

Microwave Irradiation as an Energy Source in Poly(ethylene terephthalate) Solvolysis

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ABSTRACT: Solvolysis by glycols and alcohols is an established method for the chemical recycling of poly(ethylene terephthalate) (PET). In our work, we investigated the use of microwave radiation as the energy source in PET solvolysis reactions, and the conditions that govern its effectiveness. The main advantage of microwave use are short reaction times, between 4 and 10 min, in which complete PET degradation is achieved. Solvolysis reagents used were methanol, propylene glycol, and polyethylene glycol 400. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1115–1118, 1998

Key words: waste management; recycling; poly(ethylene terephthalate); solvolysis; microwave

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a polyester plastic material widely used in the packaging industry, especially in beverage bottle production. The material has excellent mechanical, as well as chemical, properties that make it an engineering material. Wide usage of the material has led to the development of PET recycling methods, making PET one of the most widely recycled polymer materials.¹ Part of waste PET is converted through mechanical recycling, while substantial amounts are recycled chemically by a number of solvolysis methods that yield monomers, their derivatives, or oligomers as final products.^{2–6} PET solvolysis reactions are based on a reaction mechanism in which a hydroxy group of the solvolysis reagent (glycol, alcohol) attacks the ester function of the polymer, thus shortening the polymer chain. The reaction is generally performed in the presence of a catalyst,⁴ heating, and may involve elevated pressures. Several commercial PET sol-

volyses, designed either as batch or flow-through processes, are currently in use.²

The use of microwave energy as an energy source in chemical reactions requiring heating has received much attention in recent years.^{7–9} The main advantage of microwaves over conventional heating sources is that the irradiation penetrates and simultaneously heats the bulk of the material. Research efforts have thus led to numerous applications in material processing techniques that have resulted in shorter reaction times and greater convenience.

In this article, we present results of microwave energy use in PET solvolysis reactions. The goal of our work was to search for a rapid, energy efficient, and convenient method of PET degradation. Such a development should improve the economics of commercial PET solvolysis processes.

EXPERIMENTAL

PET was obtained from washed waste beverage bottles that were chopped into flakes. Flake sizes varied from 1 to 15 mm. Solvolysis reagents used were reagent grade: methanol (Merck, KGaA),

propylene glycol (Alkaloid, Skopje), and polyethylene glycol 400 (Riedel-de Haën AG). Zinc acetate (Laphoma, Macedonia) was used as the catalyst in all experiments.

Degradation experiments in a closed system (i.e., at elevated pressures) were performed in a Milestone MLS 1200 mega microwave oven. The reaction vessel was made of polytetrafluoroethylene. A single power setting was used throughout each experiment. One series of PET solvolysis experiments was performed at a constant microwave applied power of 500 W, whereas the time varied from 2 to 8 min. The second series of solvolysis reactions was conducted at a constant reaction time of 4 min, and the applied microwave power varied from 400 to 800 W. Samples were mixed by a stirring magnet supplied by the manufacturer. Open system experiments were performed in a Prolabo Microdigest A-300 microwave oven at a continuous power output of 200 W. The reaction vessel and condenser were made of glass. Magnetic stirring was not used in open system experiments.

A typical sample in degradative experiments contained 0.75 g PET flakes, 0.1 g zinc acetate, and 10.0 g of the solvolysis reagent mixed in the reaction vessel. The amount of the solvolysis reagent used exceeded the usual 1 : 3 or 1 : 4 ratio between PET and the reagent. This was due to the geometry of the reaction vessel and the size of the stirring magnet in order to ensure that PET flakes were immersed in the reagent. In the closed system, the vessel was sealed and the experiment conducted. At the end of the reaction time, the samples were taken from the oven, and closed vessels were left to cool in a cold water bath for 10–15 min. The solid remainder of PET was then separated from the solution by vacuum filtration, dried to constant weight, and weighed.

