

## RECEIVING OF TEREPHTHALIC ACID FROM POLYETHYLENE TEREPHTHALATE WASTE BY DEPOLYMERIZATION IN THE MELT.

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### Abstract

The technological method of terephthalic acid receiving by depolymerization of polyethylene terephthalate (PET) in the melt has been developed as the result of research. Mechanism of depolymerization is studied by mean of DSC analysis. It was established, that PET depolymerization in melt can be reached at atmospheric pressure, and temperature range 140-160°C during a short time with the yield of terephthalic acid close to 95-98%. Sodium or potassium hydroxide is more suitable reagents for PET depolymerization regarding technological point of view. The best found amount of alkali to be added to the polymer is 120% from stoichiometrically necessary quantity. Electrolytic method is more prominent for terephthalic acid precipitation because at the time of terephthalic acid receiving, sodium or potassium hydroxide can be regenerated by electrolysis and used in cycle. Possible use of catalyst – zinc acetate which is added into the melt to increase the degree of PET depolymerization is shown. The quantity of zinc acetate of 1% from polymer weight amount was found as optimum.

### Keywords

*Polyethylene terephthalate, depolymerization, alkali, melt, catalyst.*

### 1. Introduction

Terephthalic acid is the base for polyethylene terephthalate (PET) synthesis. Currently terephthalic acid is a strategic commodity, because the volume of PET production continuously increases. PET synthesis based on dimethyl terephthalate makes way for one based on terephthalic acid. Processing of PET waste, presented in the majority bottles and packaging waste, should be developed in several directions. The market of secondary materials cannot contain and does not require a large quantity of secondary PET processed by physico-mechanical methods. Therefore the use of PET chemical recycling with terephthalic acid receiving is necessary as alternative to the physico-mechanical processing method, despite technological complexity.

There are technologies of PET depolymerization with the use of alcohols, water, acids and alkaline reagents and even with ionic liquids use (1-butyl-3-methylimidazolium chloride) [1, 2]. Practically all of them use elevated pressure and high temperature [3]. In some cases, the process of PET depolymerization lasts several hours [4]. The best result, especially yield of terephthalic acid, in PET depolymerization has been achieved at the use of alkaline reagents because PET ester bond is more subjected and vulnerable to rupture under alkali influence [5].

But almost all developed technologies are based on the depolymerization in the solvent. The contact between alkali and polymer is not efficient. The reaction is going only on the polymer surface. Complete depolymerization takes time. Temperature, pressure and catalyst are used to accelerate the process. Zinc acetate, amines chlorides of different metals can be used to accelerate PET depolymerization. [6, 7].

A new method of PET depolymerization in the melt was discovered and the possibility of PET depolymerization in the melt was confirmed and reaction was studied by DCS analysis and realized in laboratory reactor [8]. The advantages of proposed method are the following. Method does not require a solvent; there is no evaporation of solvent in the atmosphere, no solvent recycling technics need to be used etc. Method is fast because of close contact of reagents and reaction of depolymerization is going in the volume and not only on the PET surface. Calcium hydroxide was found as the most promising and perspective reagent for PET depolymerization in laboratory condition because of its wide spreading, small cost and relative simplicity of handling and transportation. It was established, that the quantity of calcium hydroxide for complete PET depolymerization can be within the range 105-140% from stoichiometrically necessary amount. The highest reached degree of PET depolymerization was 95%. The time of depolymerization in the

melt was about 15 minutes. And the second stage of processing of melt product (hydrolysis in boiling water) took 30-60 minutes.

Technically the developed method needed to be improved in the way of reducing the quantity of technological stages. Making step from laboratory experiment to the industry, several technological complications have been arisen at the application of calcium hydroxide. We established that the use of potassium or sodium hydroxide for PET depolymerization in the melt is more justified in industrial scale.

## **2. Material and methods**

The developed chemical PET recycling process, for which colorless PET bottles crushed to the size of 5×5 mm were used, was performed under the following condition. Cut PET waste are alloyed for a certain time and temperature with an alkaline reagent in laboratory stainless steel reactor, then cooled and hydrolysed in water at steering. Terephthalic acid was regenerated by the adding of an inorganic acid or electrochemically and then filtered, washed and dried. All used alkalis and zinc acetate (chemical degree purity) were bought from Sigma-Aldrich (Singapore) and used as received.

