SOLVOLYSIS OF ON-LINE IDENTIFIED AND REFUSED HIGHLY COLOURED AND COMPLEX PET POST-CONSUMER WASTE BOTTLES AND PACKAGES

S.Arnaiz*[1], A.Asueta[1], M.Arieta-araunabeña[1], D.Manjón[1], R.López-Fonseca[2], J.I.Gutiérrez-Ortiz[2], I.Duque[2]

[1] GAIKER-IK4 Technological Centre, E-48170 Zamudio (Spain)
[2] Chemical Engineering Department, Faculty of Science and Technology, The Basque Country University - UPV/EHU, P.O. Box 644, Bilbao E-48080, Spain.
E-mail: arnaiz@gaiker.es

Abstract: The relevancy of this paper is based on the global scientific understanding and technical approach to the use of on-line polymer identification for sorting PET post-consumer waste bottles and packages in two fractions and their coupling with the requirements of their subsequent recovery steps. The fraction containing light coloured and monomaterial PET will be derived to mechanical recycling and the one having highly coloured and complex multilayered PET to feedstock recycling.This work is focused to go in deep in that need and try to correlate inlet feed properties, reaction parameters and catalyst selection with exit stream conditioning requirements and product quality.

1. Introduction

Nowadays, due to the general awareness about environmental issues in the society, it is necessary the improvement of technologies for the treatment and recycling of plastic wastes. PET consumption worldwide almost has doubled during the last years, having passed from 5 million tonne in the year 2000 to near 10 million tonne in the year 2006, being soft drink and mineral water bottles have been the applications in which major growths have been registered. In the same way that the consumption has increased, the waste generation and its collection, sorting and recycling, supported by the integrated waste management systems, have presented the same trend, so that in the year 2005 almost 2.5 million tonne were collected in the whole world, and it is foreseen that in year 2010, this quantity will reach on 4 million tonne [1].

Additionally to material itself demand, needs of content preservation have been responsible for the development of barrier materials and marketing strategies favoured the introduction of high coloured materials associated to brands and quality perception. Currently, one emerging challenge associated to PET recycling, is to provide a suitable treatment to the highly coloured and complex multilayered post-consumer waste fractions of PET. Both fractions are not convenient to be mixed with transparent and slightly coloured PET and hence does not exist for them a different alternative to disposal. These fractions are not appropriate for mechanical recycling because derived products present limitations either in colour, transparency or intrinsic viscosity, restricting their applications and value. In accordance with this, the present work proposes feedstock recycling as alternative of management for this non mechanically recoverable fractions, even though this option has not begun to apply until recent dates and at preset only covers the treatment of 0.4% of the total plastic waste collected in Europe.

In this work, NIR spectroscopy and other on-line techniques have been applied for sorting the post-consumer waste streams of PET bottles and packages in two fractions, one containing the slightly coloured and monomaterial PET, to be mechanically recycled and the other one the high coloured and complex multilayered PET to be derived towards feedstock recycling. Additionally, the study PET glycolysis process has done. The reaction consists of the degradation of polymer at temperatures in the range of 180-240°C, atmospheric pressure, with an excess of ethylene glycol (EG) and the presence of a catalyst which promote the formation of bis(hydroxyethyl) terephtalate (BHET) [2]. In principle, glycolysis conditions allows to use reduced amounts of reagents as well as low operation temperatures and pressures when compared with other methods such as methanolysis or thermal degradation [3-5], while hydrolysis under alkaline or acid conditions involve serious environmental problems associated with corrosion and management of the liquid effluent [6]. BHET, after adequate purification, is used in PET synthesis, or in the production of other polyesters, polyurethanes, plasticizers, epoxy resins, additives for textiles and biocompatible materials [7-12]. These numerous applications, in turn, provide an economical flexibility when using the raw monomer for the most profitable option upon demand.

2. Experimental

2.1 Materials

During this research work a virgin PET (Lighter S93 PET Copolymer) supplied by EQUIPOLYMERS and samples of highly coloured and complex multilayered post-consumer PET wastes provided by ECOEMBES, the Spanish integrated management system for the light packaging waste, have been used. The information related with PET materials is shown at Tab.1.

Post-consumer PET waste bottles and packages have been grinded to 5 mm flakes and, in order to avoid dirtiness effects at reaction tests, cleaned with diluted caustic soda, rinsed with water and dried. PET clean flakes have been milled by using a cryogenic mill to 250 μm to minimise diffusion controlled regimes at reactor. The solvent, EG (ehylene glycol 99%), has been purchased from ALDRICH and $Zn(Ac)_2 \cdot 2\ H_2O$ (zinc acetate dihydrate 99.5%), the catalyst, from PANREAC. Trying to simulate reaction conditions expected to be found at industrial plants, reagents have been used directly without any further purification.