Characterization of resulting solutions was performed by gel permeation chromatography: a Perkin–Elmer chromatograph with PL gel columns (upper nominal permeability limit 1×10^{-8} and 5×10^{-8} m), a diode-array LC-235 spectrophotometer, and a LC 30 refractive index detector. Polystyrene and recrystallized dimethylterephthalate were used as standards, and as effluent tetrahydrofuran at a flow rate of 1 mL min^{-1} .

RESULTS AND DISCUSSION

A series of PET solvolysis experiments under microwave irradiation was performed to determine

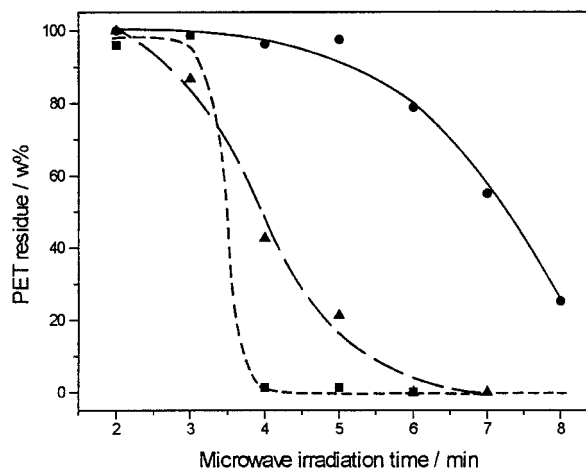


Figure 1 PET consumption versus microwave irradiation time in a closed system with (■) methanol, (▲) propylene glycol, and (●) polyethylene glycol 400 as solvolysis reagents. Applied microwave power was 500 W during all experiments.

the effect of irradiation time at a constant microwave applied power. Times ranging from 2 to 8 min were used at a constant applied microwave power of 500 W. Figure 1 shows the amounts of unsolubilized PET remaining after the reaction versus irradiation time. Complete PET degradation-solubilization was achieved in 4 min in methanol, in 6 min in propylene glycol, while more than 8 min are required in polyethylene glycol.

Data suggest that the reaction proceeds particularly fast in methanol. A 1-min reaction time difference from 3 to 4 min results in a change from virtually no degradation to complete degradation. The product of degradation in methanol was crystalline *di*-methylterephthalate (DMT), which was characterized by NMR¹⁰ (6.81 ppm, s, 4H; 3.97 ppm, s, 6H), IR¹¹ (1724, 1436, 1282, 1109, 730 cm^{-1}), and melting point¹¹ (differential scanning calorimetry, 138.8°C) determinations. These results are in accord with reports of DMT as the common product of PET solvolysis in methanol.^{2,12–14}

Degradation of PET in both glycol reagents required longer times than in methanol. This was particularly noticeable in polyethylene glycol, where no PET degradation could be observed at reaction times up to 5 min and 19% of PET still remained intact after 8 min of irradiation. PET degradation in propylene glycol follows a dependence similar to that in methanol, although it is slower. The change from no degradation to complete degradation is achieved by an increase in irradiation time from 2 to 6 min.

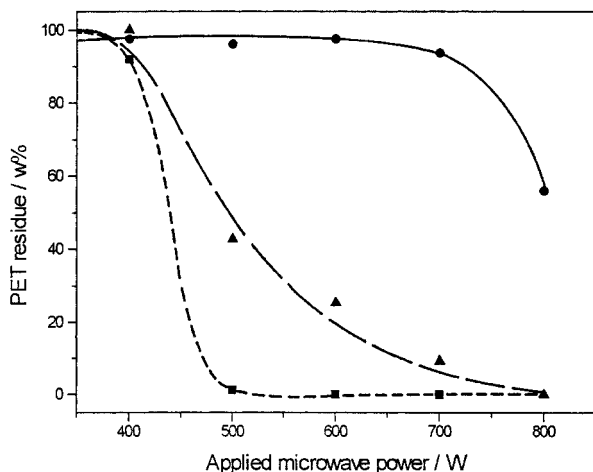


Figure 2 PET consumption versus applied microwave radiation power in a closed system with (■) methanol, (▲) propylene glycol, and (●) polyethylene glycol 400 as solvolysis reagents. Irradiation time in all experiments was 4 min.

