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Development of corrosion resistant polyurethane coating from aminolytic depolymerization of pet bottle waste

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Abstract

Disposed off PET bottles were depolymerized via aminolysis using 3-amino-1-propanol in the presence of sodium acetate as a catalyst. The product bis-(3-hydroxy propyl) terephthalamide (BHPTA) was purified and then reacted with ε-caprolactone using dibutyltindilaurate (DBTDL) as a catalyst to get a long chain saturated polyol.
Two pack coating system was formulated using the synthesized polyol as the base component and diisocyanate as the hardener component.The cured films were tested for their performance using mechanical tests such as pencil hardness, scratch resistance, impact resistance and chemical tests for resistance to acid, alkali and solvents. Anticorrosive properties were tested by salt spray test. The thermal properties of coatings were tested by Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA).The aminolyzed product of PET waste has been successfully used in preparation of corrosion resistant polyurethane coating.

Keywords: PET bottle waste; Recycling; Aminolysis; 3-amino-1-propanol, Polyurethane coating, ε-Caprolactone.

1. Introduction

Polymers are largely used in packaging industry causing equally large solid waste generation after utilization [1]. Among many, the poly (ethylene terephthalate) (PET) has gained importance due to its excellent mechanical properties, durability and low cost. The major problem of PET waste is caused by its increasing use in making of disposable soft drink bottles. Although recycling of polymer waste is relatively a better solution; it suffers from the limitation that the products obtained through recycling possess inferior properties.

Chemical recycling through depolymerization of the waste is the only sustainable approach. It involves conversion of the polymer waste chemically to generate virtual monomers which can be further used as precursors for synthesis of new utility chemicals. Glycolysis [2-4] hydrolysis [5,6], methanolysis [7] and amionolysis [8-10], are the established routes of PET degradation of which the aminolysis is comparatively less explored.

The intermediates from glycolysis of waste PET have found application in the preparation of unsaturated polyester resins [11], polyurethane resins [12], and alkyd resins [13]. Such intermediates or their mixtures with conventional monomers can significantly reduce the product cost while simultaneously imparting good properties of the terephthalate backbone to the commercial resins [14].

Aminolysis of PET waste has the advantages of formation of a single product with high yield unlike glycolysis, where in oligomers and dimers are also formed. One of the most important outcome of aminolytic chemical recycling of PET waste by ethanolamine is generation of bis- (2-hydroxy ethylene) terephthalamide (BHETA) [2]. This compound has been used in synthesis of polyurethanes [8], which have numerous applications, particularly in development of various types of coatings. The product obtained by aminolysis of PET with 3-amino-

1-propanol is bis-(3-hydroxy propyl) terephthalamide (BHPTA) which has amide linkage and terminal hydroxyl groups [15].

Polyurethanes (PU) are formed by reaction of a polyol with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts. Polyols used in polyurethane industry are usually of petrochemical origin; use of recycled product for synthesis of polyurethane would reduce the dependency on depleting natural resources. Polyurethanes are of various types such as foams (flexible, semi-rigid, and rigid), thermoplastic polyurethane, waterborne polyurethane dispersions, binders, polyurethane coatings, adhesives, sealants and elastomers, etc.[16] and they find applications in many fields that include apparel, appliances, automotive, building and construction, composite wood, electronics, flooring, furnishings, marine, medical as well as packaging.

In coatings, PUs exhibit excellent abrasion resistance, low temperature flexibility, toughness, chemical and corrosion resistance, and a wide range of mechanical strength [17].

Polyester diols possess 2 OH groups/mol, due to which the PU elastomers acheive excellent physico-mechanical properties [18]. BHPTA can thus be used as a diol for PU synthesis.

In order to make the polyurethane coatings flexible, increase in the chain length of BHPTA is desirable. For this, ε-caprolactone can be reacted with BHPTA. Studies related to ring opening polymerization of ε-caprolactone with diols such as bis 2-hydroxy ethylene terephthalate (BHETA) [19], ethylene glycol [20] and 1,4 butanediol [21] to synthesize polyurethanes have been reported.

