RESEARCH ARTICLE

Polyester Polyol Derived From Waste Poly (Ethylene Terephthalate) for Coating Application on Mild Steel

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Polyester Polyol Derived From Waste Poly (Ethylene Terephthalate) for Coating Application on Mild Steel

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Abstract
Useful coating products may be obtained by chemical valorization (glycolysis) of post consumed poly (ethylene terephthalate) (PET) wastes. Glycolysis of PET waste was carried out using poly (propylene glycol) (PPG) of molecular weight 2000. The depolymerized oligoesters obtained were trans-esterified with Castor oil and Jatropha oil which results in the formation of saturated hydroxyl-functional polyester polyols. Two-pack coating systems were formulated using these resins as base component and melamine formaldehyde resins as hardener component. Cured films were tested for their hardness, chemical and corrosion resistance performances. The glycolysis of PET using PPG and polyester polyol formation was characterized using Fourier transform infrared spectroscopy.

Keywords: PET waste; Castor oil; Jatropha oil; corrosion resistance.

1. Introduction

Polyethylene terephthalate (PET) is aromatic polyester with excellent thermal and mechanical resistance and outstanding chemical properties, which is used especially in the manufacturing of fibers, packing materials, and plastic bottles. Widespread application and non-biodegradability of PET creates huge amounts of waste and, consequently, induces a great interest for recycling this material. Therefore, a key issue nowadays is the PET conversion into reusable products [1]. With increasing application and decreasing prices, PET became the symbol of disposability in consumerism and hence a noxious material of concern in relatively recent environmental protection issue, as it is highly resistance to atmosphere and biological agent. 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 [2-5]. PET recycling is also important for conservation of oil resources, reduction of greenhouse effect, and energy preservation [6]. PET is thermoplastic polyester that is formed by a reaction between terephthalic acid and ethylene glycol [7]. Hence, its solvolytic chain cleavage is possible using various reagents like water (hydrolysis) [8–11], alcohols (alcoholysis) [12, 13], acids (acidolysis), glycols (glycolysis) [14] and saponification [15, 16]. During solvolytic chain cleavage valuable by-products are formed such as terephthalic acid (TPA), ethylene glycol (EG) or bis-hydroxyethyl terephthalate (BHET) [17], which can be used as a new raw material for preparing other polymers such as unsaturated polyester [18, 19], polyurethane [20], epoxy resin [21], alkyd resin [22] and vinyl ester resin [23].

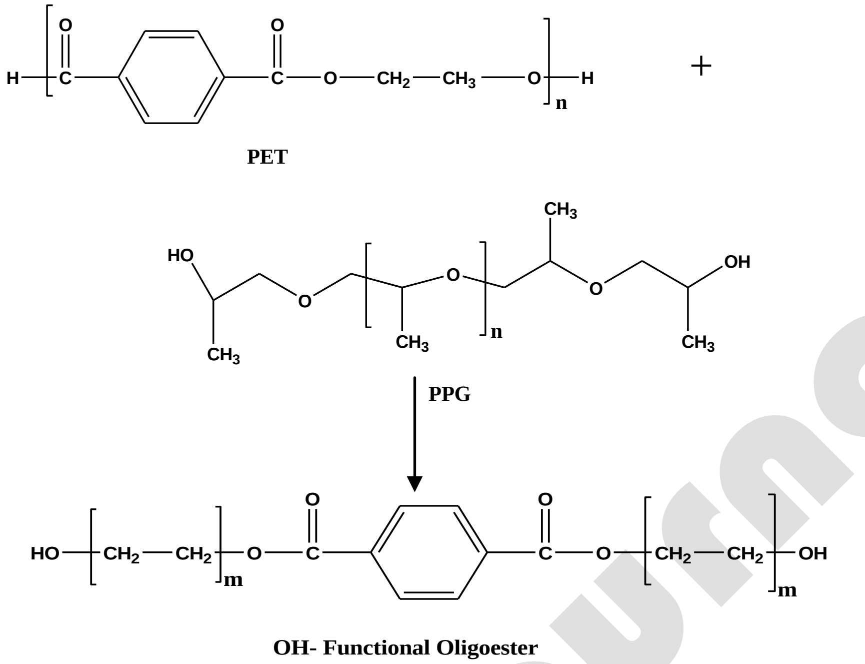
In this paper, we describe polyester polyol preparation in two stages: first, glycolysis of PET waste using PPG of molecular weight 2000; second, trans-esterification of the products formed (oligoesters) with Castor oil and Jatropha oil. The polyester polyols thus formed contain hydroxyl (–OH) and ester (–COO) functionalities. These saturated hydroxyl-functional polyester polyols were used as base materials along with melamine formaldehyde resin as a hardener in the formulation of two-pack coating systems. The performance properties of the coating systems were evaluated, revealing that coating products with a competitive performance can be produced from PET waste-based polyols. The weight ratio of hardener to base was kept constant at 1:1 to determine the effect of the amount of PET on the coating properties. The use of waste products like PET waste along with renewable material like Castor/Jatropha oil in coating systems will bring down the costs of the coatings and will also open a new market of recycled plastic materials and hence, may provide a potential solution to the problems of solid waste management.

