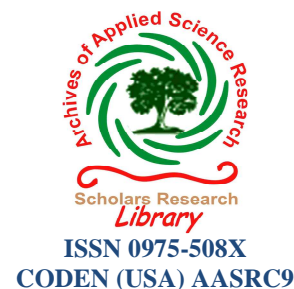




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Archives of Applied Science Research, 2012, 4 (1):85-93

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New polyester polyol derived from recycled poly (ethylene terephthalate) for coating application

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ABSTRACT

The recycling of post-consumer poly(ethylene terephthalate) (PET) is a worldwide concern due to its environmental impact and large volume of these waste materials produced by society. Current work aims at effective recycling of waste PET from soft drink bottles by glycolysis method and thereby utilization of recycled product for coating application. In the investigation, Ethylene Glycol (EG) was used for glycolysis of PET in presence of 0.5% zinc acetate as transesterification catalyst. PET & EG were taken on molar basis at 1:4 and 1:6. The glycolyzed product was characterized by hydroxyl and acid values, FTIR, ¹HNMR spectroscopy. Polyester polyol was successfully synthesized by esterification of glycolyzed product, Adipic acid, Phthalic anhydride and Neopentyl glycol. The produced resin was cured with different polyisocyanate curing agents. The mechanical properties of the cured resins were evaluated. The chemical resistances of cured coatings were evaluated for water, solvents, salt spray, acid and alkali resistance.

Keywords: waste PET; ethylene glycol; glycolysis; polyester polyol.

INTRODUCTION

Poly(ethylene) terephthalate (PET) is one of the most versatile plastics which is extensively used in the manufacture of various kinds of packaging, especially for soft drink bottles. With increasing application and decreasing prices, PET has become the symbol of disposability in consumerism.[1] The excellent properties of PET needed for its many applications are also responsible for the difficult degradation of PET and an accumulation of polymer wastes, which in turn creates serious environmental problems connected to littering and illegal land-filling or

incineration.[2] Therefore, the necessity of finding a simple economic route for the recycling of waste PET is an important practice for sustainable recycling.[3] Recycling of PET does not only serve as a partial solution to the solid-waste problem, but serve as a source of raw material to some industries and also contribute to the conservation of raw petrochemical products and energy which is of high importance due to high cost of energy.[4]

The chemical recycling of waste PET can be carried out in many ways such as glycolysis, hydrolysis, alcoholysis and simultaneous hydrolysis & glycolysis. The aim of most chemical recycling procedures is obtaining monomers such as terephthalic acid (TPA), ethylene glycol (EG), and bis(2-hydroxyethyl) terephthalate (BHET). The first two can be obtained by hydrolysis under neutral, acidic or alkaline conditions and the last by glycolysis of waste PET [5-6]. Glycolysis also makes it possible to employ very low amounts of reactants and lower temperatures and pressures compared with other recycling methods. Furthermore, unlike hydrolysis under acidic or basic conditions, glycolysis does not cause any problems related to corrosion and pollution [7]. Depolymerization of PET by glycolysis to obtain oligomeric diols such as bis(2-hydroxyethyl) terephthalate (BHET) in an excess diol, such as ethylene glycol, propylene glycol and diethylene glycol has been studied for many years [8]. Literature indicates that the product of waste PET depolymerization can be made use of in various applications such as epoxy[9], unsaturated polyesters [7,10,11], polyurethane coatings [12], alkyd resins[2,5], UV curable resins [13], hydrophobic textile dyestuffs [14] etc.

The preparation of polyester polyols usually includes two stages. In the first stage, depolymerization of PET takes place, resulting in a glycolysed product– a mixture of BHET, oligomers and unreacted glycols. In the second stage, glycolysed product is reacted with dicarboxylic acids, glycols and other additives resulting in polyester polyols. In the present paper, we report synthesis of new polyester polyol from PET recycled product and study the possibility of using this resin for producing new polyurethane coating systems. We have used Adipic acid (AA), Phthalic anhydride (PA), and Neopentyl glycol (NPG) with glycolysed PET product for the synthesis of polyester polyol. The resin was cured with different polyisocyanate curing agents.

