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Catalytic Depolymerization of PolyEthylene Terephthalate

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Depolymerization of bottle-grade commercial PolyEthylene Terephthalate by using different catalysts was studied, aiming to produce a material suitable for fabricating rigid polyurethane foams. The only catalyst which renders good results is the zinc acetate. The reaction involved was found to consist of a competition between a depolymerization and a repolymerization of the oligomers being formed.

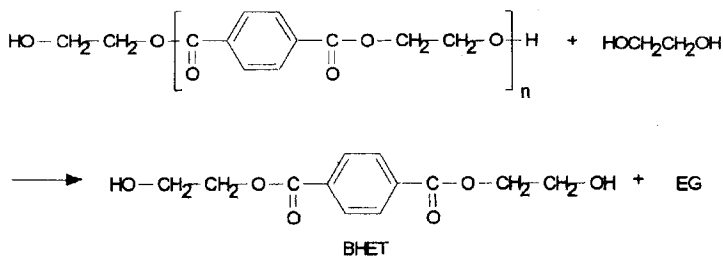
Keywords: Depolymerization; PolyEthylene-Terephthalate; catalysts

INTRODUCTION

Industrial production of PolyEthylene Terephthalate (PET) engineering resins involves the formation of various by-products, among which Bis (2-Hydroxy Ethyl) Terephthalate (BHET) oligomers have attracted a good deal of attention due to its use as a raw material for fabricating other polymeric goods of high added value, such as thermal insulating foams [1–3]. Besides the technological importance that PET oligomers

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could represent by themselves, the study of alternative methods for producing engineering materials from PET by-products also has an ecological relevance, for the oligomers being also formed during the degradation of PET by various mechanisms [4–11]. One of the most attractive possibilities consists in using them for producing rigid polyurethane foams, *via* a previous depolymerization process [8]. Two of the main degradation procedures for recycling PET are the methanolysis at high temperatures, which produces Dimethyl Terephthalate and Ethylene Glycol, and the glycolysis, which yields BHET and Ethylene Glycol, according to the following reaction scheme:



As mentioned above, BHET and related oligomers are employed in a number of industrial processes ranging from moulding components to automobile appliances [13]. In spite of this, relatively scarce work has been dedicated among the specialists to the details of the aforementioned reaction, in particular, to the role of the catalysts on the final properties of the produce. Accordingly, in this work the depolymerization of commercial PET bottles is studied in terms of the effect of various catalysts employed in the glycolysis of the PET, to produce BHET oligomers.

EXPERIMENTAL

Bottle-grade PET (Poliolos, México), Diethylene Glycol (Poliolos) were employed along with different catalyst to produce the oligomers. $\text{Ti}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$ (Poliolos), $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ (Poliolos), SnC_2O_4 (Baker), Na_2SO_4 (Baker) and SnOct (tin octate, Baker) were utilized as catalysts according to the following route: first, PET was grinded and mixed, at the molar relation established by Eq. (1), with Diethylene

Glycol in a 2 litre glass reactor. The catalyst in concentrations of 0.025, 0.05, 0.1, 0.5 and 1.0% wt, is then added and stirred and heated at different temperatures (210, 220, 230 and 240°C), for periods from 1 minute up to 9 hours. Once the reaction is completed, the solution is allowed to cool down to room temperature, filtered and the oligomers are separated by the water-extraction method [12].

ASTM standard E-326 was used to determine the number of —OH groups in the oligomer ASTM standard D-4672 allows to account for the amount of water in the specimens. Standard D-44625 was used to determine the number of carboxylic groups. Molecular weight was determined in a PL GPC apparatus. Finally, gas chromatography (Varian) was employed to follow the consumption and production of Diethylene Glycol (DEG) and Ethylene Glycol (EG).