2. Methods

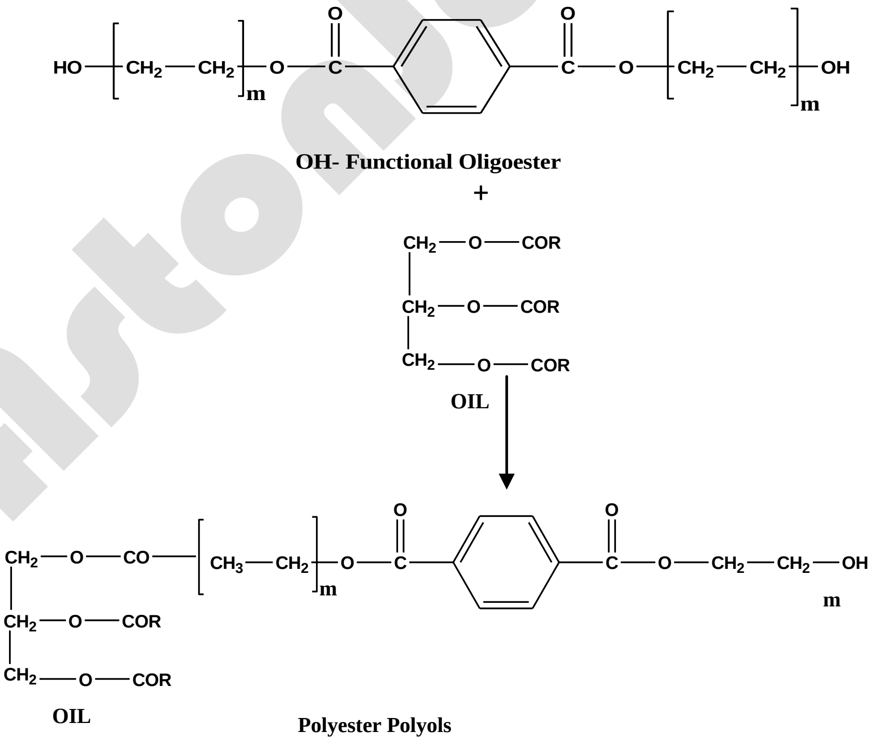
Recycled PET was obtained from a local recycling company. PPG of molecular weight 2000 was obtained from Labort Chemicals, India. Melamine formaldehyde hardener was procured from Synpol Ltd, Ahmedabad, Gujarat, India, and Castor oil was obtained from Crystal Caschem India Ltd, Ankleswar, Gujarat, India. All other chemicals and solvents used were of analytical reagent grade.

2.1 Experimental

The reaction scheme for the glycolysis of PET waste is as below:



The reaction scheme for the trans-esterification of glycolyzed products with Castor oil is as follows:



This mixture is considered as a polyol in the present study. R represents recinolic acid, which also contains a hydroxyl group.

2.1.1 Glycolysis of PET soft drink bottles

PET waste were glycolyzed using PPG (molecular weight 2000) in a three-necked glass reaction kettle equipped with stirrer, condenser. Zinc acetate (0.5%) was used as a catalyst. The content of the reaction kettle was heated at 180°C for 1 h; subsequently the temperature was raised to 210°C until all the solids disappeared. The reaction mixture was cooled and the products obtained were trans-esterified with Castor/Jatropha oil. Table 1 shows the various compositions of PET and PPG taken for glycolysis.

