

Chemical Recycling of PET Waste from Soft Drink Bottles to Produce a Thermosetting Polyester Resin

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Abstract : Poly(ethylene terephthalate) or PET waste from soft drink bottles was subjected to recycling by glycolysis. Characterization and identification were performed by the conventional method of hydroxyl and acid values, Differential Scanning Calorimetry (DSC) and Fourier Transform Infra Red (FTIR) techniques. It was found that the glycolysed product consists mainly of bis(hydroxyethyl) terephthalate (BHET) and its dimer. The glycolysed product was later polyesterified with maleic anhydride and then cross linked with styrene to produce a formulation for the resin. FTIR spectra also revealed the cross linking process between the polyester chain and styrene monomer, resulted in a final product with high densities of cross-linkages to form a network polymer. The cured resin exhibited thermal stability due to its fully curing.

Keywords: Poly(ethylene terephthalate), polyester resin, glycolysis

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Introduction

Poly(ethylene terephthalate) (PET) is one of the most valuable versatile engineering plastics which is used especially in the manufacturing of soft drink bottles. With increasing application and decreasing prices, PET became the symbol of disposability in consumerism and hence a noxious material of concern in the relatively recent environmental protection issues, as it is highly resistance to atmospheric and biological agents. Therefore, the necessity of finding a simple economic route for the recycling of waste PET is an important practice for sustainable recycling and contributes to the conservation of raw petrochemical products and energy. Most of the past research concerned, focused on the production of products obtained by using glycolysis of PET such as unsaturated polyester resin, polyurethane foam, polymer concrete and polymer composites with reinforcement [1-4].

This paper reports on the possibility of the unsaturated polyester resin derived from PET soft drink bottles through chemical recycling. This preliminary study focuses on the characterization of products from the glycolysis reaction and to the formation of the resin by monitoring its average molecular weight as well as comparing it to a commercial UPR resin, the FTIR spectrum which can justify the synthesized resin as unsaturated polyester

and finally an insight on the curing of the resin by FTIR spectrum and DSC scan.

Experimental

Materials

Post consumer PET soft drink bottles were cut into small pieces (6 mm x 6 mm). For the glycolysis of PET, ethylene glycol and zinc acetate supplied by Ajax Chemicals Ltd and Riedel-de Haën respectively were used. In preparing the unsaturated polyester resin, maleic anhydride (Aldrich Co.), hydroquinon (Merck) was used to prevent premature curing and styrene monomer from Fluka Chemika as the cross-link agent. Methyl ethyl ketone peroxide (MEKP) and cobalt octoate supplied by Fluka AG, were used as initiator and accelerator, respectively, for curing the polyester resin.

Glycolysis of PET soft drink bottles

PET wastes and ethylene glycol (PET:EG = 1:4 w/w) together with 0.5% zinc acetate based on weight of PET as catalyst were charged to a four-necked round bottom flask of 500 ml capacity, connected to a reflux condenser, N₂ gas inlet, thermometer and stirrer. The reaction was carried out under reflux in nitrogen atmosphere at 180-190 °C for 7 hr. Then, boiling water was slowly added to the

reactor and quickly filtered using a suction filter funnel with filter paper. The filter cake was collected, dried and labelled as GP-2 while the glycolysed product before having water extraction, labelled as GP-1. The filtrate was collected and stored in a refrigerator for 24 hr to allow the formation of white crystalline flakes, labelled as GP-3. All samples of GP-1, GP-2 and GP-3 were taken in order to verify monomeric materials present for each samples from its hydroxyl values.

Preparation of unsaturated polyester resin

Direct use of glycolysed product (GP-1) was used to synthesis unsaturated polyester resin by reacting it with maleic anhydride at a fixed ratio of 1.1:1 for the hydroxyl to carboxyl groups. The polyesterification was carried in a 500 ml four-necked round bottom flask connected to a partial condenser, N₂ gas inlet, thermometer and stirrer. About 10% xylol was added as solvent to help the removal of water as by product throughout the course of the reaction. The reactants were heated from room temperature to 180°C in about 1 ½ hr, then held at 180°C for 3 hr and finally raised to 200°C and

maintained until the acid value reached 20-30 mg of KOH g⁻¹. The acid value was monitored during the reaction and determined by titrating the solution of weighed resin in acetone. At the end of the reaction, the solvent was distilled. The liquid resin was then cooled to 120°C and hydroquinone, 0.45% of PET weight was added to prevent the resin from curing before use. Finally, the liquid resin was dissolved in styrene monomer at 70°C to achieve a 35% w/w styrene in the resin. In order to cure the resin, MEKP and cobalt octoate were used at a ratio of resin:MEKP:cobalt octoate of 100:1.5:0.5.