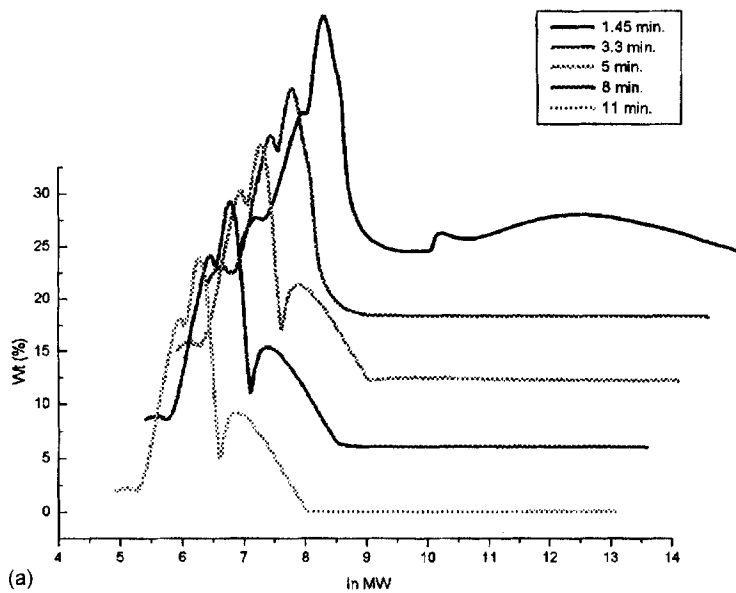
RESULTS AND DISCUSSION

The experimental design of the present study was aimed to establish the most efficient catalyst to produce an adequate raw material for fabricating polyurethane foams. Table I summarizes the industrial technical requirements for rigid foams. Therefore, only those catalysts which produced oligomers within those ranges were of interest for this study. The analysis of the whole set of data revealed that the only catalyst which produced a good material was precisely the zinc acetate, at 230°C. This agrees with previously-published results on similar reactions [11]. Therefore, from now on, the discussion will be centered around the results by using zinc acetate at 230°C.

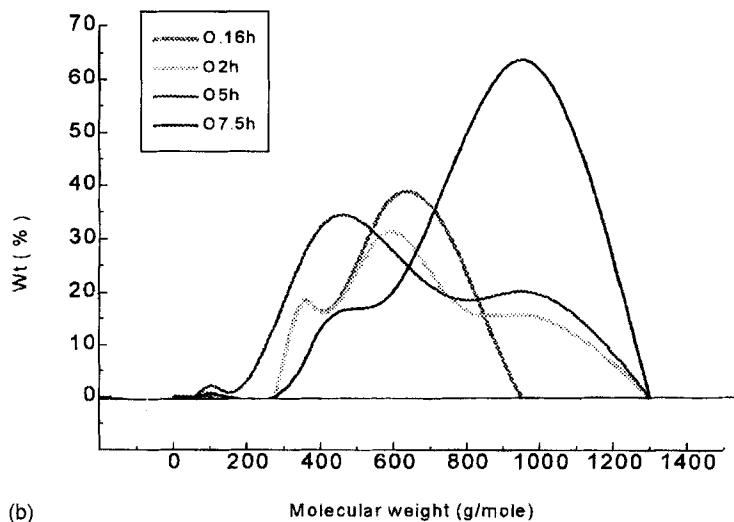
Figure 1(a) shows the GPC chromatographs of the depolymerization reaction by using the zinc acetate at various times, up to 11 minutes. Longer times can be appreciated in the plots of Figure 1(b).

TABLE I Required properties for rigid polyurethane foams

Molecular weight	650
Number of OH groups mg KOH/g	250–400
Viscosity at 25°C m Pa. S	5000
Density at 75% g/cm ³	1.15
Ignition temperature °C	210
Acidic number mg KOH/g	2.5



(a)



(b)

FIGURE 1 Gel Permeation Chromatography results by using zinc acetate in the depolymerization reaction. (a) up to 11 minutes; (b) after 11 minutes.