Table 1: Weight of PPG taken with PEG of various weights.

Molecular Weight of PPG	Weight of PET	Zinc Acetate (g)
2000	5%	0.5%
2000	10%	0.5%

2.1.2 Trans-esterification

Trans-esterification of glycolyzed oligoesters was carried out using Castor/Jatropha oil with a weight ratio of 1:10. DBTDL (Dibutyltin Dilaurate) (2 wt %) was used as a catalyst. In a typical process of trans-esterification, required amounts of glycolyzed oligoesters, Castor/Jatropha oil and catalyst were charged in a three-necked reaction kettle equipped with stirrer, vacuum line.

The reaction mixture was heated at 80°C without vacuum for half an hour; the temperature was then raised to 150°C with a vacuum of 125mmHg. The conditions were maintained for 1.5 h. The by-product formed was continuously removed by vacuum. After the completion of the reaction, the mass was cooled to room temperature and brought to atmospheric pressure slowly. The polyester polyols thus obtained were characterized using Fourier transform infrared (FTIR) spectroscopy.

2.2 Formulation of coating systems

Two-pack coating systems were formulated using the polyester polyols as base component and melamine formaldehyde as curing agent. The components were mixed in the weight ratio of 1:1. The thoroughly mixed compositions were coated on mild steel panels, using a bar applicator. The panels were placed in an oven at 120 °C for 30 min. These panels were used to evaluate various performances.

2.3 FTIR spectroscopy

Glycolysis of PET waste and the formation of polyester polyols were confirmed using FTIR spectroscopy. FTIR spectra were recorded as a film on a KBr cell using a Perkin Elmer Spectrum BX instrument.

2.4 Panel preparation

Mild steel panels (2”x 3”) were prepared, prior to application of coating, as follows. First, panels were hand scrubbed using a maroon scotch-briteR with 10% solution of Brulin 815 GDR detergent in DI water and then rinsed with DI water. They were then immersed in 10% solution of Brulin 815 GDR detergent in DI water at minimum 142 F, followed by washing with DI water. Then the panels were deoxidized for 2 min in phosphoric acid-based deoxidizing solution, followed by DI water rinse and drying, and were then stacked for 24 h before being used for application. Before coating application all the panels were washed with DI water for removal of any loose dirt on the surface.

2.5 Performance properties evaluation

Saturated polyester polyol-based coatings were applied on mild steel panels for various tests. These include MEK double rub test, pencil hardness test, chemical and solvent resistance test and corrosion resistance performance test (EIS).

2.5.1 MEK double-rub test

The MEK solvent-rub test is a well-known and frequently used test throughout the coating industry. Its primary utility to determine the extent, to which a coating is cured when interpreted properly, can be a very useful tool. The test itself is simple a cotton ball or rag is soaked in MEK and rubbed over the surface of coating a given number of times. The effect on the surface is then evaluated in terms of gloss loss, softening, or degree of rub off. The result of this type of test provides a measure of the chemical resistance of a given coating. When the results are compared to those of a control, known to be fully cured, a good qualitative determination of the degree of can be made.

2.5.2 Pencil hardness test

Pencil hardness test is a simple and quick way of estimating the extent of cure and drying of a film. Cured films of various compositions are allowed sufficient curing time. In this study, it was 14 days for room-temperature-cured coatings. The test was carried out in accordance with the ASTM D3363-00 standard. This test involves scratching a coating using pencils of increasing hardness. The coatings hardness is indicated by the first pencil which can gouge it. This test is particularly useful for room-temperature-cured coatings.

2.5.3 Chemical and solvent resistance

Chemical and solvent resistance investigations were carried out using dip tests. Mild steel coated panels were dipped in 5% NaCl, 5% NaOH, 5% HCl, water and xylene for 24 h. Panels were checked every 2 h for surface defects.