Tab.1 PET materials tested in glycolysis reactions

Origin	Virgin	Post-consume	Post-consume	Post-consume	Post-consume	Post-consume	Post-consume
Nature	Natural	Highly-coloured	Highly-coloured	Highly-coloured	Highly-coloured	Highly-coloured	Multi-layered
Colour	Transparent	Blue	Silver	Green	White	Mixed	Amber
Application	Pellet	Bottles	Bottles	Bottles	Bottles	Various	Bottles
Content	---	Water	Soft drink	Soft drink	Various	Various	Beer
Photo							

2.2 Automatic identification tests

A commercial automatic identification and sorting system, the Unisort® manufactured by RTT Systemtechnik, has been used for the post consumer waste PET packages identification and sorting tests. The system comprises: an acceleration belt, an identification belt, a sensor head with 32 probes, two nozzle groups for classification by blowing air, a collecting hood and an operation and control unit. Identification tests have been carried out with representative samples of post-consumer PET wastes in order to measure separation and purity rates.

2.3 Glycolysis of PET

Glycolysis experiments have been carried out in a 250 mL, a three necked, flat bottom glass reactor equipped with thermometer and condenser operated at atmospheric pressure. A stirrer is incorporated to the tank to assure proper mixing and turbulence. In all runs, 30 g of PET together with 1% catalyst by weight basis were charged to the reaction system. Firstly, a set of reactions with virgin PET have been carried out to assess the influences of time, temperature and EG/PET ratio and select the appropriate conditions for the depolymerisation of post-consumer highly coloured or complex multilayered PET. Recovery of product after each glycolysis run has been completed by adding boiling water into the reactor, keeping the mixture at 100°C during 20 min and stirring vigorously. Once BHET oligomers are precipitated, the mixture has been filtrated and the recovered liquid has been refrigerated at 5°C during 5 h to assure BHET precipitation. After the filtration to separate BHET from EG, BHET has been dried at 60-80°C during 3 h for later analysis.

2.4 Analysis of glycolysis products

A FTIR spectrophotometer (Nicolet Protegé 460 Model) has been used to identify the chemical structure of BHET. Samples were mixed with KBr (2:100) and the mixture was converted into a disc by mean of a press, applying a pressure of $3.5 \cdot 10^4$ $N \cdot cm^{-2}$. A DSC

(Mettler Toledo DSC822e Model), has been used for thermal analysis of BHET. Samples were heated from room temperature to 350°C with a heating rate of 10°C/min under a nitrogen stream of 15 mL/min.

3. Results and discussion

3.1 Automatic identification tests

Representative samples of the plastic fraction coming from the post consumer light packaging waste stream collected by ECOEMBES has been studied by means of a NIR spectrometer. The NIR spectra of both plastic materials (PET, HDPE, PVC, LDPE, PP, PS) and non-plastic materials (wood, paper, aluminium film), usually found due to their application at packaging, have been recorded and examined. As shown at Fig. 1 and Fig. 2 , PET spectrum presents a distinctive peak at 1,657 nm which made possible to differentiate packaging materials including this polymer from the others.

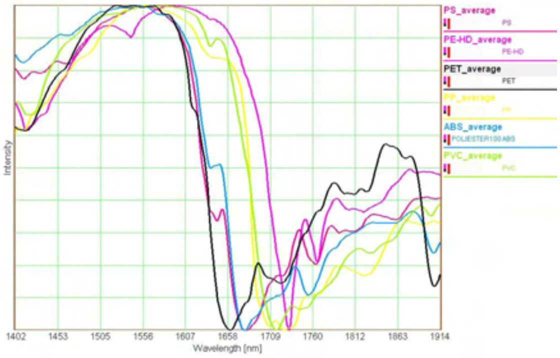

Fig. 1 PET and other polymers spectra

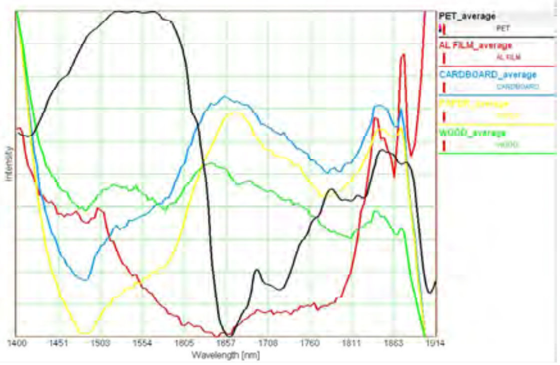

Fig. 2 PET and no-polymers spectra

On-line identification of the PET fraction and subsequent automatic sorting of it, with high yield and purity, has been possible using the Unisort® system. Recognition highly coloured and multilayered PET materials haves not been successful by NIR. Image analysis and colour sorting technology is proposed for the segregation of those fractions in a second separation step.