### **2.1. Differential Scanning Calorimetry (DSC)**

PET depolymerization reaction has been studied by differential scanning calorimetry using a TA Instruments Model Q10 DSC machine, which was equipped with a DSC Refrigerated Cooling System to achieve low temperatures. The software used was TA Instruments Control. PET flaxes grinded by mean of spherical mill with liquid nitrogen cooling have been used for DSC analysis. PET and alkalis were mixed in certain stoichiometrical proportion and placed into hermetic aluminum pans. DSC analysis was done by heating of the sample up to 400°C at the rate of 10°C per minute.

## **3. Discussion**

The method of PET depolymerization in melt with calcium hydroxide has positive and negative characteristics. Calcium hydroxide is accessible, cheap, stable and very easy to use. But from technological point of view, calcium hydroxide application has several lacks. The salt formed after melting – calcium terephthalate is insoluble in water. Therefore, simultaneous precipitation of calcium terephthalate, terephthalic acid and impurities takes place during the hydrolysis. It complicates the technology, increases the number of purification stages and leads to low purity of terephthalic acid. Moreover, the melting process should be realized at high temperature (up to 260-280°C) and if ethylene glycol is formed during depolymerization process it would evaporate from the reactor because the temperature of process exceeds its boiling point.

### **3.1. The use of different alkalis for PET depolymerization in melt.**

The use of potassium or sodium hydroxide for PET depolymerization in the melt appeared more preferably due to several technological reasons. Potassium or sodium hydroxide is more expensive and aggressive compared to calcium alkali. But several advantages of the use of potassium or sodium hydroxide cover all negative moment and lacks.

The use of potassium hydroxide allows to reduce the temperature of depolymerization in the melt. It can be seen on DSC curves (figure 1) that depolymerization of PET in the presence of potassium hydroxide occurs at 140-160°C.

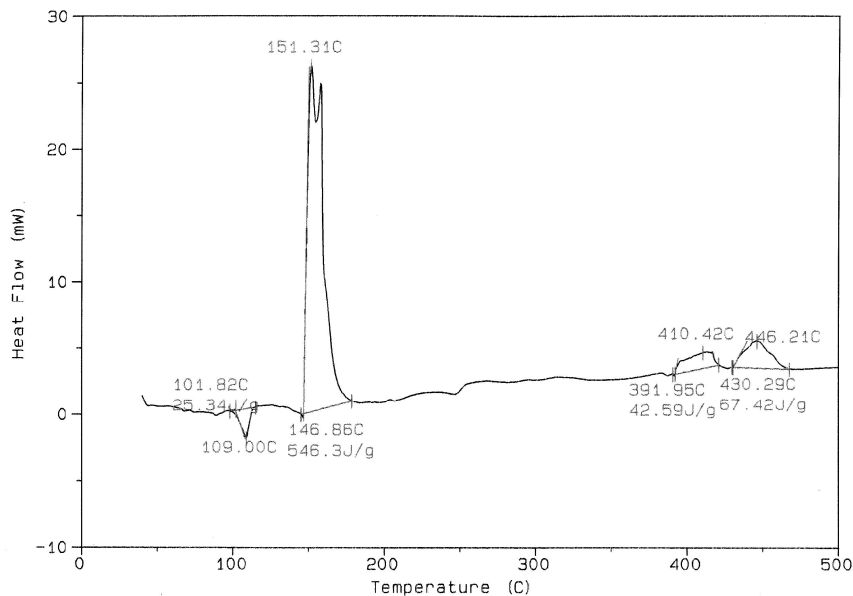


Figure 1. DSC analysis of PET depolymerization at the presence of potassium hydroxide.

Considering the splitting of main exothermic peak into two tops, we can suppose that there are two steps of depolymerization. The results shows the possibility to make depolymerization very fast because the process is exothermic and can be realized at lower temperature compared to the use of calcium hydroxide. It saves the time, energy for heating and mixing and decreases the lost of ethylene glycol because its boiling point is 197.3°C [9].