Results and Discussion

Characterization of the glycolysed product

The hydroxyl value of the glycolysed product was found to be 615 mg KOH g⁻¹ for GP-1 and 366 mg KOH g⁻¹ for GP-2. This suggests that the glycolysed product consists of monomer and its dimer (values between theoretical hydroxyl value of pure BHET monomer; 441.5 mg KOH g⁻¹ and its dimer; 251.3 KOH g⁻¹) [5].

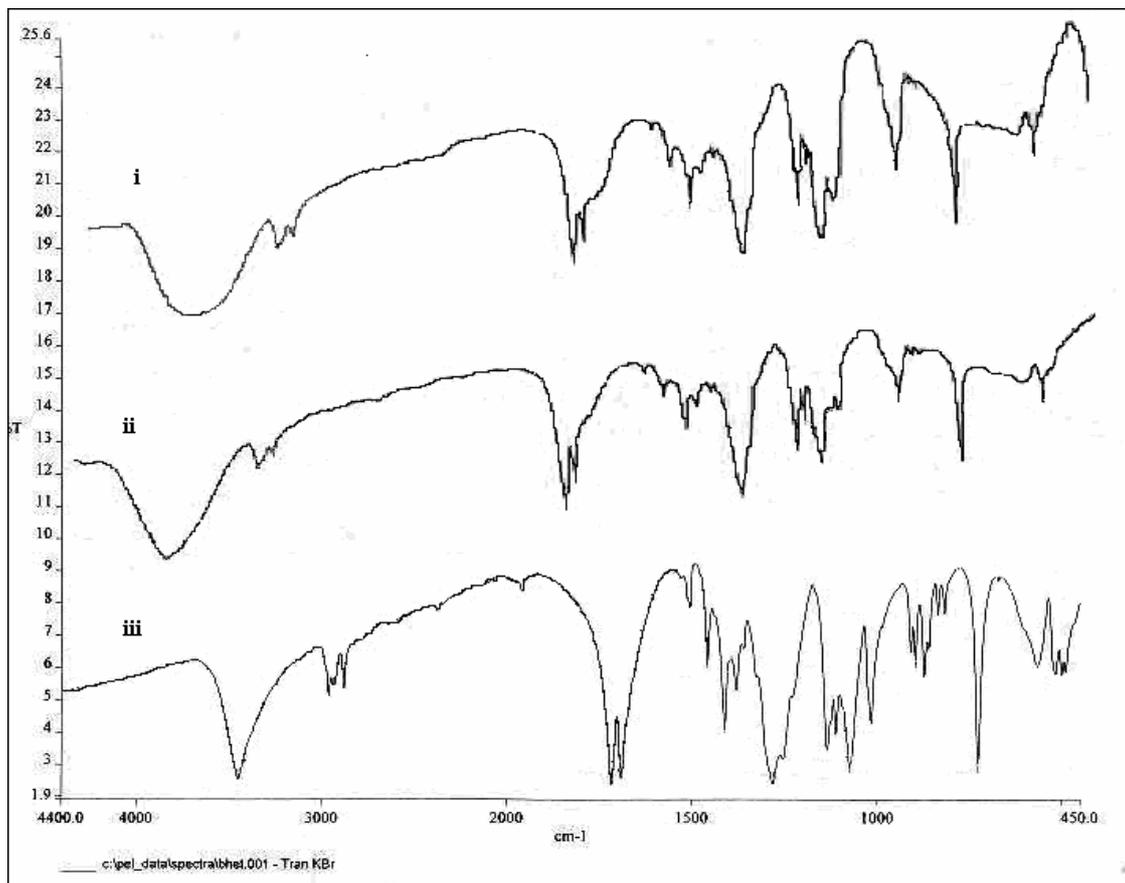


Figure 1 : FTIR spectra for glycolysed product (i) GP-1 (ii) GP-2 (iii) GP-3.