MATERIALS AND METHODS

2.1 *Materials*

The PET utilized was obtained from waste soft drink bottles, which were cut into pieces. It was then washed and dried. The chemicals ethylene glycol, phthalic anhydride (PA), adipic acid (AA), neopentyl glycol (NPG), p-toluene sulphonic acid (p-TSA) and zinc acetate were obtained from commercial sources and were used without any further purification.

2.2 *Glycolysis of PET*

Waste PET chips and EG were reacted with zinc acetate in a reactor equipped with stirrer, thermometer and reflux set. PET and EG were charged at molar ratios of 1:4 and 1:6 along with 0.5% zinc acetate catalyst. The glycolysis reaction was carried out at 180-200 °C under reflux in nitrogen atmosphere for about 4 hours. The reaction product was then quenched on ice. The solid precipitate was separated and washed with hot water. The product was later washed with ethyl

acetate to remove un-reacted PET. The purified product was dried and stored. The glycolyzed product was confirmed by ^1H NMR and FTIR analysis.

2.3 Preparation of Polyester Polyol (PE Polyol)

Glycolyzed product was used for the synthesis of PE polyol. Adipic acid, phthalic anhydride and neopentyl glycol were charged along with glycolyzed product on fixed acid to hydroxyl ratio of 1:1.3 and 0.5% of *p*-toluene sulphonic acid (*p*-TSA) catalyst. The reaction was carried out in a reactor equipped with stirrer, thermometer, nitrogen inlet and reflux set. Xylene was added as solvent to help the removal of water as by product throughout the course of reaction. The polyesterification reaction was carried out at 180-190 $^{\circ}\text{C}$ and was monitored with acid value. The reaction was stopped when the acid value of the reaction mixture reached below 20 mg KOH g^{-1} . Polyester product was then cooled and stored.

2.4 Preparation of PE Polyol based coatings

PE polyols were cured with different polyisocyanate curing agent. The detail information of these curing agents is as shown in table 1. Both the components were taken on equivalent basis with NCO:OH ratio of 1:1. Dimethyl formamide was used as solvent to the system. The coating film was applied on mild steel panels (150 mm* 100 mm * 0.5 mm) and cured at 180 $^{\circ}\text{C}$ for 1 hour. Coating film was also applied on aluminum panels for determination of flexibility.

2.5 Testing

The depolymerized PET was analyzed by FTIR Perkin-Elmer Spectrum 100 Instrument and Mercury Plus ^1H NMR spectrometer. Coating films were analyzed for Tg using DSC Q-100 equipment over the range of -50 to 150 $^{\circ}\text{C}$ at a heating rate of $10^{\circ}\text{C}/\text{min}$. All the coating properties were evaluated according to ASTM methods.

RESULTS AND DISCUSSION

The aim of this study was to use the oligoester diols produced from PET recycling as potential raw material for synthesis of PE polyol. In order to fulfill these goals, PET was glycolyzed using excess ethylene glycol and the glycolyzed products were used to produce PE polyol which are used as organic coating component. The coating was then characterized for different mechanical and chemical properties.

3.1 Glycolyzed PET

The glycolyzed product was purified with ethyl acetate to remove unreacted PET. The dried product was obtained in a powder form which was characterized for hydroxyl value, SAP value, ^1NMR and FTIR. The hydroxyl and SAP values of both the reaction products using PET:EG of 1:4 and 1:6 is shown in table 2. Increased ethylene glycol content resulted in enhanced glycolysis of PET to generate BHET which can be seen from increased hydroxyl number in case of PE polyol-2 [7].