### 3.2. Use of catalyst to increase the degree of PET depolymerization.

Process of PET depolymerization can be improved by catalyst use. Many works have been done in the area of catalyst for PET depolymerization. Catalytic activity in PET depolymerization process has been revealed at the following chemicals: acetates of magnesium, zinc, tin, aluminum, copper etc [10, 11]. We studied the effect of zinc acetate added to the mix of PET and different amount of potassium hydroxide. PET depolymerization has been realized in laboratory reactor with mechanical steering. PET flakes, alkali and zinc acetate were added subsequently to the reactor preheated up to 100°C. One and three weight percents of zinc acetate (from polymer amount) were used to study the influence of catalyst on depolymerization process. Potassium terephthalate received after depolymerization was dissolved in water and insoluble part (impurities and unreacted PET) was filtered, dried and weighted. Amount of products insoluble in water after PET depolymerization with the use of different quantity of zinc acetate is presented in figure 2.

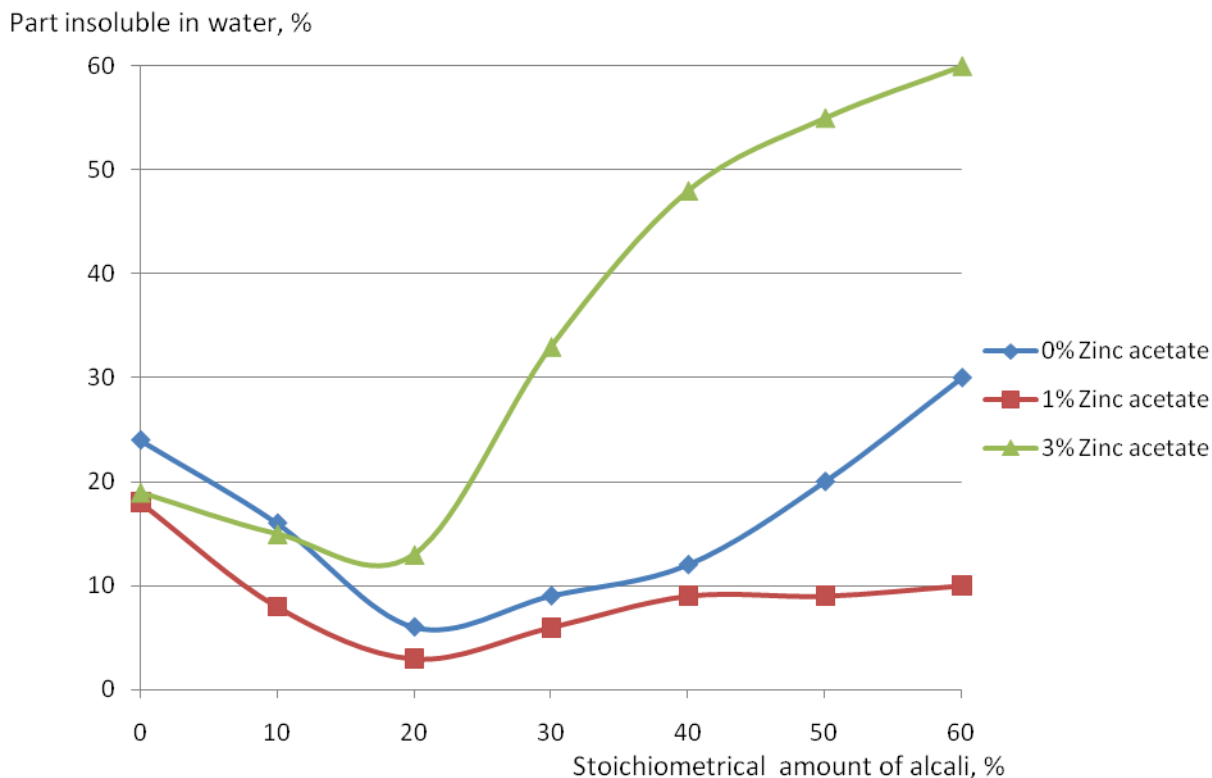


Figure 2. Influence of catalyst on degree of PET depolymerisation.