The present communication deals with the results on the utilization of bis-(3-hydroxy propyl) terephthalamide (BHPTA) obtained by aminolytic depolymerization of PET bottle waste for the synthesis of polyol and formation of polyurethane there from. The synthesized polyurethane was characterized by melting point, IR spectroscopy and DSC and tested for gel time, scratch hardness, impact resistance, flexibility, percentage adhesion as well as chemical and solvent resistance.

2. Experimental

2.1 Materials

Waste PET bottles were obtained from local market. These bottles were cut into small pieces of approximate size 6 × 6 mm after removing the non-PET components such as labels and caps. These were boiled first in a nonionic detergent solution (2 g/L) for 1 hr to remove any dirt present followed by thorough washing with water and drying in an oven at 85^0C.

2.1.1 Chemicals

Sodium acetate, dibutyltin dilaurate (DBTDL), sodium bicarbonate, methylene chloride were of Laboratory Reagent (LR) grade and 3-amino-1-propanol of Guaranteed Reagent (GR) grade were procured from SD Fine Chemicals, India. Isophorone Diisocyanate (IPDI) was procured from Bayer India. All the chemicals were used as such without any further purification.

2.2 Aminolysis of PET waste material

The aminolysis of PET waste material was carried out using 3-amino-1-propanol in the molar ratio 1:5 (PET: 3-amino-1-propanol) under reflux for 4 hr in the presence of 0.5% (w/w) sodium acetate as catalyst. Experimental conditions for the aminolysis have been reported earlier.[15] At the end of the reaction, cold distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the product. The filtrate mainly contained unreacted 3-amino-1-propanol and little quantities of a few water soluble PET depolymerization products. The precipitate thus obtained was dissolved in distilled water by boiling for about 30 min. White crystalline powder of bis-(3-hydroxy propyl) terephthalamide (BHPTA) was obtained by first concentrating the filtrate by boiling and then chilling it. It was further purified by recrystallization in water, dried in an oven at 80^0C and weighed for estimating the yield. BHPTA was characterized using TLC, FTIR, NMR and DSC.

2.3 Synthesis of Polyol

Pure BHPTA obtained was reacted with ε-caprolactone (mole ratio 1:20) to synthesize the polyol through ring opening polymerization at 130^0C using 1 wt% dibutyltin dilaurate (DBTDL) as catalyst for 3.5 hr in a round-bottom flask equipped with a condenser, stirrer, nitrogen gas-inlet tube and thermometer. At the end, the reaction mass was cooled to obtain the light-yellowish waxy product, polyol which was used for the synthesis of polyurethanes.

2.4 Synthesis of polyurethanes and application on panels

A two pack polyurethane coating system was formulated using the polyol obtained from aminolytic depolymerization of PET bottle waste and isophorone diisocyanate (IPDI) as a hardener component. The polyol was dissolved in xylene, mixed with IPDI and then applied to mild steel panels using bar applicator.

The coated panels were allowed to cure completely for three days at 100^0C and after seven days the panels were tested for their performance properties.

2.5 Characterization of products

Melting points of the products, BHPTA and polyol were determined in an open capillary. Infrared spectrum was recorded on Shimadzu FTIR-470 spectrophotometer.

The thermal characteristics were determined by differential scanning calorimeter (DSC) (Shimadzu 60). All runs were carried out with sample consisting of ≈2–6 mg of compound. They were carefully put into an aluminum pan while another empty aluminum pan was used as a reference. Scans were performed at the heating rate of 10^0C/min from 30 to 300^0C in nitrogen atmosphere.

2.6 Surface preparation of mild steel panels

The dimensions of mild steel panels taken for experimental purpose were of 150mm* 100mm* 0.5mm. The mild steel panels were washed with tap water and dried. The panels were polished with Emery paper 800.

2.7 Performance evaluation

Adhesion of the developed coating to mild steel panel was tested by cross cut adhesion method according to ASTM D-3359. With the help of cross hatch cutter, a lattice pattern of cuts with similar spacing was made and commercial cellophane tape was applied over the lattice pattern of cut. Impact resistance and flexibility were tested according to ASTM D-2794 and ASTM D-522, respectively. The impact resistance of the coating was measured on the impact tester with maximum drop height of 60 cm and load of 1.36 kg. The pencil and scratch hardness of the applied coating was measured according to ASTM D-3363 and ISO-104, respectively. Chemical resistance of the coated panels to acid and alkali was evaluated by immersion method according to ASTM D-1308 and ASTM D-870, respectively. The rub test method was used to measure the solvent resistance of the coating using MEK and xylene as solvents as per ASTM D-4752.

