

CHAPTER III

LITERATURE REVIEW

Baliga and Wong [2] studied poly(ethylene terephthalate) recycled from post-consumer soft-drink bottles is depolymerized by glycolysis in excess ethylene glycol at 190 °C in the presence of a metal acetate catalyst.

This work summarized that the glycolyzed products consist mostly of the PET monomer, bis (hydroxyethyl) terephthalate and the dimer, and after long reaction time (up to and longer than 8 h), an equilibrium is 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 is best in terms of the extent of depolymerization, that is, the relative amount of monomer formed. The presence of green pigment in one type of recycled PET apparently has no effects on the glycolysis reaction.

Vaidya and Nadkarni [3] studied glycolysis of PET waste by propylene glycol at different weight ratios. The glycolyzed products were analyzed for hydroxyl value, number average molecular weight, and the amount of free glycol. The glycolyzed products were reacted with maleic-anhydride at a hydroxyl to carboxyl ratio of 1.1. The control resin was a general purpose unsaturated polyester prepared by reacting phthalic anhydride, maleic anhydride, and propylene glycol. The heating schedule of the polyesterification was comparable to that normally employed in the industrial process, with two isothermal plateau of 3-4 h. at 180 and 200 °C. The rate of reactions and rate constants were determined separately at 180 and 200 °C. The kinetics of the PET-based unsaturated polyesters was compared with that of the general purpose resin.

The results of this work were concluded that the PET waste could be depolymerized by propylene glycol to a molecular weight range of 276-480 . The polyesterification reactions followed a third - order kinetics. The rate of polyesterification of PET based systems were higher than that of the general purpose resin PET-based systems took about 10h to reach an acid value of 32 mgKOH/g whereas the general purpose resin took about 25h to reach the same acid value.

Tong et al [8] prepared a series of unsaturated polyesters based on bis (2- hydroxyethyl) terephthalate, ethylene glycol, propylene glycol , diethylene glycol , maleic anhydride and styrene. Properties of these casting were investigated and compared with those analogue based on dimethyl teraphthalate or polyester digomers formed by depolymerization of poly (ethylene terephthalate).

This work summarized that properties of casting based on bis(2-hydroxyethyl) terephthalate are superior to those based on polyester oligomer . When compared with those based on dimethyl terephthalate ,the castings have higher hardness and heat distortion temperature, but lower tensile strength and elongation; other properties are very similar.

Vaidya and Nadkarni [9] studied the kinetics of polyesterification of the glycolyzed PET waste with adipic acid. Glycolysis of PET waste was carried out with ethylene glycol at three different ratios of PET waste to glycol. The glycolyzed products could be readily polyesterified by reacting with adipic acid , to give polyester polyols with low acid number. Kinetics of polyesterification of the glycolyzed product made from 62.5 % ethylene glycol (EG) and 37.5 % waste were investigated further at different hydroxyl to carboxyl ratios. Reaction conditions were nonisothermal , comparable to the industrial process scheme consisting of two isothermal regions at 170 and 200 °C. The kinetics results of the polyesterification of glycolyzed PET waste are compared to the polyesterification of pure diols, namely ethylene glycol and bis(hydroxyethyl) terephthalate (BHET) with adipic acid. The reactions follow second-order kinetics

at 170 °C and the rate of polyesterification of the mixed diol system from PET waste lies intermediate between those of the pure diols, namely, EG and BHET. Ethylene glycol exhibited the highest reactivity. At 200 °C the kinetic plots of the mixed diols from PET waste were nonlinear, and thus the reaction may not follow second-order kinetics. The nonlinearity is explained in terms of the different reactivities of the different diol species in the reaction mixture. The polyester polyols, when cured with polymeric 4,4 - diphenyl methane diisocyanates, gave polyurethane rigid foams and elastomers.

Chen et al. [10] investigated the process of depolymerization of PET resin by EG glycolysis under pressure. The kinetics of this pressurized depolymerization of PET resin is discussed.

The results of this work were concluded that the rate of depolymerization is dependent of temperature, pressure, and concentration ratio of EG to PET. The rate of depolymerization is proportional to the square of EG concentration and faster than that under atmospheric pressure. Glycolized products under pressure consist of the PET monomer, BHET, and oligomers, mostly dimer and trimer. An equilibrium between BHET and oligomers is attained quickly soon after the depolymerization step is completed in the case of a higher ratio of EG/PET used. In the case of lower ratio of EG/PET, the final product now consists of higher molecular weight of oligomers rather than monomer, dimer and trimer.

Fujita et al. [11] investigated depolymerization of poly(ethylene terephthalate) to bis-hydroxyethyl terephthalate and/or its oligomer (BHET) by supplying the scrap, together with ethylene glycol, to a reactor containing molten BHET under the following conditions

- a) the molten BHET has a glycol to acid component equivalent ratio of 1.3 to 2.0
- b) the ratio by weight of the acid component of the molten BHET to that of the polyester scrap is 1/4 to 2/1

- b) the ratio by weight of the acid component of the molten BHET to that of the polyester scrap is 1/4 to 2/1
- c) the ratio of polyester scrap to ethylene glycol is such as to have a glycol to acid component equivalent ratio between the limits of 1.3 to 2.0

The depolymerization is performed at 215 to 250 °C with agitation of the reactions, after which a part of the product in the reactor be removed to a polymerizing reactor.



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