an aluminum DSC pan.

#### 1) Isothermal Kinetic Study

The isothermal analysis is performed by monitoring the heat flow at a constant cure temperature. The sample in the container was placed in the thermal chamber, preheated at a specific isothermal temperature and heating was continued for 150 min. All the measurements were conducted in the inert atmosphere of nitrogen at a gas flow rate of 30mL/min. The isothermal temperatures used for the study were 100, 110 and 120°C. The exothermic heat flow generated at each isothermal temperature was recorded as a function of time. The completion of the reaction was indicated by the response of the DSC curve to the baseline following a linear pattern at high temperature. With the intention of ensuring completion of the reaction and quantifying any residual heat, a temperature scan was performed immediately after the isothermal measurement. The sample was cooled to -60°C at the cooling rate of 50°C/min, held for one minute, and then heated from -60°C to 250°C at 10°C/min. Data obtained were analysed by using Star-e Mettler Toledo analytical software.

Kinetic analysis by DSC assumes the amount of heat generated from a reaction ( $\Delta H_T$ ) is directly proportional to the

degree of cure and therefore the rate of cure ( $da/dt$ ) can be related to the heat generated by **Equation (1)** [11, 12]:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T} \frac{dH}{dt} \quad (1)$$

where  $dH/dt$  is the differential heat flow during cure.

In isothermal mode, the total heat released ( $\Delta H_T$ ) is given by **Equation (2)**:

$$\Delta H_T = H_{iso} + H_{res} \quad (2)$$

where  $\Delta H_{iso}$  is the heat released during the isothermal measurement and  $\Delta H_{res}$  is the residual heat measured dynamically after each isothermal cure.

#### 2) Dynamic Calorimetric Measurement

The dynamic DSC analysis is performed by monitoring the heat of reaction at a constant heating rate. In this study, this measurement was performed at various heating rate i.e. 5, 10, 15 and 20°C/ min over the temperature range of 25 – 200°C. Exothermic peak temperatures, as well as the overall heat of reaction of curing, were determined. In dynamic mode,  $\Delta H_T$  is the total heat per gram of mixture, which is determined by measuring the area underneath the exothermic curve. The ratio of the partial area over total area thus corresponds to a certain degree of conversion, assuming one of the reactants has been entirely consumed. Consequently, the ratio of partial area over total area under the exothermic curve is equivalent to the ratio of partial enthalpy ( $\Delta H_t$ ) over total enthalpy as in **Equation (3)** [13]:

$$\alpha = \frac{\Delta H_t}{\Delta H_T} \quad (3)$$

### D. Working Life of Polyurethane Adhesives

The working life of PU adhesives were performed according to ISO 10364:1993. About 5 g of each PU samples (PU1.3, PU1.5, PU1.7 and PU2.0) were set in a test tube. The adhesives were slowly stirred with a glass rod until the adhesive mixture gelled and stuck to the glass rod. The gelation time was recorded as the pot life or working life of PU samples.

## III. RESULTS AND DISCUSSION

### A. Effect of Heating Rate and NCO: OH Ratio on the Degree of Cure

Fig. 1 shows the thermograph of dynamic scan for uncured PU1.7 with different heating rates of 5, 10, 15 and 20°C /min. It was found that the temperature exothermic peak (first scan) increases as the heating rate increased while the height of exothermic peak also ascends. This behavior is a result of the kinetics reaction of PU. Due to the increasing of heating rate, there is a hydroxyl and an isocyanate group that has yet to react present at higher temperatures. This applies regardless of the reaction order and had been seen in the PU [14].