3. Results and discussion

BHPTA obtained from aminolysis of PET by the earlier reported method [15]. The pure BHPTA obtained with 68% yield was reacted with ε -caprolactone for the synthesis of polyol. Synthesized polyol was cured with IPDI isocyanate and used for coating application. Reaction scheme for synthesis of coating from PET waste has been shown in (Fig.1).

3.1. Chemical characterization

Chemical characterization of the synthesized polyol was carried out. The results are given in table no. 1.

Table 1: Chemical characterization of synthesized polyol resin

Sr. No	Parameter	Value
1	Acid Value	22.5 mg of KOH/gm of sample
2	Hydroxyl Value	250 mg of KOH/ gm of sample
3	Isocyanate content of IPDI	42%

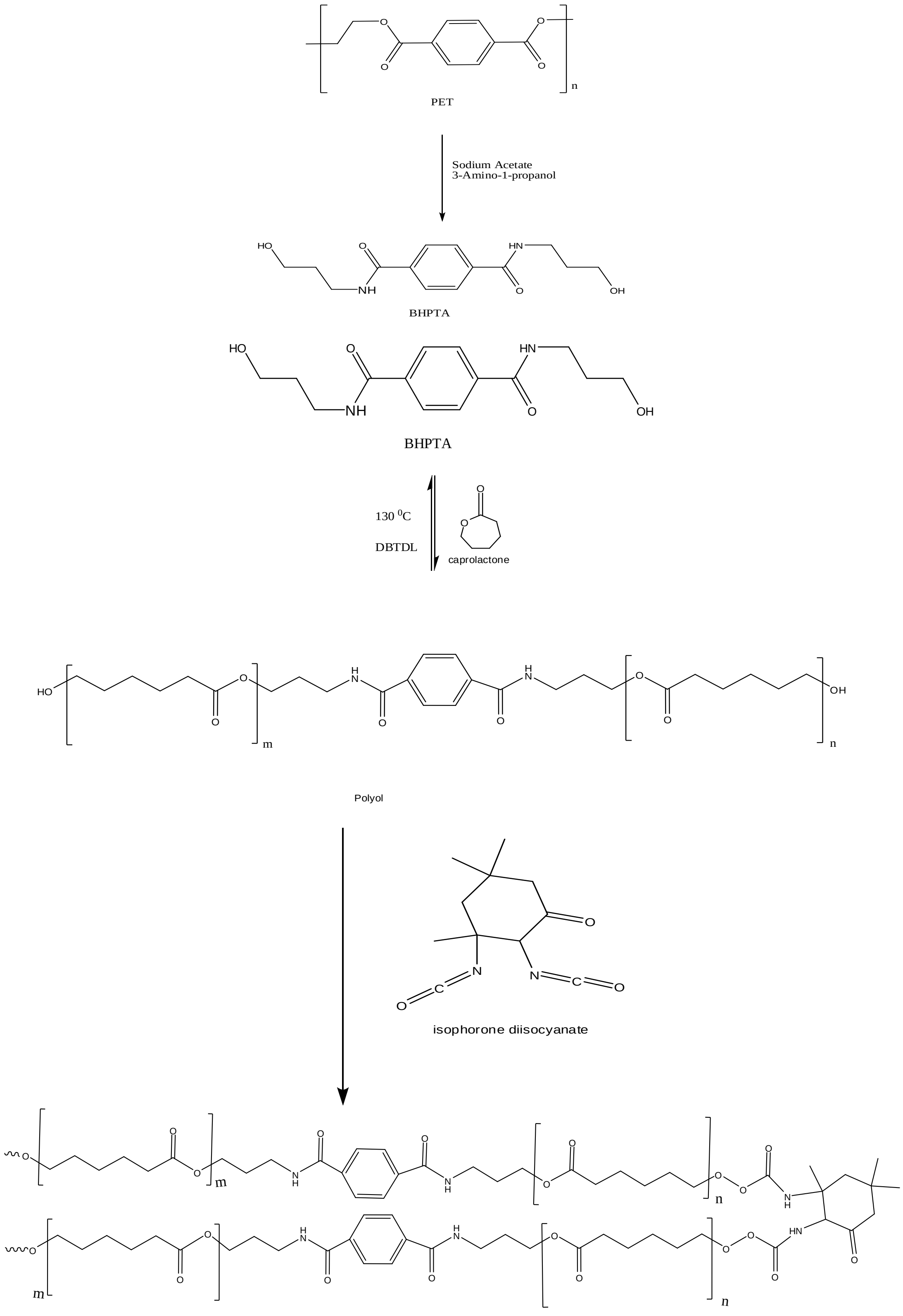


Figure 1: Reaction scheme for synthesis of coating from PET.

3.2. Dry Film Thickness

The dry film thickness of the film was found to be 70µ.

3.3. Gloss

The gloss of the panels at an angle of 600 was found to be 65.

3.4. Gel time

Gel time is very important for a two-pack coating system, as it indicates the maximum length of time during which the system remains in fluid condition. The gel time for the formulation was found to be 4 hr.

3.5. Impact Resistance

It evaluates the ability of a coating to withstand impact without cracking when the sudden deformation takes place. It passed from a drop height of 60 cm with 1.36 kg load.

Impact properties perform best if the energy of impact is dissipated uniformly over the film. For this, free volume between the chains plays a crucial role. Impact resistance of the developed system was excellent because the film passed the impact test when the indenter was released from a drop height of 60 cm and also the coating passed the flexibility test without any cracking. This may be attributed to adequate contribution of the linear caprolactone structure.

3.6. Scratch Hardness

Scratch hardness of a coating indicates its resistance to abrasion. It passed the test for 3.0 Kg. Scratch resistance and Pencil hardness of PU coating showed excellent results because of polyurethane linkage and aromatic content present in BHPTA. PU films formed hard structure due to di-functional isocyanate cross linker.

3.7. Flexibility