The glycolyzed products are characterized by FTIR and ^1NMR as shown in figure 1 & 2, figure 3 & 4 respectively. FTIR confirms presence of hydroxyl and ester groups which can be related to peaks seen at 3500 and 1700 cm^{-1} . The signals at chemical shifts 8.1, 4.7 and 4.3 ppm, represent *p*-substituted phenyl group, $\text{OOCCH}_2\text{CH}_2$ and OCH_2CH_2 of glycolyzed PET, respectively,

were observed in all ^1H NMR spectra. The signal observed at 3.7 ppm in both the spectra, which represent OH group of glycolyzed PET, indicate the presence of terminal OH in all glycolyzed PET samples.

3.2 PE Polyol

The PE polyol was prepared via polyesterification reaction of the glycolyzed product, adipic acid, phthalic anhydride and neopentyl glycol. The reaction was monitored with acid value of the reaction mixture. Reaction charge of different starting materials is shown in table 3. The polyester polyol products are characterized for hydroxyl value and SAP value shown in table 4.

3.3 Coating Properties.

The PE polyols were cured with different polyisocyanate curing agents at 180 $^{\circ}\text{C}$ for 1 hour. Dimethyl formamide was employed as solvent to achieve proper viscosity of coating system. The coatings were applied on surface pretreated mild steel panels. A digital electromagnetic thickness gauge instrument was used to measure the dry film thickness (DFT) of each coating. Each coating showed excellent gloss; however there was no significant difference observed in gloss of these two PE polyol based coatings. Excellent gloss of the coated films can be attributed to increased cross-link density which enhances the crystallinity of the three dimensional structure. The detailed characteristics of each coating system are as shown in table 5 and table 6. Glass transition temperature increases with increasing NCO content of the hardener which is again a result of increased cross-linked density.

Coated aluminum panels were tested for flexibility by Conical Mandrel Bend method. It was observed that these coating systems possessed excellent flexibility. Impact resistance was determined using impact load of 1.36 Kg which was dropped from constant height of 24 inch for both intrusion and extrusion. Both the coating systems showed excellent impact resistance and no cracks were observed on any of coatings. Excellent flexibility and impact resistance can be a result of both, high cross-link density and presence of longer soft polymeric segments [9]. Thus the cross-linked structure maintains a balance between its hard nature and flexible soft segments. The dry tape adhesion of all the coating films was observed to be 100%.

Scratch hardness for coatings based on PE Polyol-1 was observed to be better than that based on PE Polyol-2. This could be due to presence of oligomers such as dimer or trimer in depolymerized product which results into increased aromatic concentration. In case of PE Polyol-2 based coatings the increasing scratch hardness is again result of increasing cross-linking density. Both coating system showed very good pencil hardness. DSC curves representing Tg for these coatings are shown in figure 5 & 6. It can be seen that the Tg value increases with increasing crosslinking density.

Table 1: Polyisocyanate Curing Agents

| Polyisocyanate Grade | Percentage (%) NCO | Non-volatile matter (%) | Equivalent weight |
|------------------------------------|--------------------|-------------------------|-------------------|
| Aliphatic Biuret (HDI Based): N-50 | 11 | 50 | 382 |
| TDI Based Polyisocyanate: N-67 | 12 | 67 | 350 |
| Aliphatic Biuret (HDI Based): N-75 | 17 | 75 | 255 |

Table 2: Depolymerized product

| Designation | Mole ratio of PET:EG | SAP value (mg KOH/g) | Hydroxyl value (mg KOH/g) |
|-------------|----------------------|-------------------------|------------------------------|
| DEP-1 | 1:4 | 580 | 80 |
| DEP-2 | 1:6 | 440 | 140 |

Table 3: Formulations for PE Polyol synthesis

| Starting Material | Acid/Hydroxyl Equivalent | Charge(gm) | |
|--------------------|--------------------------|-------------|-------------|
| | | PE Polyol-1 | PE Polyol-2 |
| Adipic acid | 1.6 | 12.4 | 18.4 |
| Phthalic anhydride | 0.4 | 3.1 | 4.5 |
| NPG | 1.6 | 8.8 | 13.1 |
| DEP-1 | 1 | 75.2 | - |
| DEP-2 | 1 | - | 63.5 |
| p-TSA | - | 0.5 | 0.5 |
| Total | - | 100 | 100 |