TABLE I. ISOTHERMAL DATA OF POLYURETHANE SYSTEM AT DIFFERENT TEMPERATURE

Sample	Heating rate (°C/min)	$\Delta H_T$ , (J/g)	$\Delta H_{res}$ , J/g	$T_{peak1}$ , °C	$T_{peak2}$ , °C	$\alpha$ (%)
PU1.3	5	97.38	1.26	107.56	160.97	98.7
	10	113.66	0.78	122.08	180.61	99.3
	15	118	-	127.15	-	100.0
	20	119.76	-	135.22	-	100.0
PU1.5	5	51.05	7.36	100.27	153.5	87.4
	10	100.94	-	119.74	-	100.0
	15	107.17	-	123.44	-	100.0
	20	96.88	-	127.76	-	100.0
PU1.7	5	70.59	-	101.71	-	100.0
	10	74.28	-	114.4	-	100.0
	15	95.37	-	123.12	-	100.0
	20	76.45	-	124.49	-	100.0
PU2.0	5	86.58	-	98.38	-	100.0
	10	62.56	-	110.54	-	100.0
	15	54.58	-	118.05	-	100.0
	20	74.93	-	121.37	-	100.0

From the Table 1, all samples except PU2.0 indicate the exothermic peak of the second dynamic scan has been detected at lower heating rates (5 °C /min). In addition, at 10 °C / min, PU1.3 also showed the presence of exothermic peaks in the second scan, while other samples showed an absence of such an exothermic peak. Flores [15] states that the absence of the residual of the exothermic peak in the second scan confirmed that the curing reaction was completed during the first scan.

Overall, there is no significant change in the total enthalpy ( $\Delta H_T$ ) when the heating rate is increased. The ratio of NCO: OH also has not substantially affected the  $\Delta H_T$ . This is because the amount of heat or enthalpy changed with the mass or weight of the sample [16]. Using thermal analysis software; Star-e Mettler Toledo, plot degree of cure ( $\alpha$ ) for PU1.7 versus curing temperature for each heating rate can be produced and shown in Fig. 2. It was found that the curing reaction has been shifted to the higher temperatures at the higher heating rates.

The effect of NCO: OH ratio on PU adhesive curing reaction is shown in Fig. 3 and 4. It was found that the temperature and height of the exothermic peak decrease as the ratio of NCO: OH increase. It is also observed from the Fig.4 that the plot is shifted to a lower temperature when the ratio of NCO: OH increased. This indicates that curing rate of PU2.0 is faster compared with the adhesive at lower NCO: OH ratio. This was agreed by Popovic et. al [17] which he studied the curing kinetics of two types of urea-formaldehyde adhesives. He suggested that the adhesive that exhibits a lower

exothermic peak temperature has higher reactivity and curing rate. Instead, PU1.3 experienced a slower curing rate as it showed the highest exothermic peak temperature, hence lower its reactivity and the curing process will be longer.

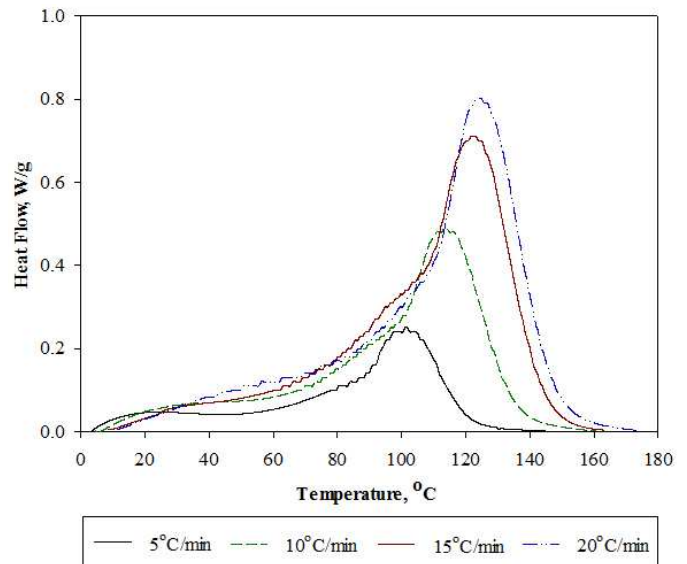


Fig. 1. Effect of heating rate on the cure of uncured PU1.7.