2.5.4 Corrosion resistance performance test (EIS)

Polarization measurements were carried out using the instrument CH Electrochemical analyzer model 608 C (USA). Electrochemical experiments were performed in a conventional three electrode electrochemical cell at 25± $^{\circ}\mathrm{C}$ with a working electrode (WE) of the mild steel, a pure platinum counter electrode (CE) and saturated calomel electrode (SCE) as a reference electrode. The WE was first immersed into the test solutions for 30 min to establish a steady state of open circuit potential (OCP). Polarization resistance measurements were first carried out with a scan rate of 0.01 V/s at −10 to +10 mV versus corrosion potential (E_{corr}) of the WE. The mild steel electrodes were immersed for 24 h in the test solutions for the impedance measurements which were carried out at the E_{corr} . Electrode surface area exposed to testing solution (3.5 wt. % NaCl) was 1 cm^2.

3. Results and Discussion

3.1 FTIR spectroscopy

3.1.1 Glycolysis

Glycolysis of PET using PPG was confirmed using FTIR spectral analysis. Figure 1 shows comparative FTIR spectra of Glycolyzed PET oligoesters obtained from glycolysis of different amounts of PET by glycolysis. Figure 1 shows that –C=O stretching around 1720 cm^{-1} is a key band appearing due to ester formation on the glycolysis of PET using PPG. This can be directly compared with the PPG FTIR spectra which do not contain any band around 1750 cm^{-1}. From Figure 1 it can also be seen that the peak around 1720cm^{-1} becomes sharper and more intense with an increase in the amount of PET which is due to an increase in the number of ester linkages formed in the glycolyzed oligoesters. The band around 3400 cm^{-1} is due to free hydroxyl groups present in glycolyzed PET oligoesters. Thus, the FTIR spectral analysis confirms the glycolysis of PET using PPG.

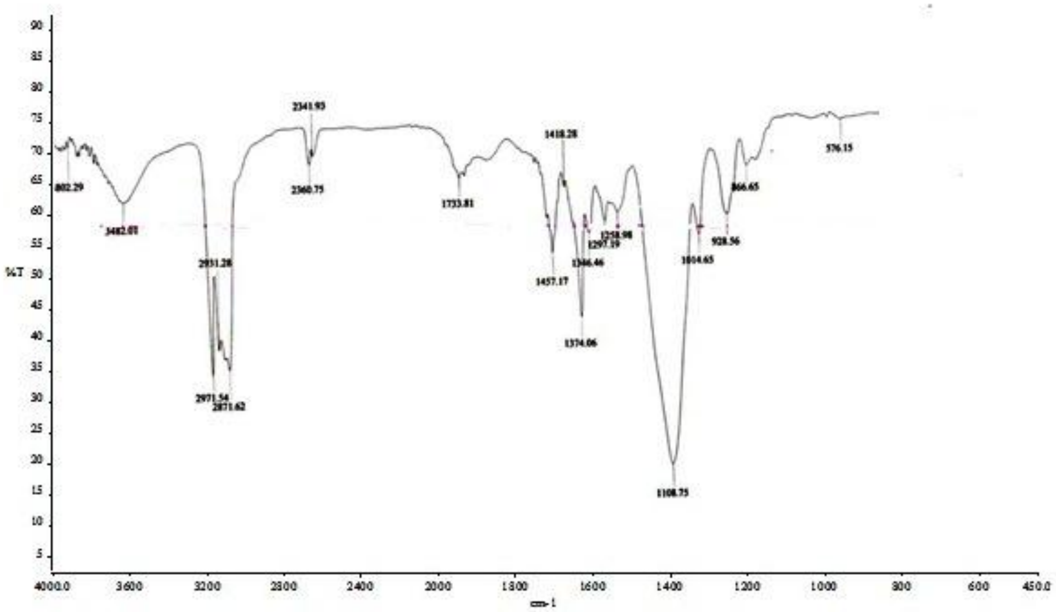


Figure 1: FTIR spectra of glycolyzed PET oligoesters.

3.1.2 Trans-esterification process

Polyester polyol formation by reaction of oligoesters obtained on glycolysis and Castor oil was also confirmed by FTIR spectral analysis. Figure 2 shows FTIR spectra of polyol formed on the trans-esterification of oligoesters with Castor oil. A sharp band at 1736 cm^{-1} confirms polyester formation. The band at 3435.8 cm^{-1} is due to the presence of free hydroxyl groups in the polyols. The strong band at 2864 cm^{-1} is due to the OH stretching of methylene groups present in fatty acid radicals.