The FTIR spectrum of the glycolysed product is shown in Fig. 1. It can be seen that GP-1 and GP-2 show absorptions at 3200-3550 cm^{-1} due to the -OH, 2840-3000 cm^{-1} for the C-H stretching, 1720 cm^{-1} for the carbonyl group (C=O), 1100 cm^{-1} for C-O-C and at 675-900 cm^{-1} for the aromatic ring. Both absorption peaks are almost similar except that the peak at 3200-3550 cm^{-1} for GP-2 is much sharper. GP-3 shows quite a similar trend, however absorptions at 3200-3550 cm^{-1} is sharper and much closer to 3500 cm^{-1} . The FTIR spectrum can only reveal that the molecular structure of each sample do not defer much from each other. However due to a

higher purity of sample achieved by sample GP-3, a much sharper peak is shown from the spectrum.

As shown in Fig. 2 that the DSC thermogram supported that GP-1 and GP-2 consist mainly of the monomer and dimer of PET where GP-1 and GP-2 both has two peaks associated to the melting point of the monomer and dimer. GP-3 however, due to its higher purity, has a single sharp peak at 110 $^{\circ}\text{C}$, which corresponds to the monomer's melting point. The reaction mechanism suggested in order to produce the glycolysed product from PET and ethylene glycol under the mentioned experimental condition is shown in Fig. 3.

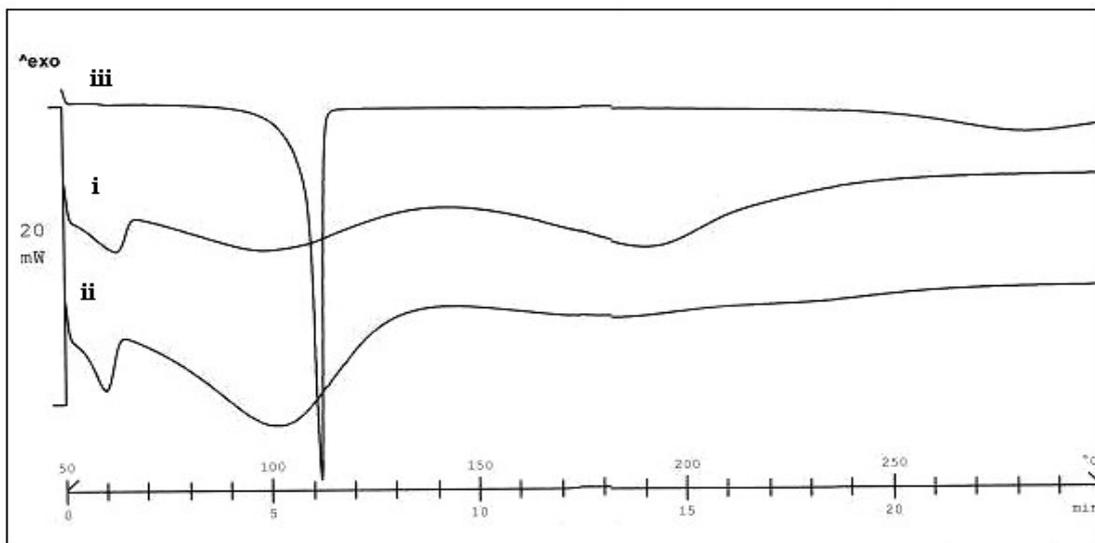


Figure 2 : DSC thermogram for glycolysed product (i) GP-1; (ii) GP-2; (iii) GP-3.