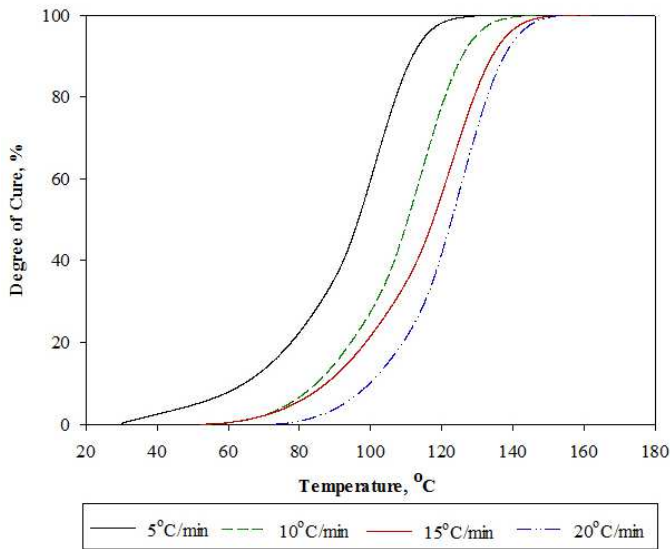


Fig. 2. Effect of heating rate on the cure temperature of PU1.7.

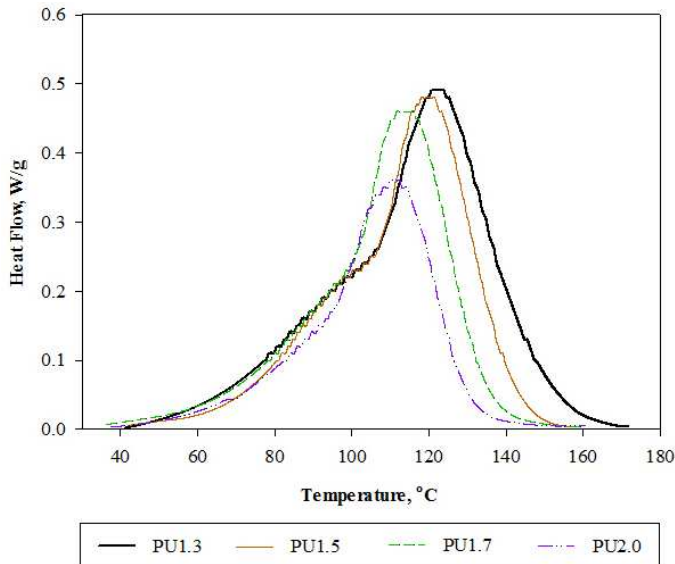


Fig. 3. Effect of NCO: OH ratio on curing behavior of PU adhesives at 10°C/min

**B. Effect of Isothermal Cure Temperature on the Degree of Cure**

Fig. 5 indicates DSC isotherm thermograph for sample PU 1.7 at three different curing temperatures, namely 100, 110 and 120°C. It was found that the time required for the exothermic reaction to occur is getting shorter when the isotherm temperature is increased. That means when the temperature is increased, the curing rate will also increase. The effect of temperature on the degree of cure can be observed in Table II. From the table, it was found that at a temperature of 100°C and 110°C, the exothermic peak occurs in the second scan. That means the degree of cure at both temperatures do not reach up to 100% [15].