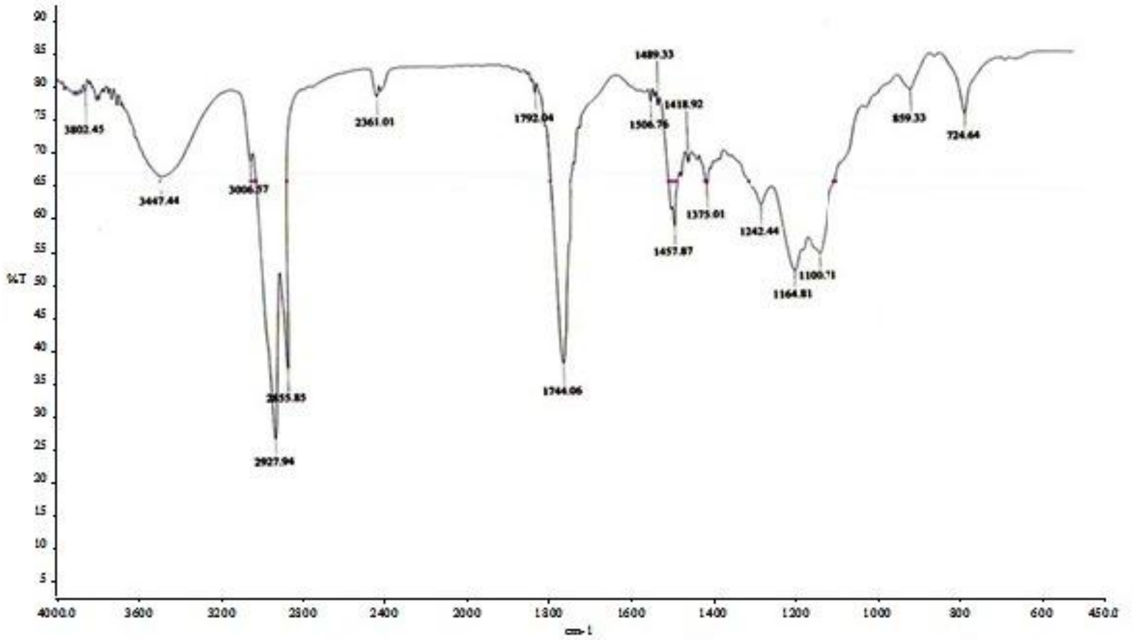


Figure 2: FTIR spectra of polyester polyols.

3.2 Performance properties

Coated panels were evaluated for MEK double rub test, pencil hardness test, chemical and solvent resistance and corrosion resistance test.

3.2.1 MEK double rub and pencil hardness test

The results of MEK double rub on coatings systems are shown in Table 2. As the amount of PET increases in Castor oil based coatings system, the MEK double rub increases from 90 to 170. In the Jatropha oil based coatings system, MEK double rub increases from 80 to 150. The point where a visible defect is observed on the coating was considered as the MEK double rub number.

The results of pencil hardness on coatings systems are shown in Table 3. An increased amount of PET in both Castor oil and Jatropha oil based coatings system leads to increase in the hardness from 1H to 2H; the addition of PET to the formulation makes it more dense and hard.

Table 2: MEK double rub resistance.

S. No.	Coatings System	PET (%)	MEK double rub resistance
1	Castor oil	5%	90
		10%	170
2	Jatropha oil	5%	80
		10%	150

Table 3: Pencil hardness test.

S. No.	Coatings System	PET (%)	Pencil Hardness
1	Castor oil	5%	1H
		10%	2H
2	Jatropha oil	5%	1H
		10%	2H

3.2.2 Chemical and solvent resistance

The chemical and solvent resistance was found to be satisfactory. However, alkali resistance was found to be somewhat poor because of the ester linkages and the presence of oil in the polymer. The results are given in Table 4.

Table 4: Chemical and solvent resistance.