Table 4: PE Polyols

| PE Polyol | Acid value (mg KOH/g) | SAP value (mg KOH/g) | Hydroxyl value (mg KOH/g) |
|-------------|--------------------------|-------------------------|------------------------------|
| PE Polyol-1 | 15 | 572 | 85 |
| PE Polyol-2 | 10 | 654 | 80 |

Table 5: Coating properties

| PE Polyol | Curing agent | Designation | DFT (μ) | Gloss (60°) |
|-------------|--------------|-------------|---------------|----------------------|
| PE Polyol-1 | N-50 | Coating 1 | 105 \pm 5 | 85 |
| | N-67 | Coating 2 | 110 \pm 5 | 86 |
| | N-75 | Coating 3 | 165 \pm 5 | 89 |
| PE Polyol-2 | N-50 | Coating 4 | 135 \pm 5 | 87 |
| | N-67 | Coating 5 | 110 \pm 5 | 90 |
| | N-75 | Coating 6 | 160 \pm 5 | 88 |

Table 6: Mechanical Properties

| Coating | Adhesion | Flexibility (mm) | Impact Resistance (Kg-Inch) | Scratch hardness (Kg) | Pencil Hardness | Tg ($^\circ$ C) |
|-----------|----------|---------------------|--------------------------------|-----------------------|-----------------|---------------------|
| Coating 1 | 5B | 0 | >32 | 4 | 4H | 27.52 |
| Coating 2 | 5B | 0 | >32 | 4 | 4H | 28.64 |
| Coating 3 | 5B | 0 | >32 | 4 | 4H | 37.52 |
| Coating 4 | 5B | 0 | >32 | 2.7 | 4H | 8.22 |
| Coating 5 | 5B | 0 | >32 | 2.7 | 4H | 45.60 |
| Coating 6 | 5B | 0 | >32 | 3 | 4H | 47.86 |

Solvent resistance of coating film was investigated according to ASTM D-4752 method. The coated films showed excellent resistance to xylene and methyl ethyl ketone which could be attributed to absence of major interaction between solvent and the polymer structure. Acid and alkali resistance was also investigated according to ASTM D-1308 method. All the coated films showed good resistance to acidic environment whereas in alkaline environment, loss of gloss was observed for each film. It was also observed that PE Polyol-2 based coating systems showed less

effect which could be eventually due to lesser number of ester linkages in depolymerized product DEP-2 than DEP-1. This can be confirmed by SAP values as shown in table 2.

Figure 1: FTIR spectra for depolymerized product (EG:PET = 4:1)