As can be observed in both figures, the system first produces a depolymerization, during the first 10 minutes, as expected. However, at longer periods, a polymerization occurs. This indicates that in reality there exists a competition between the polymerization and depolymerization processes. Indeed, the results show that first oligomers with molecular weights of around 370 are formed, and are subsequently polymerized to oligomers with molecular weights of around 950. Figure 2 shows graphically the evolution of these two types of oligomers. Figures 3(a) and 3(b) show the corresponding polydispersities up to 11 minutes and beyond, respectively.

The above results can be better understood by analyzing the gas chromatographs of Figures 4(a) and 4(b), which correspond to the evolution of DEG and EG, respectively. In principle, as DEG reacts, a product of the reaction is precisely EG. However, at higher temperatures, EG is dimerized producing again DEG. This cycle is broken by the transesterification of the oligomers, which thus show a tendency to

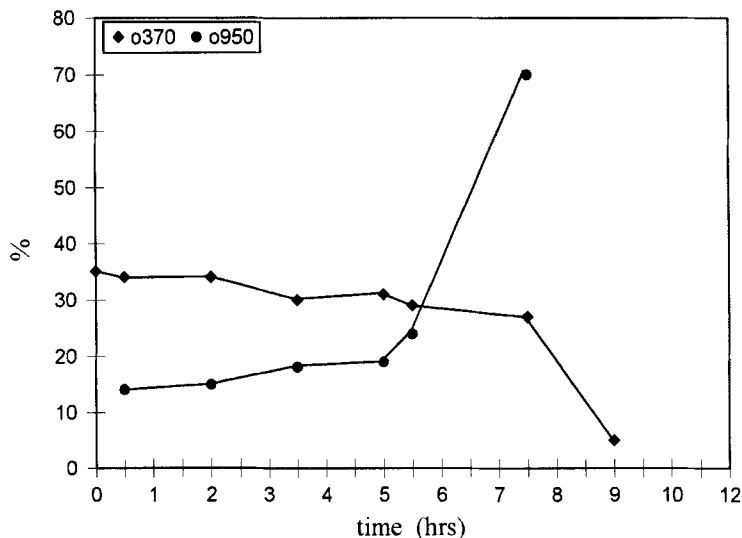
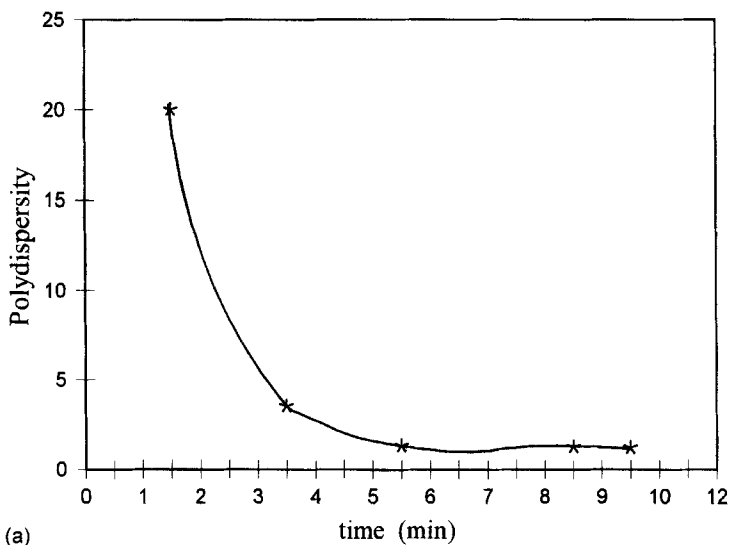
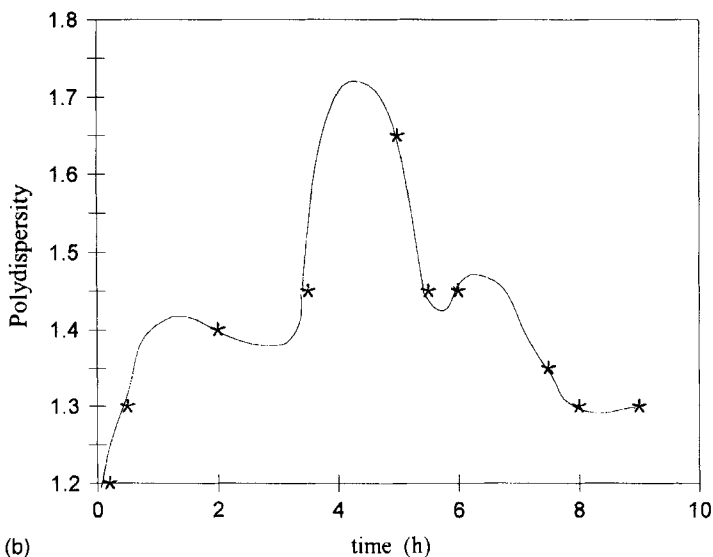