S. No.	Coatings System	PET (%)	5% NaCl	5% NaOH	5% HCl	Water	Xylene
1	Castor oil	5%	1	6	3	1	1
		10%	1	1	1	1	1
2	Jatropha oil	5%	1	7	4	1	1
		10%	1	2	1	1	1

1 = No effect; 2 = soften; 3 = loss in gloss; 4 = loss in adhesion; 5 = lifting; 6 = blistering; 7 = rupture. Results are reported as condition obtained after 24 h.

3.2.3 Corrosion resistance

E_{corr} and corresponding I_{corr} values were obtained by using tafel analysis method as shown in Figure 1. E_{corr} and I_{corr} values are shown in Table 5. The corrosion current density I_{corr} value of Castor oil based coating system having a 10% PET is found very low in comparison to all other coatings. In general, lower I_{corr} value for all coatings compare to bare substrate indicating that coating indeed can provide a physical barrier for blocking the electrochemical process.

Table 5: Corrosion resistance performance.

S. No.	Coatings System	PET (%)	I_{corr}	E_{corr} (mV)
1	Bare	0	$1.1x10^{-3}$	-7952
2	Castor oil	5%	$1.5x10^{-4}$	-7582
		10%	$3.1x10^{-5}$	-7352
3	Jatropha oil	5%	$2.6x10^{-4}$	-7664
		10%	$5.4x10^{-5}$	-7482

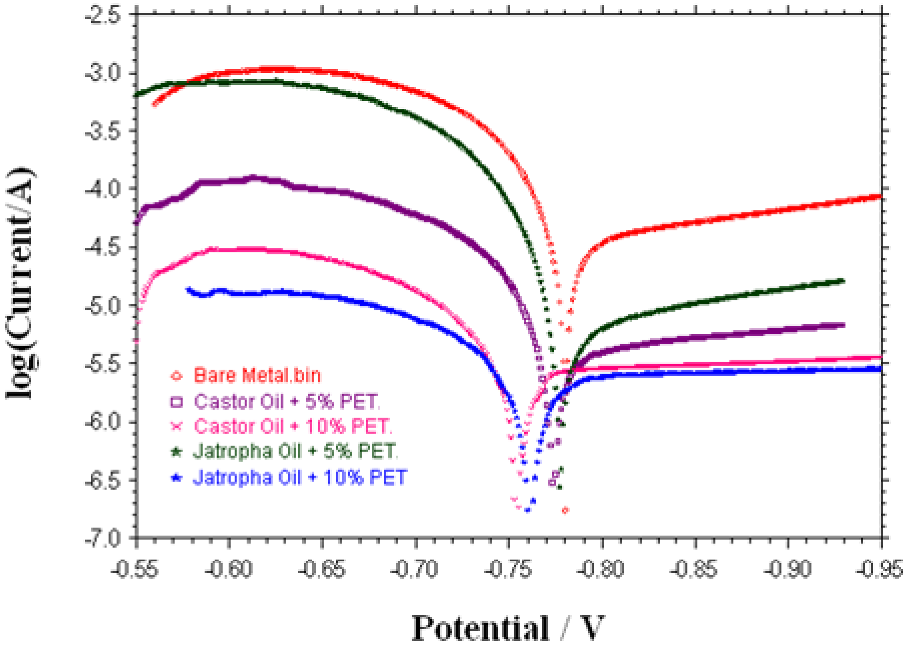


Figure 3: Tafel plot for coating systems.

4. Conclusion

PET can be successfully glycolyzed using PPG. The oligoesters obtained were trans-esterified with Castor oil and Jatropha oil to obtain hydroxyl functional polyester polyols. The resins were cured using melamine formaldehyde in equal weight proportions. The results obtained showed that the coating properties are influenced by the amount of PET used for glycolysis, and type of oil used for trans-esterification. As the percentage of PET increased from 5 to 10%, properties like corrosion resistance, MEK double rub resistance, pencil hardness, solvent and chemical resistance were increased. Potentiodynamic polarization study clearly shows much lower corrosion current densities (reduced corrosion rate), indicating the formation of dense coatings, with Castor oil based coating system having a 10% PET showing the best performance.

Competing Interests

None declared.

Authors' Contributions

All authors contributed equally to this work.

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