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Chemical degradation of PET: Waste with different catalysts

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Abstract

This paper presents a review of work that covers chemical degradation of polyethylene terephthalate, known as PET. In this Paper, Several processes for PET degradation which is carried out by using glycolysis processes with ethylene glycol (EG) or other glycols in the presence of different simple chemicals acting as catalysts, namely, categorized in ionic liquids, metal salts, hydrotalcites, and enzymes have been discussed. From every process, some materials as a sample were used, and the one which is going to bring the best result is noted. The effect of some parameters such as degradation temperature, pressure, amount of sample, material ratio, and stirring rate was investigated. As a result we compared the methods and finally the best method for shown for PET waste degradation into monomers or oligomers is shown.

Keywords: Polyethylene terephthalate, waste, glycolysis. Catalyst, polyester

Introduction

Polyethylene terephthalate (PET) is a thermoplastic polymer with long branches of those which their wastes can be useable and bring economic benefits by using appropriate recycling methods ^[1]. It is used for tape recorders and videos and is largely used in packaging industry in different forms; The synthetic polymer industry is demanding an efficient sustainable ecologically friendly, less energy consumption and clean process for degradation of waste PET-bottles. In recent years, researcher's efforts have been made to find other stable, more environment friendly eliminate the use of expensive catalyst, solvents used in conventional recycling of waste PET techniques ^[2]. A variety of new techniques of mechanical and chemical recycling of waste PET have been employed along with the conventional process to increase the efficiency and purity, still the use of toxic and expensive reagent catalysts, impure monomer, low yield and discharge of byproduct waste circumvent these processes from industrial application ^[3]. Today several countries have realized the importance of this issue and started to recycle PET bottles and turn them into recycled polyesters in both mechanical and chemical methods according to their needs. Through mechanical recycling, waste PET bottles can be found in films, sheets, strapping packaging, and fiber used for sacking and their usage for insulation and for floor covering has also been studied ^[4]. Many processes for chemical degradation of waste PET have been put forward such as the methanolysis process with methanol ^[5] glycolysis process ^[6, 7], hydrolysis with TPA based monomer under the promotion of acidic or basic conditions ^[8, 9], however there exist advantages and disadvantages in these processes ^[10].

The primary objective of chemical degradation of PET is to increase the monomer yield while reducing the reaction time and/or carrying out the reaction under mild conditions. Continuous efforts of researchers have brought about great improvements in the chemical degradation processes ^[11]. Methanolysis is usually carried out at relatively high pressure and temperature, moreover it involves the volatilization of methanol. The main drawback of the glycolysis process is that reaction products are not discrete chemicals but the BHET monomer along with higher oligomers are formed which are difficult to purify with conventional methods ^[6]. Many researcher have reported chemical recycling of PET by strong acids or bases as effective

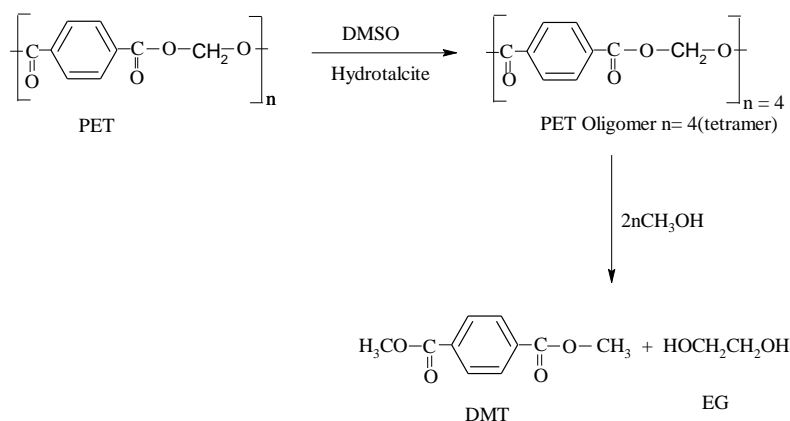
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catalysts for hydrolysis of PET to give TPA [12, 13] but the corrosion of the equipment and separation of EG from the waste acids were critical problems in these processes. Chemical degradation of waste PET by Ionic liquids can be good alternative, yet these reactions require high temperature, pressure and longer reaction time (10h) [18], so it is economically not feasible. Therefore there is a target for polymer chemist to develop an economically cheaper, highly pure and eco-friendly method for chemical degradation of PET which work under ambient conditions so that the

technology could be easily adopted by the plastic industry.

