

CHAPTER III

LITERATURE REVIEW

In this chapter reports about the researches of poly(ethylene terephthalate) and polyurethane, from 1980 - 1996. Baliga and Wong (1989) studied about poly(ethylene terephthalate), recycled from post - consumer soft-drink bottles was depolymerized by glycolysis in excess ethylene glycol at 190 °C in the presence of a metal acetate catalyst. The glycolyzed products consisted mostly of the PET monomer, bis(hydroxyethyl) terephthalate, and the dimer, and after long reaction time (up to and longer than 8 hours) an equilibrium was attained between these two species. No other higher PET oligomers were detected in the study. Of the four metal acetate (lead, zinc, cobalt, and manganese) tested, zinc acetate was the best in terms of the extent of depolymerization.

Chen, Uo, Hu and Lin (1991) studied about depolymerization of PET resin by ethylene glycol glycolysis under pressure was investigated. The kinetic of this pressurized depolymerization of PET resin was found that the rate of depolymerization was dependent of temperature, pressure and concentration ratio of EG to PET. The rate of depolymerization was proportional to the square of ethylene glycol concentration and faster than that under atmospheric pressure. The glycolyzed product under pressure consisted of the PET monomer, BHET and oligomers, mostly dimer and trimer. In case of lower ratio of EG/PET, the final product now consisted of higher molecular weight of oligomers rather than monomer, dimer and trimer.

Yoshioka, Sato and Okuwaki (1993) studied about the hydrolysis of waste PET by sulfuric acid at 150 °C. In this work, waste PET powder was hydrolyzed to TPA and EG in relatively dilute sulfuric acid (< 10 M.) and the sulfuric acid could be reused by recovery methods. PET powder was put in sulfuric acid in a sealed Pyrex tube and heated to 150

°C for 1-6 hours. After the reaction, a mixture of PET residue and TPA deposited was filtrate. The filtrate solution contained sulfuric acid and ethylene glycol. TPA was separated as terephthalate from the unreacted PET by dissolving with NH_3 . TPA insoluble in acid solutions was precipitated again in the filtrate containing sulfuric acid. The degree of degradation of PET and yield of TPA were determined by weight. The yield of ethylene glycol was measured by HPLC.

Comparative three procedures from three journals concluded that glycolysis in excess ethylene glycol procedure were easier than hydrolysis procedure. Depolymerization of PET was chosen to produce the chain extender because the final product had terminated-hydroxyl group (oligomer, BHET and excess ethylene glycol). The terminated-hydroxyl group is the suitable character to use as chain extender and the procedure is conveniently. The final product from hydrolysis consists of terephthalic acid, ethylene glycol and sulfuric acid, thus sulfuric acids must be separated out of the final product, this is difficult procedure.

The work of Baliga and Wong, and the work of Chen and the others were different when the equilibrium of depolymerization of PET was approached. Baliga and the other found dimer and BHET at the equilibrium, while Chen and the others found trimer, dimer and BHET. From two works concluded that the pressure had the effect on the quantity of the product of depolymerization. In this thesis was referred to glycolysis in excess ethylene glycol to depolymerize PET because no - pressure controlled in this procedure, to operate at low cost.

Lee, Sze and Lin (1994) studied about polyurethane synthesized from polyester polyols derived from PET waste. The PET waste was first depolymerized by glycolysis. The glycolyzed products were reacted with adipic acid to yield polyester polyols, and the polyester polyols were then reacted with either MDI or TDI to obtain polyurethanes. The polyurethane from this procedure had T_g that range from $-21.7\text{ }^\circ\text{C}$ to $16.3\text{ }^\circ\text{C}$, indicating elastomeric characteristics at room temperature and had a higher decomposition temperature in the range of $352.1\text{ }^\circ\text{C}$ to $365.9\text{ }^\circ\text{C}$, indicating good thermal stability. They were found that polyurethane having molecular weight of around 1000 in higher weight

percent of hard segment, that could attain about 90 kg./cm.³ in tensile stress, with about 320% in the elongation, with the modulus of about 170 kg./cm.³.

The researches about polyurethane elastomer described about the effect of the quantity of polyols, diisocyanate and chain extender on the properties. There were the researches from 1980 to 1996. Neirzwichi and Wysocka (1980) studied about polyurethane elastomers. They studied the amount of chemical cross-linking and microphase separation and found that had the effect on mechanical properties of the elastomers. The mechanical properties and glass transition temperature increased when the two factor in this work was swelled. In this work concluded that the mechanical properties of urethane was influenced directly to NCO/OH ratio and the excess of isocyanate groups was able to take part in cross-linking reaction through formation of allophanate or biuret linkages.

Deanin, Muraaka and Kapasi (1985) studied the effect of polyol molecular weight, polyol functional group and NCO/OH equivalent ratio. Polyurethane were prepared from isocyanate 125 - M MDI, and three polyester polyols that had different molecular weight, (1000,2000and 3000). The comparative polyurethane based-on polyester polyol and polyurethane based-on polyether polyol,the polyurethane were repeatedly prepared, but this preparation used polyether polyols instead of polyester polyols. The three polyether polyols had different molecular weight, (650, 1000 and 2000). This work concluded that increasing NCO/OH ratio also increased hardness, tensile modulus, ultimate tensile strength, ultimate elongation and rebound. Polyether polyols gave higher hardness, ultimate tensile strength, tensile modulus, tear strength and rebound than polyester polyols which gave higher ultimate elongation. The hardness, tensile modulus, ultimate tensile strength and tear strength of short-chain polyol were higher than the long-chain polyol. On the other hand, the higher ultimate elongation and rebound of long - chain polyol were higher than the short chain polyol.

Protrovic and Simendic (1985) studied the effect of soft - segment length and concentration of the soft segment on the properties of polyurethane. In this work three molecular weight of polytetramethylene oxide diols were varied. (Mw.650, 1000 and 2000).

The polytetramethylene oxide diols was mixed with 1,4 - butanediol and diphenylmethane diisocyanate. The maximum tensile strength obtained soft-segment concentration (the concentration of polytetramethylene oxide diols) was 40 - 50% and fixed NCO/OH ratio at 1:1. This result was explained by a specific interlocking morphology. The elongation at break increased linearly with polytetramethylene oxide diol concentration. On the other hand, hardness modulus and tear strength depended on hard segment concentration (1,4 - butanediol and diphenylmethane diisocyanate).

Harris et al (1990) studied the effects of isocyanate index in chemical composition of 4,4'- methylene - di(phenyl isocyanate) and 1,4- butanediol on properties which had constant quantity of poly(ethylene ether carbonate) diol. This work concluded that the melting point, hardness and tensile strength were improved when the isocyanate index in chemical composition were increased.

N. Maneerattanaroongrun (1994) studied about the polyurethane elastomer using brick powder as filler for saving the cost of paving surface. This work compared the properties of unfilled polyurethane and filled polyurethane. The polyurethanes were prepared by polyester polyol polymeric MDI, 1,4 - butanediol. The result were concluded that the suitable compositions for paving surface was 10% by weight of the brick powder.

Panich Olanwanich (1996) studies about development of polyurethane using diethylene glycol as a chain - extender and using brick as filler. The result of this work concluded that the suitable molar ratio of polyester polyol:MDI:diethylene glycol which gave the best properties was 1:4:3 at two NCO/OH ratio, one was at 1.02 and the other was at 1.11. The suitable composition of the brick was 10% by weight, the best percent of brick modified the hardness and tensile of polyurethane and loss the cost.

จุฬาลงกรณ์มหาวิทยาลัย