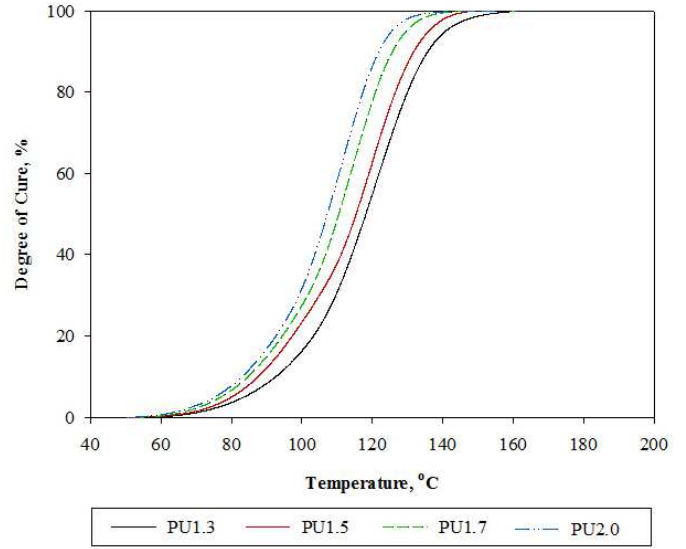


Fig. 4. Effect of NCO: OH ratio on the degree of cure of PU adhesives at 10°C/min.

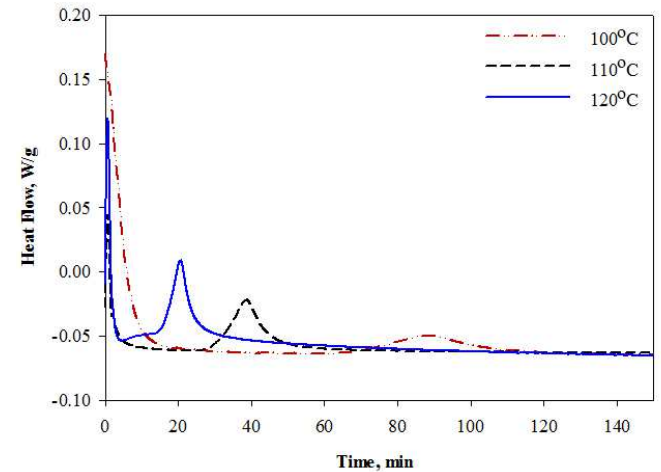


Fig. 5. DSC isotherm curve for PU1.7 at different curing temperatures.

TABLE II. ISOTHERMAL DATA OF POLYURETHANE SYSTEM AT DIFFERENT TEMPERATURE

$T_{iso}$ (°C)	$\Delta H_T$ (J/g)	$\Delta H_{res}$ (J/g)	$\alpha$ (%)
100	18.77	6.87	73.2
110	17.91	2.53	87.6
120	18.86	0	100.0

Fig. 6 shows the effects of different NCO: OH ratios on the time taken by the PU adhesive to completely cured. It was found that the higher the ratio, the shorter the fully cured time where PU1.3 required for about 56 minutes to fully cured while PU2.0 shows the shortest curing time (33 min).

As the curing reaction start ( $t=t_0$ ), small molecules of adhesive react and becomes a bigger molecule. This process continues until the reaction touches the gelation point ( $t=t_{gel}$ ), where the adhesive molecules connected. At this point, the first structure of crosslink is formed, and then the adhesive experiences the phase transition from liquid (sol) to the solid network (gel) [18]. Continuous of curing reaction would create a crosslinking network until it reaches the maximum level ( $t=t_{cured}$ ). The schematic of crosslink growth during the adhesive curing reaction is illustrated in Fig. 7. This is agreed by Jaruchattada et al. [19] in their study on the rheological investigation of cure kinetics and adhesive strength of polyurethane acrylate adhesive.

Table III shows the working life and gelation time of PU adhesives at a temperature of 25°C. It was found that the gelation time decreased with the increase of NCO: OH ratio. Similar patterns can be observed in the life working life of PU adhesive where the working life also decreased. The working life of PU1.3 recorded for 90 minutes while the PU2.0 recorded time to a very short working life, i.e. 5.5 minutes. That means after 5.5 minutes, the PU 2.0 cannot be applied over the substrate anymore as the adhesive is already in the solid state. It may affect the durability of adhesive if the working life is the too short. This is because the carbon dioxide (CO<sub>2</sub>) gas that resulting from the PU reaction is possible to be trapped in the polymer matrix and at the interface of adhesive and substrates that are also known as voids.