It was established, that the quantity of alkali for complete PET depolymerization can be within the range 105-130% from stoichiometrically necessary amount. The highest degree of PET depolymerization (96-98%) can be reached when the amount of alkali is 115-120%. Larger quantity of alkali invokes additional oxidation and degradation reactions that sharply augment the output of water insoluble products.

Zinc acetate improves the depolymerisation when it was added at the quantity 1% of polymer weight. We suggest that the highest amount of catalyst leads to redundant of transesterification reactions and formation of different condensed products that reduces the yield of potassium terephthalate and increases the amount of insoluble part. But we suppose, the use of catalyst in industrial scale is not well-grounded economically cause of small difference in results obtained for 0% and 1% of catalyst added to the melt (figure 2).

### 3.3. Terephthalic acid regeneration.

The product of PET processing in the melt represents very fragile material which can be directly put in reactor for hydrolysis. The grinding is no needed because sodium or potassium terephthalate is soluble in water even at room temperature. Formation of sodium or potassium salt of terephthalic acid, compared the calcium one, allows to omit the step of grinding and realize the dissolution at room temperature. Solubility of sodium/potassium terephthalate gives an advantage to filter the solution and separate all insoluble impurities. Filtered solution goes to the next technological stage of terephthalic acid precipitation.

There are some possibilities to regenerate terephthalic acid from solution of sodium or potassium terephthalate. Electrochemical and chemical methods can be applied. The choice of the best method for developed technology depends of the quantity of processed PET waste and amount of impurity and other possible local factors. When the amount of processed PET waste is not large, the use of chemical methods for terephthalic acid regeneration is more justified. For example, formation and sedimentation of terephthalic acid occurs at the addition of nitric or hydrochloric acid to the hydrolysis solution. Then terephthalic acid is filtered, washed out and dried in the vacuum oven. Potassium hydroxide is regenerated from potassium nitrate or chloride solution. Electrochemical method is more complicated from technological point of view, but it can combine several

technological steps: precipitation of terephthalic acid and regeneration of sodium/potassium hydroxide. Water can be used several times for hydrolysis, accumulating ethylene glycol which is well soluble in water. When certain concentration of ethylene glycol is reached, solution need to be regenerated by means of distillation or membrane separation. We aimed on terephthalic acid receiving in this method. Ethylene glycol might be considered as a secondary value product, because of two reasons. Theoretical weight yield of terephthalic acid is 2.5 times more than ethylene glycol because, for example, 1 ton of PET after depolymerization gives about 855 kg of terephthalic acid and 320 kg of ethylene glycol. And secondly, market price of terephthalic acid is much higher that one of ethylene glycol.

#### 4. Conclusions

New PET depolymerization method in the melt was developed and maximum approached to the industrial requests as a result of research. Alkaline reagent – sodium or potassium hydroxide allow to realize PET depolymerization during several minutes at the temperature 140-160°C.

Developed process of PET depolymerization differs from existing technologies by simplicity of the main reaction, use of cheap reagents – alkalis in solid state, absence of elevated pressures, supercritical temperature and long time of processing. Presence of impurity such as paper and other polymers does not affect the depolymerization process and terephthalic acid quality that is extremely important at waste processing. PET waste containing 90% of sand formed at the PET synthesis plant was successfully processed, with terephthalic acid received during the trial attempt. The quantity of technological steps was reduced to the minimum. Method of terephthalic acid receiving consists in the following technological steps: depolymerization of PET in melt in presence of sodium or potassium hydroxide; dissolution of received salt of terephthalic acid in water; filtration of solution to separate insoluble impurities; regeneration and precipitation of terephthalic acid by chemical or electrochemical methods; separation of terephthalic acid by filtration; drying of terephthalic acid in vacuum oven; regeneration of alkali; regeneration of ethylene glycol by distillation of membrane technology application.

Obtained terephthalic acid can be used as a product for chemical synthesis, for PET and heat-resistant polyester fibers production.

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