Flexibility is the ability of the material to be bent or flexed without cracking or undergoing any failure. [22] The mild steel panel coated with uniform thickness was allowed to cure. The cured panel was then subjected to conical mandrel test and it successfully passed the test as there was no loss of adhesion or cracking. Coating showed excellent mechanical properties since it has proper balance of hardness and flexibility due to aromatic linkage present in BHPTA. Use of ε -caprolactone provides flexibility and IPDI as a curing agent provided good weatherability, hardness and flexibility. Hence excellent scratch hardness as well as flexibility without cracking was observed.

3.8. Percentage Adhesion

It is the degree of attachment between a coating film and the underlying material which may be another film of paint or any other material or substrate. It is measured in terms of force required to remove the coating from the substrate under controlled conditions.[23] The percent adhesion for the coatings was determined by the cross hatch test. The percent adhesion of the coatings to mild steel panels was found to be 100% for all the panels.

3.9. Chemical Resistance

Coating showed excellent acid resistance with no damage whereas in case of alkali exposure, slight loss in the gloss of coating was observed. The film showed good resistance to solvent rub by xylene (non-polar) which could be due to polar nature of the film. Resistance to MEK could be correlated to complete curing of the resin.

3.10. Anticorrosive properties

Anticorrosive properties of coating were characterized by salt spray and Electron Impedance Spectroscopy (EIS) testing. Salt spray testing was carried out according to ASTM B 117 by exposing the coated panels to salt spray corrosion cabinet maintained at 35^0C and 0.82 bar pressure for 500 hr. (Fig.2) represents photographic references of panels before and after the test. It was observed that corrosion started at cross cut lines, but there was no loss of adhesion and also no rust formation. Blistering was observed throughout the panel after exposing it up to 500 hr. Thus, corrosion resistance of the coating was found to be good which was also proved by EIS testing.