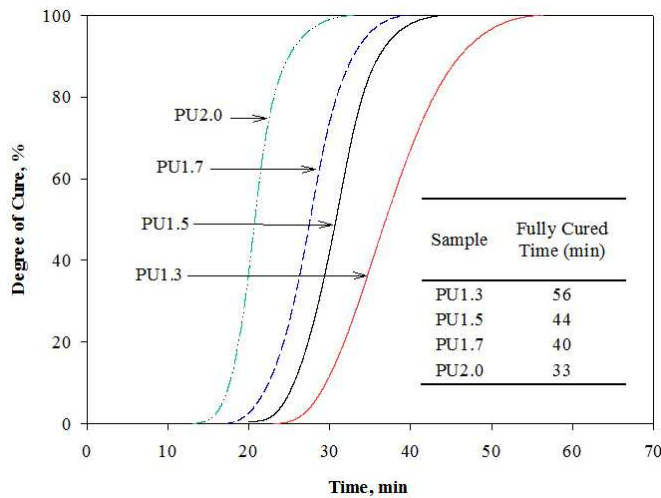


Fig. 6. Effect of different NCO: OH ratio on the PU adhesive curing time at 120°C.

TABLE III. GELATION TIME AND WORKING LIFE OF POLYURETHANE SYSTEM

Sample	Gelation Time at 25°C (min)	Working Life (min)
PU1.3	45±1.0	90±2.0
PU1.5	8±0.5	10±1.0
PU1.7	6±0.03	7±0.03
PU2.0	5±0.02	5.5±0.01

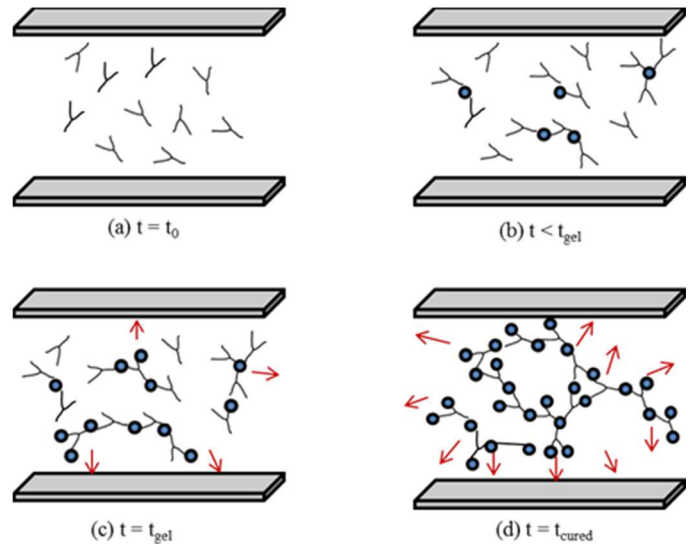


Fig. 7. Curing mechanism of PU adhesive.

#### IV. CONCLUSIONS

Four series of PU adhesives were prepared, and their cure behavior and working life were investigated. It was found that cure kinetic of green PU adhesive is depending on the NCO: OH ratio and isotherm temperature. The higher the isotherm temperature, the faster the rate of cure. PU 2.0 is found to have the shortest working life and PU1.3 has the longest. Nevertheless, the selection of the parameter in PU production depends on the mold geometry and also the durability of the PU adhesive itself.

#### ACKNOWLEDGEMENT

The authors would like to thank Universiti Kebangsaan Malaysia and Universiti Kuala Lumpur for the financial support of this research project.