PET degradation products in propylene glycol and polyethylene glycol remained in solution. The products were characterized by gel permeation chromatography. In the case of reactions in polyethylene glycol, a UV detectable broad peak was obtained at the relative peak molecular weight (PMW) of 1330. The peak had the same substructure as the peak for pure polyethylene glycol at approximately PMW 600. We thus assumed a glycol-terephthalic acid-glycol adduct as the main degradation product. In reaction mixtures where propylene glycol was used, the highest peak was found at PMW 440. This could be ascribed to an oligomer composed of three propylene glycol molecules connected through two terephthalic acid moieties. Weak peaks for additional oligomers at PMW 300 and 740 were also observed. The composition of solutions resulting from PET degradation in both glycols did not differ significantly with changes of irradiation time and power.

A second set of experiments was conducted at a constant reaction time of 4 min, while the output power was varied from 400 to 800 W. The dependencies of PET degradation on reaction conditions are shown in Figure 2. They are similar to those obtained from constant power experiments. Degradation in methanol yielding DMT shows a step-like dependency and has the lowest power requirement among the selected systems giving complete degradation at 500 W. PET degradation in propylene glycol has an intermediate power requirement (700 W), whereas PET in polyethylene

glycol is consumed only at applied power values above 700 W (42% at 800 W). The rapid degradation of PET in methanol found in both sets of experiments is most likely due to the low reagent boiling point that causes high pressures in the sealed vessel during the experiment. This strongly affects the position of the equilibrium degradation reaction. Pressures obtained with propylene glycol and polyethylene glycol are lower due to their higher boiling points, which is reflected in the difficulty/ease of PET depolymerization.

The significant influence of elevated pressure was confirmed by parallel experiments performed in a microwave oven equipped with open vessels that were kept at ambient pressure during the entire experiment. Due to evaporation, methanol could not be successfully used in this setup, whereas less than 10% of PET could be degraded in either propylene glycol or polyethylene glycol in irradiation times up to 15 min. The relatively ineffective PET degradation is most likely due to the low applied microwave power that may not be sufficient for the reactions to take place. An additional factor in favor of low PET consumption is the ambient pressure in the reaction vessel.

The second factor leading to rapid degradation of PET is the use of a stirring magnet that serves as an effective microwave energy absorber. Preliminary experiments performed without a stirrer resulted in a substantially lower PET degradation.

The described results show that, by using microwave radiation in a closed system, it is possible to achieve rapid PET degradation. Other authors have reported much longer reaction times for comparable reactions performed with conventional heating. Vaidya and Nadkarni³ reported a reaction time of 8 h in propylene glycol, whereas 6 h were required for PET consumption in polyethylene glycol.¹⁵ The difference is less in the case of methanol, where reaction times from 7 to 13 min were reported for a method developed by Hoechst in which the reagents are preheated.¹⁶

Zinc acetate was used as the catalyst in all experiments. Although the list of possible catalysts that have been studied in connection with PET solvolysis reactions is extensive, we chose zinc acetate because it seems to be the most commonly used.^{2,3} The amount of catalyst added to the reaction mixtures was kept constant, so no conclusion can be given as to the optimal reactant ratios.

CONCLUSIONS

The presented results show that the use of microwave radiation as the energy source in PET solvolysis resulted in the short reaction times needed for complete PET degradation, compared with reactions with conventional heating methods. Complete PET degradation in methanol and propylene glycol was achieved in 4 and 6 min, respectively, whereas up to 81% PET was consumed in 8 min in polyethylene glycol 400. Based on these results, we may expect to find similar advantages of microwave radiation use also in PET solvolysis reactions with other reagents. We have shown that the use of a catalyst, elevated pressure, and magnetic stirring contributes strongly to rapid PET consumption.

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