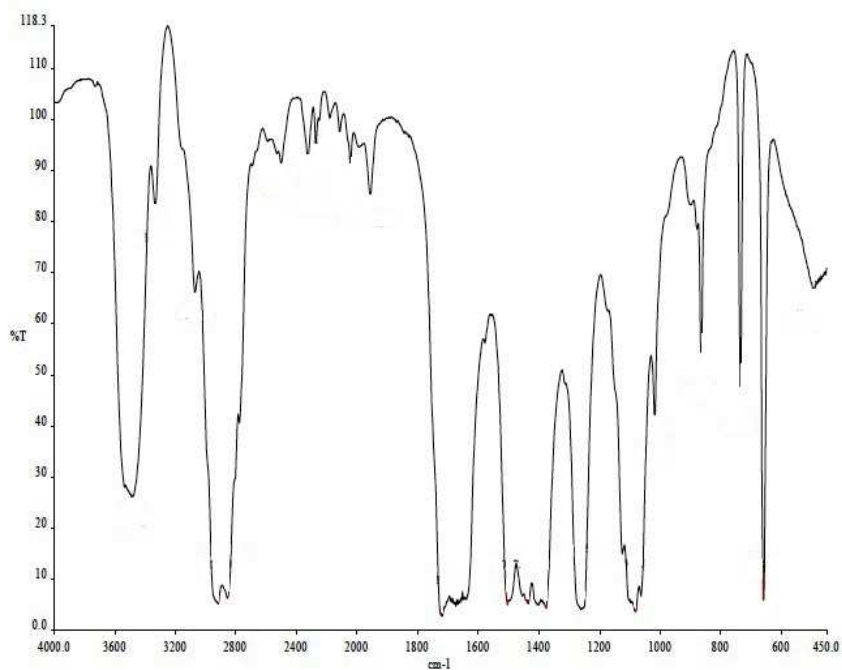


Figure 2: FTIR spectra for depolymerized product (EG:PET = 6:1)

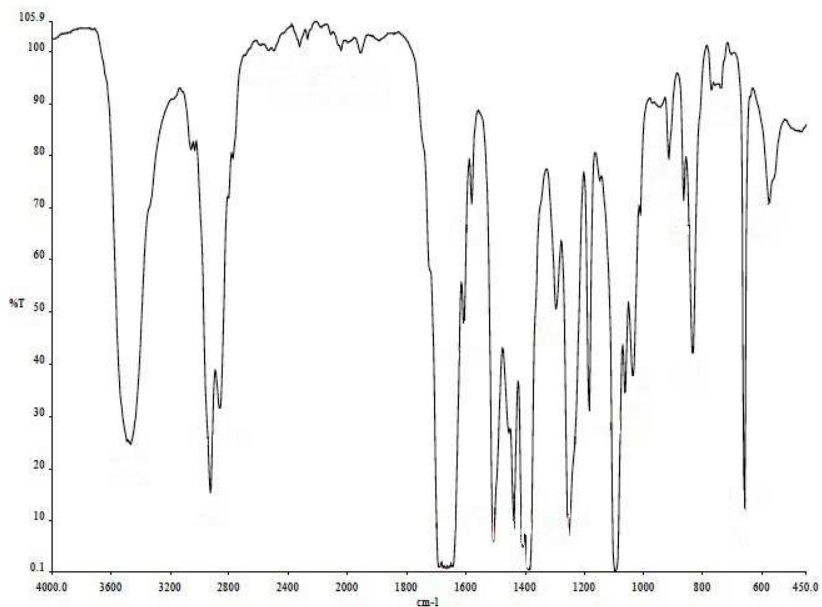


Figure 3: ¹HNMR spectra for depolymerized product (EG:PET = 4:1)

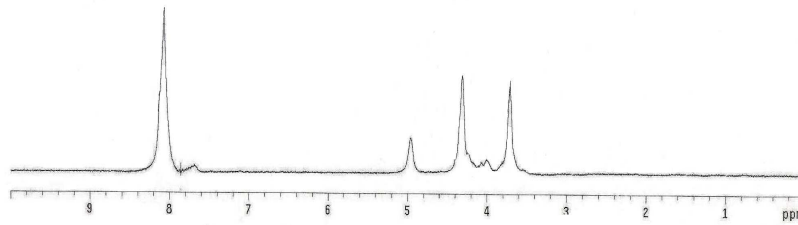


Figure 4: ¹HNMR spectra for depolymerized product (EG:PET = 6:1)

