CHAPTER 1

GENERAL INTRODUCTION

1.1 Polymer recycling

Polymer recycling is the processes of recovering the polymer scrap or waste and reprocessing the material into useful products and this can be completely different in form from their original state. Recycling of those polymers especially synthetic polymers such as plastic is good for the environment, plastic is bad for the environment because it takes hundreds of years to biodegrade. Furthermore less money is spent on using more resources to make plastic, and less energy is used to make newer plastic, which saves the economy some money. However the recycling process can be costly and difficult because of constraints on waste contamination and inadequate separation prior to recycling. Another barrier to recycling is the widespread use of fillers, dyes and other additives in the synthetic polymer. The polymer is generally viscous to economically remove fillers and would be damaged by many of the processes.

1.2 Recycling methods

Polymer waste can be recycling by mechanical recycling. In the mechanical recycling of plastics this process involves a number of operational steps which are separation of plastics by resin type, washing to remove dirt and contaminants, grinding and crushing to reduce the plastics' particle size, extrusion by heat and reprocessing into new plastic goods. This type of recycling is mainly restricted to thermoplastics because thermosets cannot be remoulded by the effect of heat. This process is limited by the compatibility between the different types of polymers. Presence of a polymer in a matrix of a second polymer may change the properties and hinder the possibilities to use it in the conventional applications. In addition, most polymers suffer certain degradation during their use due to effects of temperature, ultraviolet radiation oxygen and ozone. Therefore recycled polymers exhibit lower properties and performances than the virgin polymers and are usually useful for lesser value applications. Chemical recycling of plastics, also referred as feedstock recycling is based on the decomposition of polymers by means of heat, chemical, or catalytic agent, to yield a variety of products ranging from the chemical monomers to a mixture of compounds with possible applications as a source of chemicals or fuels [20]. There are few alternative methods in chemical recycling such as hydrogenation, gasification, chemical depolymerisation, thermal cracking and catalytic cracking and reforming. In the hydrogenation method, the polymer is degraded by the combined actions of heat, hydrogen and many cases catalysts. Gasification is a process where plastic wastes react with oxygen and/or steam to produce synthesis gas which is carbon monoxide and hydrogen gas. In chemical depolymerisation, plastic wastes react with certain agents to yield the starting monomers while in thermal cracking, plastic wastes are decomposed by the effect of heat in an inert atmosphere. In catalytic cracking and reforming method the polymer chains are broken down by the effect of catalyst, which promote cleavage reactions.

1.3 Poly(ethylene terephthalate)

Polyethylene terephthalate which is commonly abbreviated as PET is a thermoplastic polymer resin of the polyester family and consists of polymerized units of the monomer ethylene terephthalate, with repeating $C_{10}H_8O_4$ units.

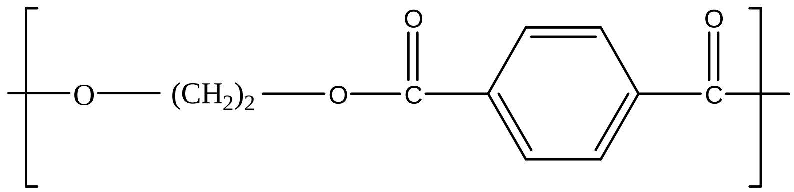

Figure 1.0 Repeating unit of PET.

PET is considered as one of the most important engineering polymers due to rapid growth in its use. It is regarded as an excellent material for many applications. It has excellent tensile and impact strength, chemical resistance, clarity, process ability, colour ability and reasonable thermal stability.

PET products are widely used in the manufacture of high strength fibers, photographic films and food packaging especially soft-drink bottles for replacing poly(vinyl chloride) and glass bottle. However because of its high resistance to the atmospheric and biological agents [1], the disposal of a large number of PET bottles has caused serious environmental problems [2]. The empty PET bottles are discarded by the consumer after use and become PET waste. In the recycling industry, this is referred to as 'post-consumer' (postc-PET) bottles. The postc-PET recycling industry started as a result of environmental pressure to improve waste management. The other aspect that acts as driving force for PET recycling industry is that PET products have a slow rate of natural decomposition. PET is a non-degradable plastic in normal conditions as there is no known organism that can consume its relatively large molecules. Complicated and expensive procedures need to be operated in order for PET to degrade biologically.

Since the postc-PET can find a secondary usage as new resources in different polymer productions, a lot of scientific work has been done on the development of new methods for recycling of postc-PET. This can economically reduce the PET waste. On the other hand, as the price of virgin PET remains stable, cheaper technologies for recycling PET give an added value to the PET recycling industry by providing industry with relatively cheaper PET.