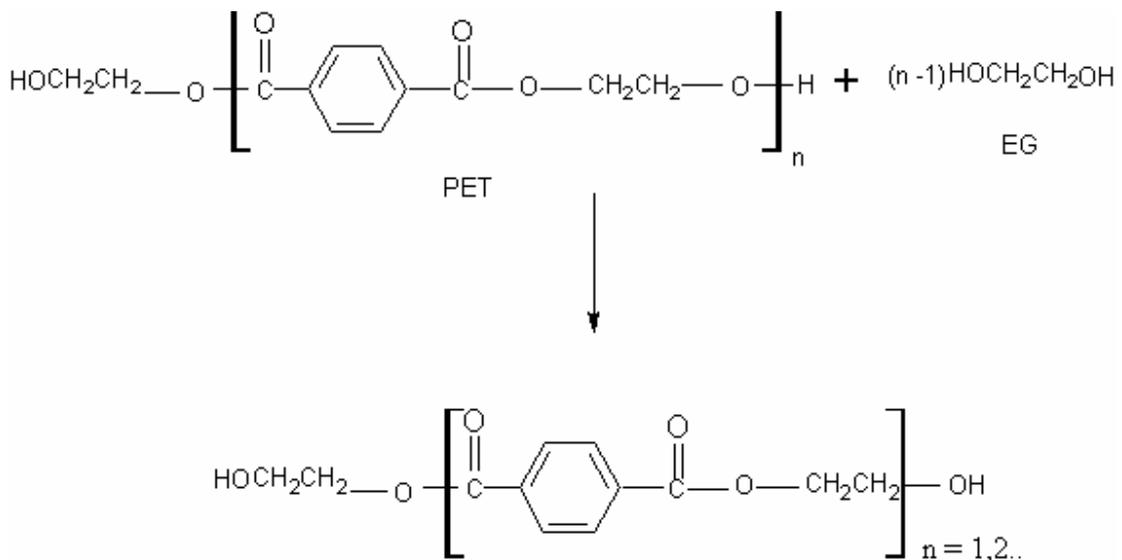


Figure 3 : Reaction mechanism of glycolysed PET.

Characterization of the unsaturated polyester resin

Hydroxyl value, acid number and number average molecular weight of the prepared resin and the commercial resin are shown in Table 1. Unsaturated acids in polyesters resins can be detected on the basis of C=C band at 1639 cm⁻¹ (from this experiment achieved at 1641 cm⁻¹) and the C=C bond is likely to be responsible for the absorption at 772 cm⁻¹ (again hereby at 780 cm⁻¹) [6]. Both C=C are from polyester chain and vinyl group in styrene respectively.

FTIR spectra of the prepared resin after curing in Fig. 4 showed that the result of their heating (during curing process) diminished the bands: 780 cm⁻¹; characteristics of C=C vinyl (in styrene), 981 cm⁻¹ characteristics of C-H out of plane bending in CHR=CHR (in polyester) and 1641 cm⁻¹; indicative to the C=C in polyester. Thus, suggests that cross-linking occurred between polyester chain and styrene monomer, both at their unsaturation active sites. The absent of these bands is also being observed from the spectra of polymerized material in unsaturated polyester resins [6].

Table 1 : Hydroxyl value, acid number and number average molecular weight of the resin.

Resin	Hydroxyl value (mg KOH/g)	Acid number (mg KOH/g)	Number average molecular weight (g/mol)
Prepared resin	26.0	22.2	2328
Commercial resin	39.1	22.8	1812