EIS results for Tafel plot and Potentiostatic EIS was represented in (Fig.3) and (Fig. 4) the corresponding values of Icorr, Ecorr and Corrosion rate are represented in Table no. 2.

In tafel plot corrosion current is low before immersion and after immersion in 3.5 wt% NaCl solution for 5 days corrosion current is increased but not significant increase is observed. Corrosion rate also get slightly affected by immersion. In Potentiostatic EIS also impedance value is high before immersion (>1 M) and impedance value decreases after immersion (< 1M) due to starting of corrosion which is also matches with salt spray results. The reason for starting the corrosion is presence of ester linkage in resin and ester linkage is prone to the hydrolysis. Once the corrosion started diffusion of corrosive ions through the coating may enhance further corrosion, but presence of BHPTA which has amide linkage helps to increase the corrosion protection at the same time. Amide linkage has lone pair and on application of coating on metal surface which contain vacant d orbital, due to donar-acceptor type conditions better adhesion of coating to the metal surface takes place. Since adhesion of the coating to metal surface is good and through chemical type of linkage (donor-acceptor) type, diffusion of the corrosive species underneath the coating is decrease, it helps to increase the corrosion resistance. Since amide linkage gets attached to the metal surface the remaining part of BHPTA, i.e. aromatic ring and another part get away from surface towards bulk coating. This acts as a hydrophobic part and form additional protective layer, hence water and other aggressive chemicals remain away which helps to enhance anticorrosive properties. Hence as mention in EIS, even though corrosion current and corrosion rate is increasing and in potentiostatic EIS even though impedance value decreases after 5 days of immersion, it is not enhance drastically and shows good anticorrosive properties.

Table 2: Tafel plot results for polyurethane system.

Parameter	Before	After
I_{corr}, μA	-8.1539e^{-04}	-5.0549e^{-05}
E_{corr}, mV	27.12	-57.34
Corrosion Rate, mmpy	-1.3551e^{-06}	-8.4007e^{-08}