3.2 Glycolysis reactions

Time, temperature and PET/EG ratio have been chosen as the independent variables for the glycolysis study, setting catalyst/PET ratio on 1% by weigh. Run #1 at Tab. 2 has been carried out using virgin PET for studying the evolution of BHET yield with time. Reaction progress at 20 min, 40 min, 1, 2, 3, 4, 5 and 8 h is shown on the curve at Fig. 3. Run #2 has been used to compare reaction rate without catalyst that has been confirmed slower. Although run #1 verified that catalysed reaction reached equilibrium after 2 h, in order to shorten duration of preliminary work, it has been selected a time of 1 h to determine the influence of the independent variables. Runs #1, #3 and #4 have been respectively carried out at 165, 180 and 196°C and confirmed the need for operating at the maximum reachable temperature that, in practice, corresponds to the closest one to the boiling point of glycol at atmospheric pressure. The achieved BHET yields at a given time with temperature are represented at Fig. 4. Finally, runs #5 and #6 have been completed at 1:4.5 and 1:6.75 PET/EG molar ratios and verified that the 1:9 is the value required for getting a reasonable BHET yield as plotted at.Fig.5.Runs #7 to #12 at Tab. 2 are the glycolysis of the highly coloured and complex multilayered post-consumer PET wastes after 2 h at 196°C and 1:9 PET/EG ratio. After representing at Fig.6 the BHET yields it has been found that the PET nature does not have significant influence but on the cases of white and multilayered materials.

Tab. 2 Glycolysis reactions with virgin PET and post-consumer waste PET

Run	t (h)	T (°C)	PET Nature	PET (g)	PET/EG (mol/mol)	$ZnAc_2$/PET (w/w)	BHET yield (%)
#1	8	196	Virgin	30	1:9	1%	79.06
#2	8	196	Virgin	30	1:9	---	67.74
#3	1	165	Virgin	30	1:9	1%	46.99
#4	1	180	Virgin	30	1:9	1%	78.77
#1	1	196	Virgin	30	1:9	1%	79.99
#5	1	196	Virgin	30	1:4	1%	61.96
#6	1	196	Virgin	30	1:6.75	1%	75,70
#1	2	196	Virgin	30	1:9	1%	79.32
#7	2	196	Blue	30	1:9	1%	76.16
#8	2	196	Grey	30	1:9	1%	80.20
#9	2	196	Green	30	1:9	1%	78.37
#10	2	196	White	30	1:9	1%	72.99
#11	2	196	Brown	30	1:9	1%	80.46
#12	2	196	Multilayered	30	1:9	1%	69.86

3.3 Analysis of glycolysis products

DSC and FTIR analysis of BHET produced after the glycolysis of highly coloured and complex multilayered post-consumer waste streams of PET at runs #7 to #12 are illustrated in Fig. and Fig. and compared with the one derived from virgin PET at run #1. In both figures, curves have been shifted to provide a better comparison. According to previous DSC analysis, in which melting temperature of BHET and dimmer have been verified to be around 110°C and 170°C respectively, it has been assumed that main glycolysis product is BHET. On the other hand, regarding FTIR studies it has been confirmed that, for a pure BHET, the absorptions at 3.400, 3.000-2.800, 1.750 and 1100 cm^{-1} are respectively due to -OH, C-H, C=O and C-O verifying that infrared spectra of glycolysis products correspond with the BHET one.

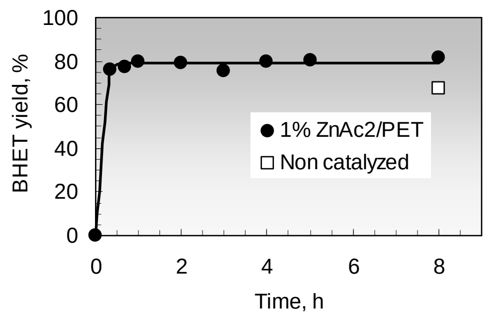

Fig. 3 Time effect on BHET yield (virgin PET glycolysis at T=196°C, PET/EG=1/9)