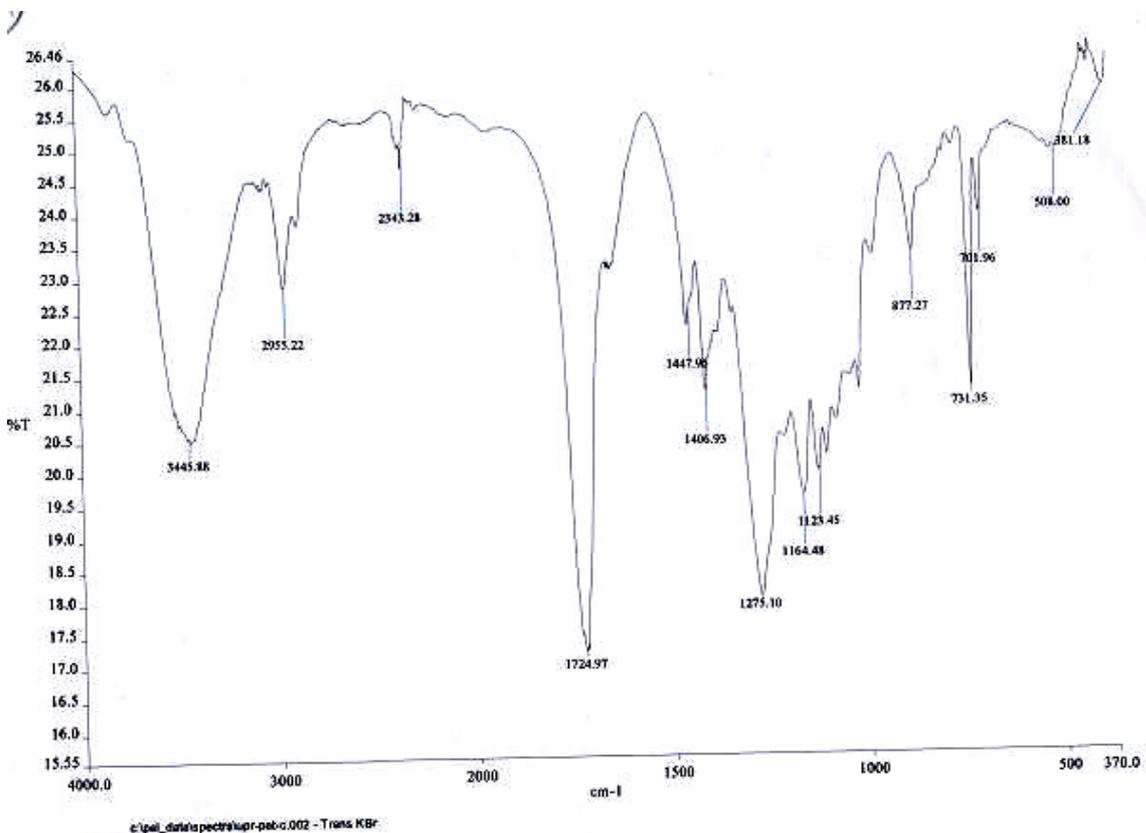


Figure 4 : FTIR spectra of the prepared resin.

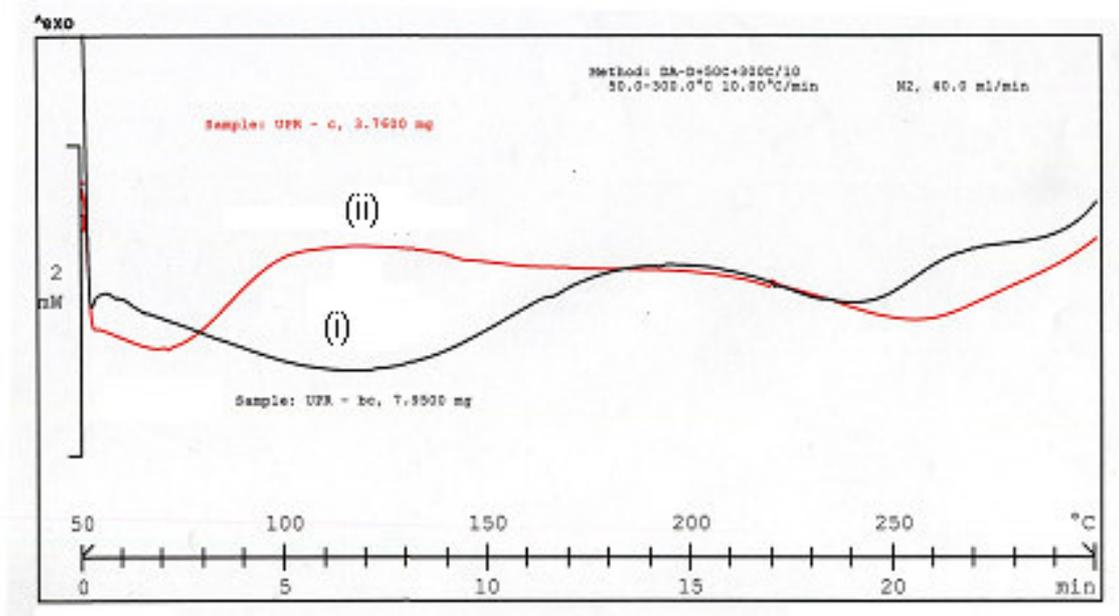


Figure 5 : DSC thermogram of the prepared resin (i) before and (ii) after curing.

Fig. 5 shows the DSC thermogram for the prepared resin which was scanned twice using DSC analysis. The first run was to see the curing behaviour that occurred in a temperature range of room temperature to 300°C. The first run showed two endothermic, one at the range of 50-190°C (approx.) and another one at 200-270°C. These two curves can be related to the cross-link process and to the thermal polymerization of polyester-styrene, as described by other authors [7]. The second run, showed nearly a baseline, and the diminishing of this endotherm is always associated with the well curing of the sample.

Conclusions

Recycling of PET waste through glycolysis was successfully performed after 7 hrs, cracking the polyester's molecular structure into monomer and dimer, while polyesterification of the glycolysed product with maleic anhydride within 5 hrs of reaction was complete to produce an unsaturated polyester resin. The unsaturated polyester resin then cross linked with styrene can be fully cured with MEKP and cobalt octoate. It was found that the samples were fully cured at temperatures at 60°C for 6 hr and post cured at 100°C for 4 hr.

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