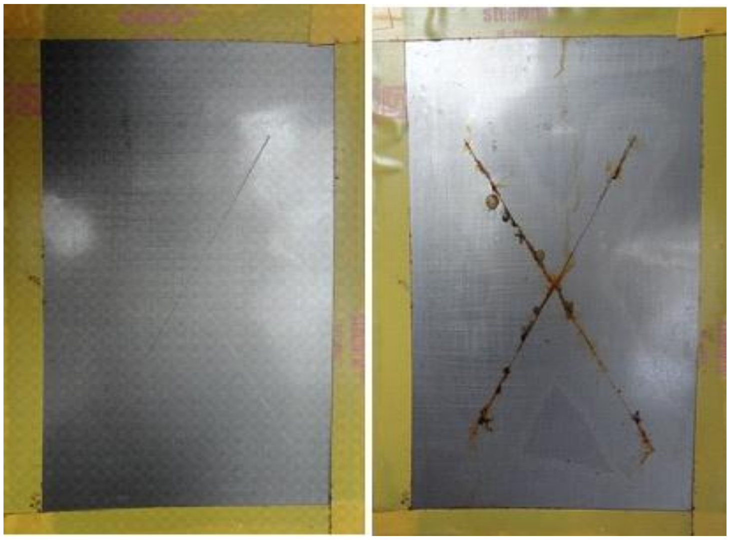


Figure 2: Mild steel panel before and after salt spray test

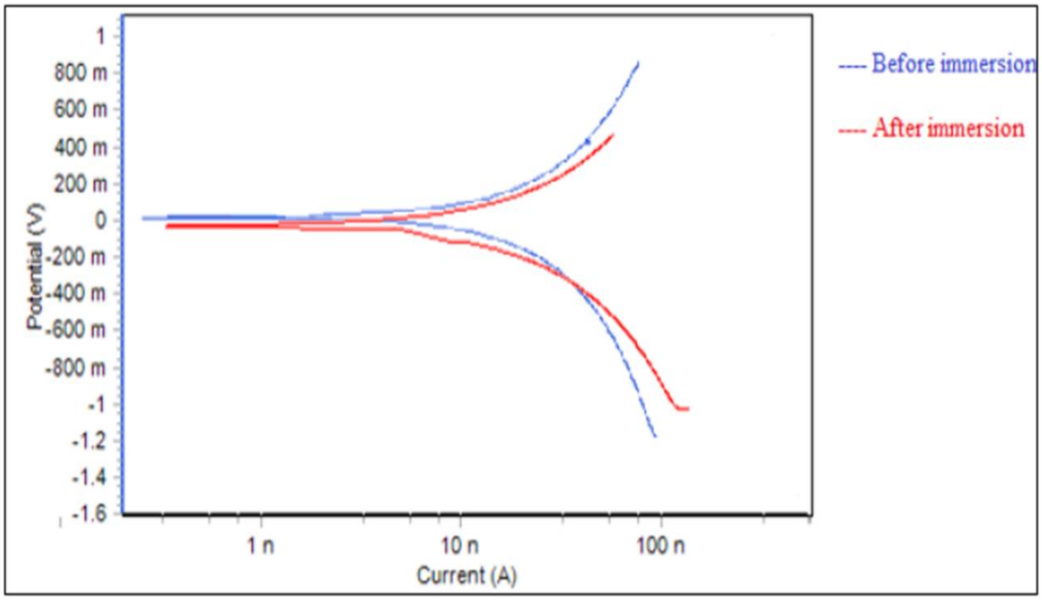


Figure 3: Tafel plot for coating

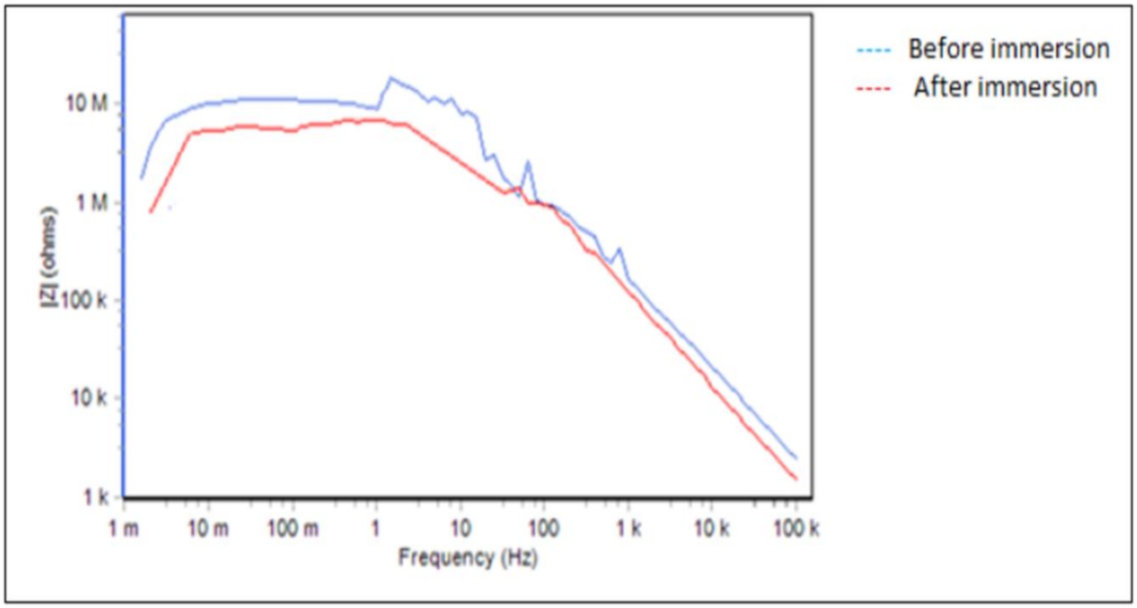


Figure 4: Potentiostatic EIS plot for coating

3.12. Thermal Properties

Thermal properties of all the coatings were evaluated by DSC and TGA. (Fig. 5, 6) Coating showed higher thermal stability due to the presence of aromatic structure in the cross-linked backbone. The coating started degrading at 284^0C.