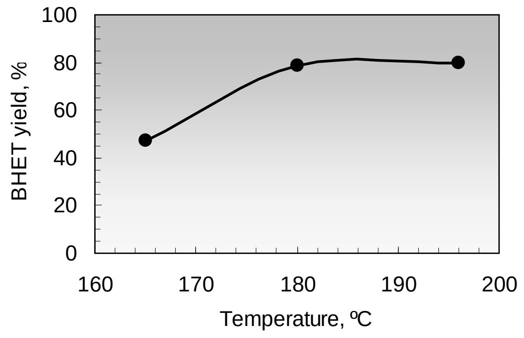

Fig. 4 Temperature effect on BHET yield (virgin PET glycolysis at PET/EG=1/9, t=1 h)

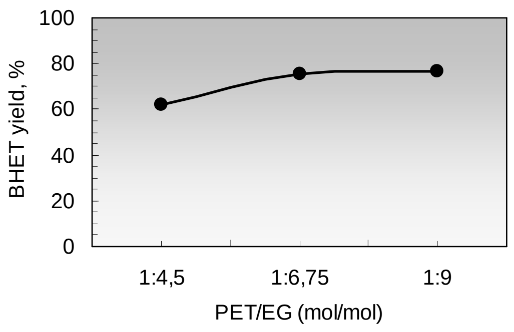

Fig. 5 PET/EG ratio effect on BHET yield (virgin PET glycolysis at T=196°C, t=1 h)

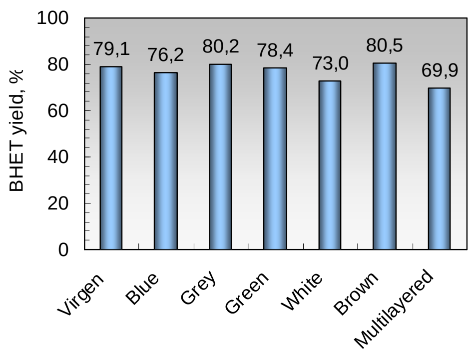

Fig. 6 PET nature effect on BHET yield (glycolysis at T=196°C, PET/EG=1/9, t=2 h)

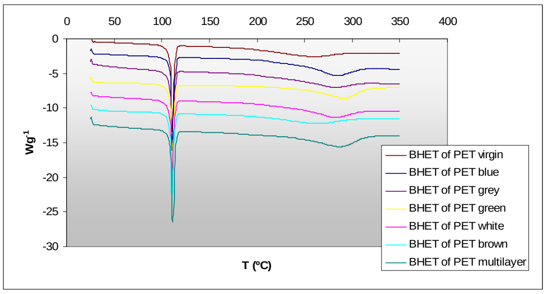

Fig. 7 DSC thermal analysis curves of BHET

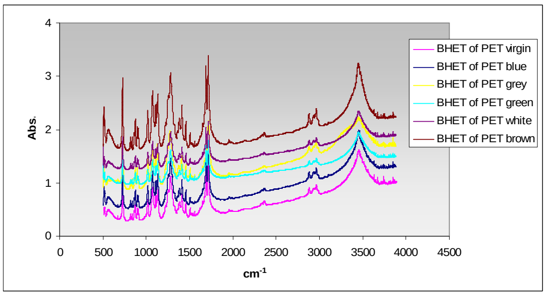

Fig. 8 IR analysis curves of BHET

4. Conclusions

On-line NIR identification tests of PET materials for their subsequent automatic sorting have been carried out by means of a commercial system. Results have shown that NIR is a feasible technology for sorting a PET fraction from other non-polymer and polymer based materials at packaging waste stream but fails on the recognition highly coloured and multilayered PET fractions among them that will requires image analysis and/or colour sorting technologies for its segregation.

The glycolysis of virgin PET has been carried out under atmospheric pressure, with an excess of ethylene glycol as chemical agent and zinc acetate dihydrate as catalyst. The influence of glycolysis time, temperature and PET/EG ratio has been investigated, showing that conversion rate depends significantly on these factors. The main products have been BHET and oligomers. Once defined suitable operating conditions, highly coloured and complex multilayered post-consumer PET wastes have been depolymerised, getting BHET yields up to 80%. These values have been similar to the one coming from virgin PET, demonstrating that PET nature and colour has less influence on BHET yield than expected. The DSC and FTIR results have verified that the BHET products derived from highly coloured and complex multilayered post-consumer waste streams of PET have been equivalent to the one derived from virgin PET. As a first step in a large project, glycolysis has been verified as a promising option for the recycling of these non-mechanically recoverable PET wastes that probably can be recycled by glycolysis as a mixture of highly coloured and complex PET materials.

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