Degradation reaction

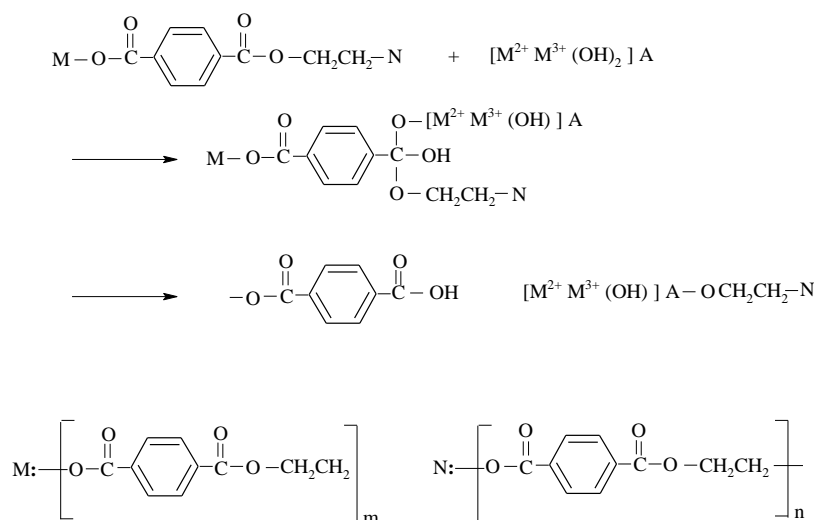
The degradation of PET-bottle was achieved in 10 minutes using hydrotalcite (Al:Mg:CO₃) as catalyst in solvent dimethyl sulfoxide (DMSO). The oligomer on treatment with sodium hydroxide in methanol at room temperature resulted in the precipitation of dimethyl terephthalate (DMT) and ethylene glycol in methanol, according to the following chemical reaction [14]:



The effect of degradation temperature on the degradation of PET with hydrotalcite catalyst in temperature range (120°C-190°C) at different time periods. The results show that the catalytic activity increased with an increase in reaction temperature and the rate of degradation is also enhanced as the reaction temperature rises and maximum conversion of 98% was observed at 190°C in 10 minutes. The remaining 2% oligomer stay dissolved in DMSO which got separated on recovery of DMSO by distillation. Hence this temperature was selected for further studies. It was observed that degradation was slow at 180°C and degradation was completed in 180 minutes and further decreases in temperature from 180°C to 160°C and 160°C to 120°C increased degradation time from 180 to 360 minutes and 360 to 540 minutes respectively. Different concentration of catalyst but PET was completely depolymerised at 0.5 g hydrotalcite in 10 minutes. At lower concentration of catalyst (0.05) PET was not completely depolymerised and conversion time is too high [14].

Mechanism of the process

For PET degradation a mechanism as shown in scheme 1 is proposed. During the degradation process, DMSO first penetrated into the PET chips, causing swelling of the chips. The metallic group of the hydrotalcite interacts with the carbonyl oxygen O=C in the ester. mean while the OH⁻ attacks the carbon atom of the ester group leading to the formation of a tetrahedral intermediate. These two interactions result in the breakage of the C=O bond as well as the decrease of the mol. wt. of PET [19]. The degradation increases with increase in temperature and time (Fig 8). Similar behavior has been observed by Bendak *et al.* [33] The solubility of oligomer only in DMSO help in higher activity. This may be due to improved desorption of product from the catalyst surface [34]. This supports the observation that high polarity of DMSO and solubility of oligomer in DMSO play an important role [14].



Scheme 1 Possible mechanism of the degradation of PET using hydrotalcite [14].

Conclusion

It can be concluded that hydrotalcite in presence of dimethyl sulfoxide (DMSO) as solvent can degrade PET within 10 minutes to afford oligomer (Tetramer), mol.wt.934 and molecular formula $\text{HOOC}[\text{C}_6\text{H}_4\text{COO}(\text{CH}_2)\text{OOC}]_4\text{C}_6\text{H}_4\text{COOH}$ (Lit. ^[15] Tetramer). The oligomer (Tetramer) using sodium hydroxide can be transesterified to dimethyl terephthalate (DMT) and ethylene glycol (EG) at room temperature ^[14] while other catalyst (like sodium hydroxide, zinc chloride, lithium chloride, magnesium chloride and ferric chloride) ^[16, 17, 18] required high temperature, pressure and longer reaction time (8-10 hrs.). Hydrotalcite enhances rate of the reaction due to large surface area, weak Lewis acidity, high adsorption capacity while other commonly used catalyst like (sodium hydroxide, metal acetate (lead, zinc, cobalt, and manganese) ^[19] shows low surface area. Hydrotalcite can be easily recycled and reused and easily separated from the product while various other catalysts, such as titanium-phosphate ^[6], metal acetate (lead, zinc, cobalt, and manganese) ^[20] and solid superacids ^[21] are difficult to separate from the products ^[22]. Thus hydrotalcite has the advantage of high reactivity, recyclability, nontoxicity, and ease of separation. The oligomer formed can be easily converted to DMT at room temperature resulting in zero effluent reaction ^[14].

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