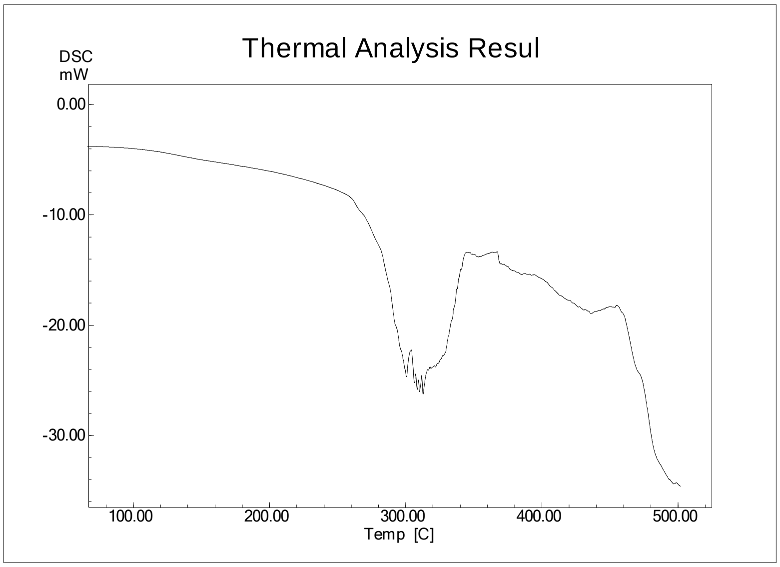


Figure 5: DSC of PU coating

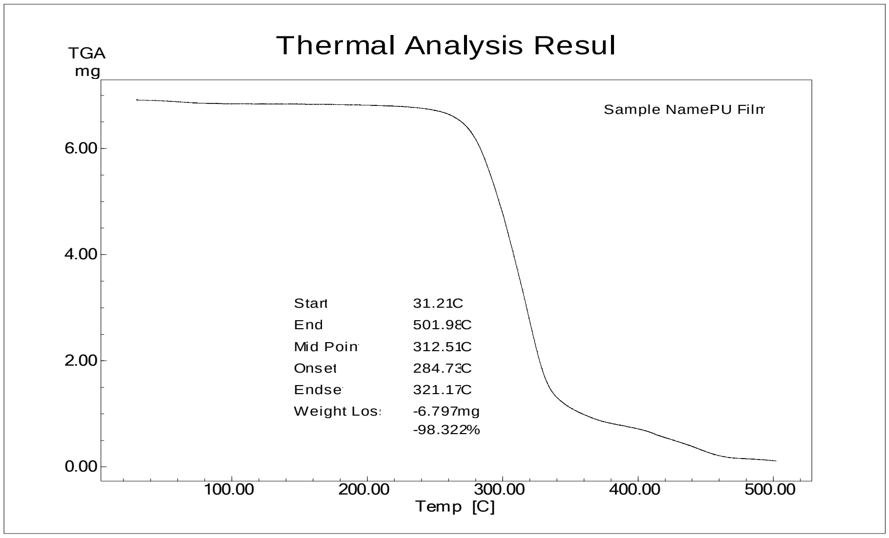


Figure 6: TGA of PU coating

3.13. FTIR Spectroscopy

The FTIR spectrum of the polyurethane is as shown in the following figure 7. There are distinctive transmission peaks at 3332 cm^{-1} (bonded – NH groups), 2947 and 2864 cm^{-1} (asymmetric and symmetric CH2 groups), 1728 cm^{-1} (overlapped carbonyl groups of polycaprolactone and urethane linkages), 1635 cm^{-1} (C=C stretching vibration in aromatic ring), 1548 cm^{-1} (-CO-N amide), 1461 and 1357 cm^{-1} for various modes of CH2 vibrations, 1236 and 1161 cm^{-1} are the stretching vibrations for the ester group.

3.14 ^{1}H NMR. The NMR results are as shown in (Fig.8, 9). The NMR peaks were observed at 7.940 δ(d, 4H, Ar-H) indicates the presence of the four aromatic ring protons. The peak at 4.151 δ(s, H, A-OH) corresponds to AOH groups; 4.043 δ(m, 2H, -CH2-) and 2.871 δ(m, 2H, -CH2-) corresponds to aliphatic (ACH2) proton.