1.4 Chemical Recycling of PET

Recycling processes are the best way to reduce postc-PET waste. In view of the recent sharp increase in the price of petroleum, the cost of PET products has also increase significant. Recycling PET has become more attractive, leading the development of new technologies. Currently, PET bottles have become one of the most valuable and successfully recyclable materials.

Generally in recycling of PET, there are two ways that have to be differentiated. First is mechanical recycling where the original polymer properties are being maintained. This process consists of the collection, disintegration and granulation of waste PET followed by their recirculation into production. The other way is chemical recycling, where the PET will return back to the initial raw materials purified terephthalic acid (PTA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) where the polymer structure is change completely, or in intermediates like bis-ß-hydroxyterephthalate.

Processes of chemical recycling of waste PET involved a few methods such as methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis and other processes. Methanolysis is the degradation process of PET by methanol at high temperatures and under high-pressure conditions. The products obtain are dimethyl terephthalate (DMT) and ethylene glycol (EG) which are raw materials for the production of PET. This process is used by large PET manufacturers just as Hoechst (Brandrup, 1975) , Eastman (Mush et al., 1992) and DuPont (Firm booklet, 1992) as well as lesser manufacturer (Kapelanski et al., 1995), quoted by Paszun et al. (1997).

Glycolysis degradation is carried out most frequently using ethylene glycol [3-5], diethylene glycol [6, 7], triethylene glycol [8] and propylene glycol [9, 10]. The process is conducted in a wide range of temperatures from 180-250 °C [1-8] and various reaction times. Hydrolysis can be performed in acid, alkaline or neutral condition. For acid hydrolysis, concentrated sulfuric acid is frequently used while alkaline hydrolysis is usually carried out with the use of an aqueous solution of NaOH [11, 12] of a concentration of

4-20% [1]. Water or steam is used in neutral hydrolysis [13] where the process usually runs at a pressure of 1-4 MPa at temperature of 200-300 °C. The other method of chemical recycling of PET is aminolysis. This process usually carried out using primary amine aqueous solutions in the temperature range of 20-100 °C and deep aminolysis yields corresponding diamides of TPA and EG [1]. TPA amide is produced by the reaction of anhydrous ammonia on PET in an ethylene glycol environment under ammonolysis process [14]. It was carried out under a pressure of about 2 MPa in a temperature range of

120-180 °C for 1-7 h.

All of these processes have both advantages and disadvantages. However, chemical glycolysis method makes it possible to employ very low amounts of reactants as well as application of lower temperatures and pressures in contrast with other methods such as supercritical methanol and thermal degradation while, hydrolysis under acidic or basic conditions may cause corrosion and pollution problems.

1.5 Production of PU foam from recycled PET

Under the chemical glycolysis, past researchs have suggested the synthesis of unsaturated polyester (UP) from PET waste [7, 9, 15] and investigated the kinetics of glycolysis on several glycols. Moreover, glycolysed PET find application in the manufacture of polyurethane foams [16] and polyisocyanurate foams [17]. Little of literature concerning polyurethane synthesis from PET waste has appeared. The literature mostly deals with rigid foams and polyurethane elastomers made by using ethylene glycol [16]. Method in producing foam was developed by using a mixture of polyols. This creative way successfully diversified foam characteristics for various applications and that is the reason why using polyol mixtures in the preparation of polyurethane foams is already known [18, 19].

1.6 Scope of work

The PU industry has been growing over 7% p.a. for the last 15 years and even in times of economic recession has maintained its global sales. In PU chemistry, the predominant reaction involves partners of the isocyanates and polyols. There are two main classes of commercial polyols currently used are the polyesters and the polyethers which have –OH terminals and both of the polyols are made from chemicals derived from petroleum, which are not sustainable and will rapidly diminish.

At the same time, the use of PET bottles is widespread causing the post-consumer PET bottles to increase rapidly. Therefore, the recycling of PET through the glycolysis process and producing a new polymer from the glycolysed PET, will not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy [7].

This work has investigated the use of PET glycolysed by glycerol to produce PET waste-based polyols for making new polyurethane system for various applications.

Objectives:

- To recycle postc-PET bottles by glycolysis method

  Waste of postc-PET bottle is glycolysed using glycerol. The influences of glycolysis time, glycolysis temperature and the equivalent weight ratio of PET to glycerol 9amount of glycerol) on glycolysis conversion are presented.

- To synthesize polyols from the degraded materials

  The reaction time and temperature of glycolysis are optimized and the glycolysed PET are further analysed for its hydroxyl value, acid value, FTIR and NMR.

- To develop a new polymer (PU foam) from the waste materials

  The glycolysed PET is used as a raw material in making PU foam after some modification to produce the semi-rigid foams.

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