FIGURE 2 Evolution of oligomers with molecular weight of 370 and 950, as the reaction proceeds.



(a)



(b)

FIGURE 3 Polydispersity of oligomers produced. (a) up to 11 minutes; (b) after 11 minutes.

polymerize, as observed. The evidence of this is the small shoulder on the right hand side of the DEG chromatograph, which indicates a slight increase in DEG, in spite of some evaporation which is likely to occur.

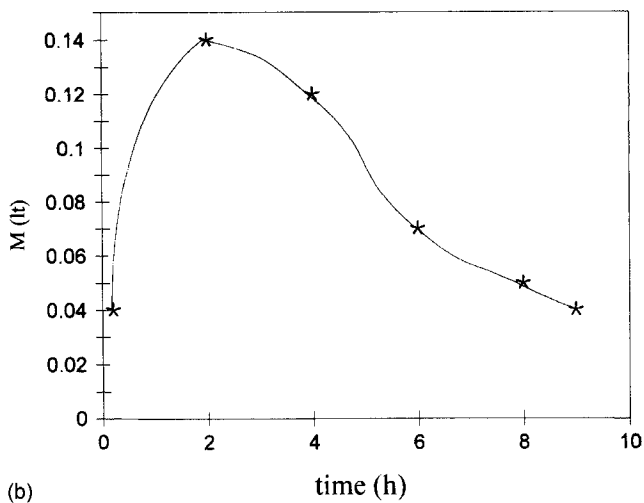
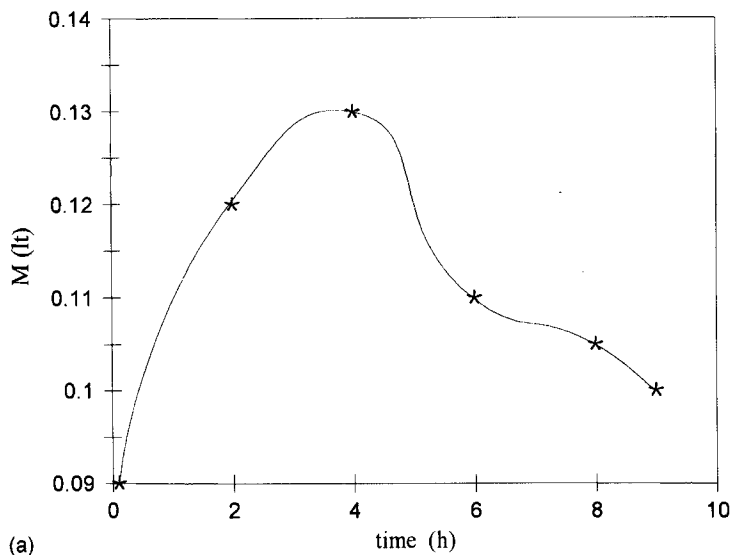


FIGURE 4 Gas chromatography characterization of the evolution of: (a) DEG and (b) EG.