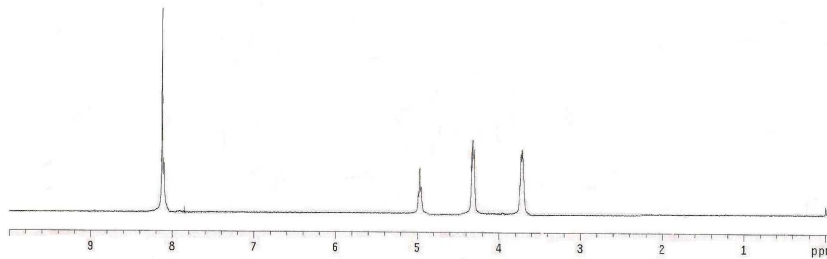


Figure 5: DSC scan for coatings based on Polyol 1

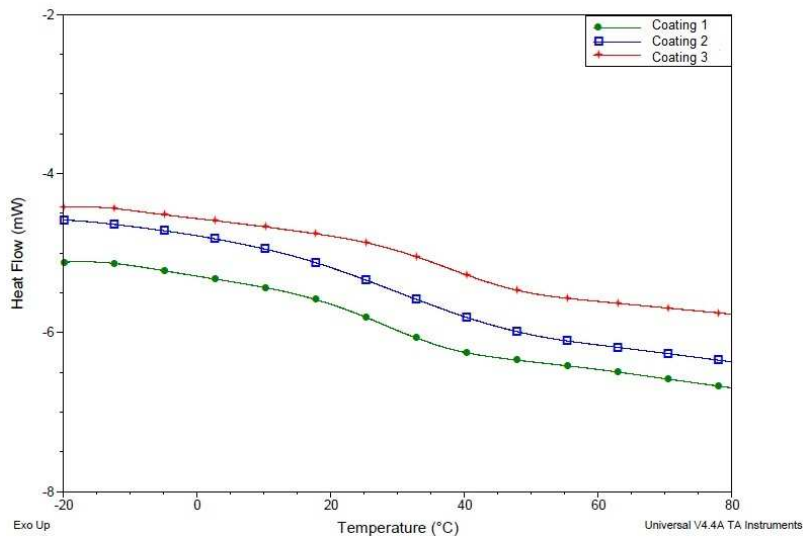
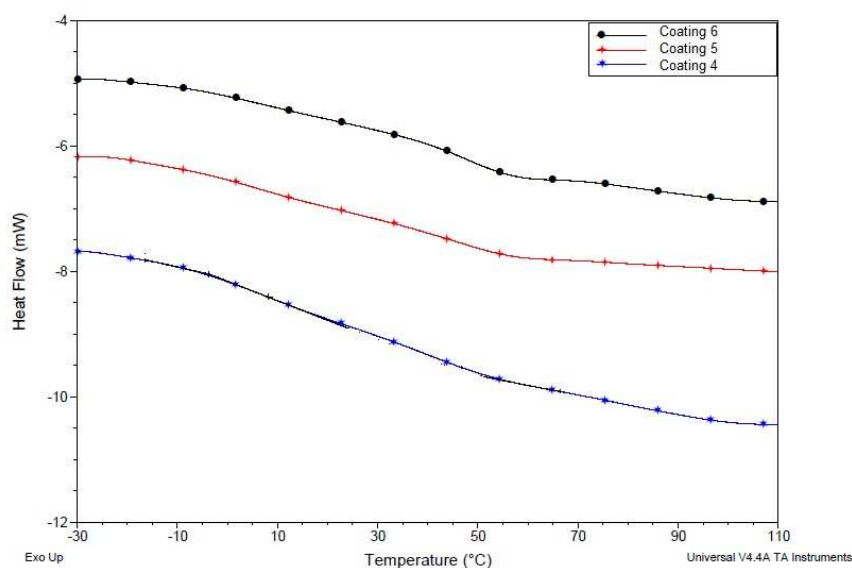


Figure 6: DSC scan for coatings based on polyol 2



CONCLUSION

Waste PET was successfully depolymerized via glycolysis using ethylene glycol and the glycolyzed product was used for synthesis of new polyester polyol. The polyester polyol was used for coating application and thereby it can be concluded that the coating films had excellent mechanical properties like flexibility, impact resistance, scratch and pencil hardness. This can be attributed to increased functionality and hence increased cross-link density of network. The coatings also showed very good chemical resistance.

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