#### REFERENCES

- [1] V. Mittal, Thermoset Nanocomposites. John Wiley & Sons, 2013.
- [2] R. Kotsilkova, Thermoset Nanocomposites for Engineering Applications. Rapra Publishing, 2007.
- [3] M. Biron, Thermosets and Composites: Technical Information for Plastic Users. Elsevier, 2003.
- [4] S. Lampman, Characterization and Failure Analysis of Plastics. ASM International, 2003, pp.89 – 104.
- [5] J. D. Menczel, and R. B. Prime. Thermal Analysis of Polymers, Fundamentals and Applications. 1<sup>st</sup>ed. New York: Wiley, 2009.
- [6] H. Vaskova, and V. Kresalek. "Raman spectroscopy of epoxy resin crosslinking." In: 13th WSEAS International Conference on Automatic Control, Modelling & Simulation (ACMOS '11). Lanzarote, Canary Island, Spain: WSEAS Press, 2011. 357-361.
- [7] R. Hardis, "Cure kinetics characterization and monitoring of an epoxy resin for thick composite structures", Master Thesis, Iowa State University, 2012.

- [8] E. Phil and C. Soutis, *Polymer Composites in the Aerospace Industry*. Elsevier, 2014.
- [9] J. Mijovic, M. Kenny, A. Maffezzoli, A. Trivisano, F. Belluci and F. Nicolais, "The principles of dielectric measurements for in-situ monitoring of composite processing," *Compos Sci Technol.*,49(3), pp.277 – 290, 1993.
- [10] N.M. Zain, S.H. Ahmad, E.S. Ali, N.A. Ahad, S.A. Zubir, "Characteristics of Hydrolysis Resistant Polycaprolactone/Palm Kernel Oil based Polyol," *Adv Mater Res*, vol. 576, pp. 334-337, 2012.
- [11] C. D. Han, K.-W. Lem, "Chemorheology of thermosetting resins. I. The chemorheology and curing kinetics of unsaturated polyester resin," *J. Appl. Polym. Sci.*, 28, pp. 3155 - 3183. 1983.
- [12] E. Papadopoulos, M. Ginic-Markovic and S. Clarke, "Reaction Kinetics of Polyurethane Formation Using a Commercial Oligomeric Diisocyanate Resin Studied by Calorimetric and Rheological Methods," *Macromol. Chem Phys*, 209, 2008.
- [13] F. Hernandez-Sanchez, H. Vazquez-Torres, "Activation energy for urethane-linkage formation. An improved calculation from the differential scanning calorimetry data," *J. Polym Sci.: Part A: Polym. Chem.* 28, pp.1579 - 1592,1990.
- [14] Dodge, J. "Chapter 4 Polyurethanes and Polyureas" In Rogers, M. E. & Long, T. E. (Ed.). *Synthetic Methods in Step-Growth Polymers*. pp. 197. New Jersey: John Wiley & Sons, 2003.
- [15] J. D. Flores, "Chemical and two-step cure kinetics of a high performance epoxy adhesive system," Master Thesis, Wichita State University, 2006.
- [16] Anon. 2014. "Best Methods of Increasing Cure Speed". <http://www.masterbond.com/techtips/best-methods-increasing-cure-speed> [16 January 2014].
- [17] M. Popovic, J. Budinski-Skimendic, M. Jovicic, J. Mursics, M. Diporovic-Momcilovic, J. Pavlicevic, & I. Ristic, "Curing kinetics of two commercial urea-formaldehyde adhesives studied by isoconversional method," *Hemijska Industrija*, 65, pp.717 – 726, 2011.
- [18] J. P. Pascault, H. Sautereau, J. Verdu and R. J. J. Williams, *Thermosetting Polymers*, 1st ed.; Marcel Dekker: New York, 2002.
- [19] J. Jaruchattada, A. Fuongfuchat & C. Pattamaprom. "Rheological investigation of cure kinetics and adhesive strength of polyurethane acrylate adhesive", *J. Appl Polym Sci*, 123:2344 – 2350, 2012.