On the other hand, Figure 5 shows the evolution of acidic number, expressed in mg of KOH per gram of produce, according to the ASTM standard mentioned in the previous section of this manuscript. The high values at the beginning of the reaction are attributed to the fact

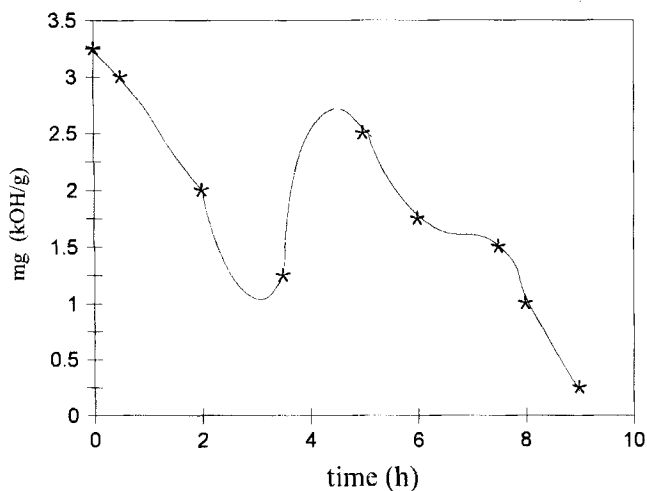


FIGURE 5 Acidic number of the product of the reaction.

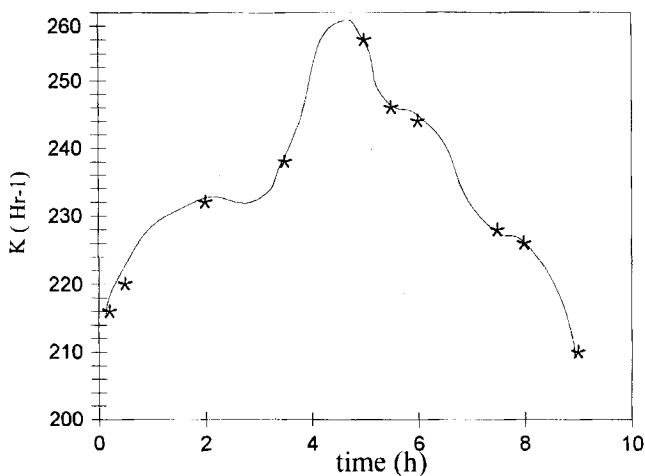


FIGURE 6 Number of OH groups as a function of reaction time.

that, when PET is dissolved into the DEG, an equilibrium situation is established. As the reaction proceeds and the DEG is consumed, the equilibrium is displaced and the acidic number diminishes. At around 5 hours of reaction an increase is observed. This is the same time at which the polymerization begins, according to the GPC (see Fig. 1).

Finally, the number of OH groups is extremely relevant if the product of the reaction is to be utilized for fabricating polyols suitable for producing rigid polyurethane foams. Figure 6 shows the evolution of the number of OH groups in terms of the reaction time. At the beginning, there exist an increase in the number of —OH groups produced, up to 5 hours of reaction. The further decrease is associated to the polymerization detected by the other techniques.

The above results lead to think that the depolymerization achieved was only partial, producing a mixture of monomers, dimers and trimers, as revealed by the corresponding molecular weights. The re-polymerization is likely due to the breaking of higher molecular weight oligomers, since the depolymerization competes with a degradation of the PET. This breaking produces oligomers with active groups which would react to re-polymerize.

CONCLUSIONS

Among all the different catalysts tested, only zinc acetate produces a material suitable for producing rigid polyurethane foams, according to the industrial requirements. The zinc acetate favors the depolymerization reaction up to 230°C. Above this temperature the degradation of the PET is so severe that the effect of the catalyst is negligible. The reaction is more complex than thought in other reports, for a re-polymerization competes with the desired depolymerization, as observed in this present work.

Acknowledgement

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