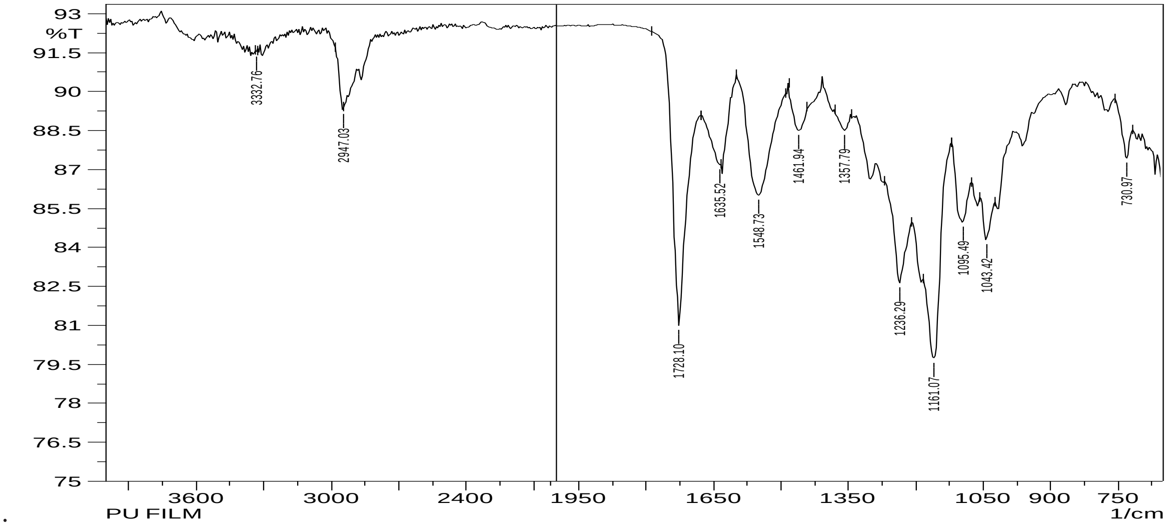
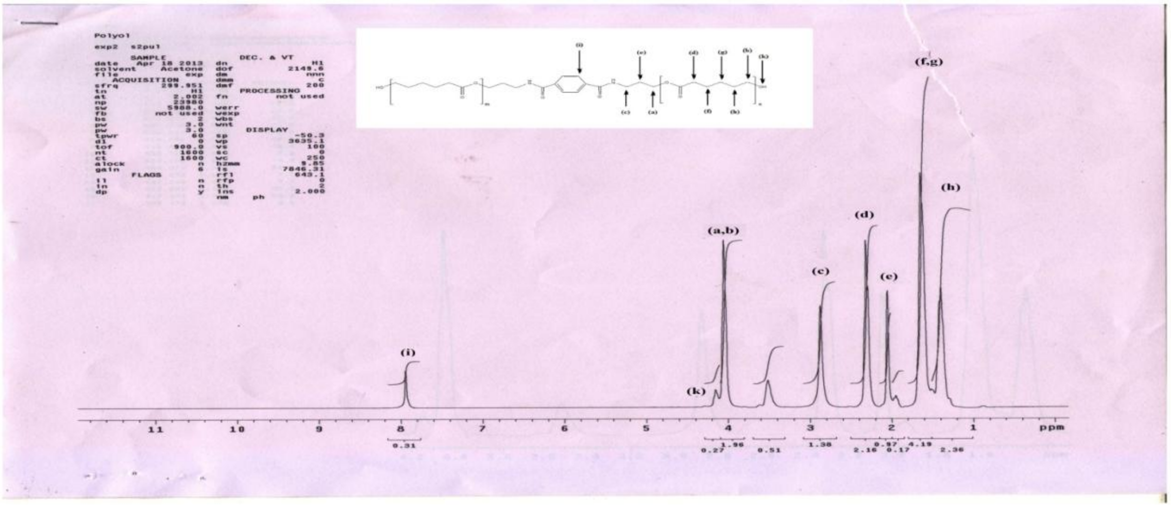


Figure 7: FTIR spectra of PU coating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Polyol
exp2   s2pul
        SAMPLE                 DEC. & VT
date    Apr 18 2013    dn            H1
solvent     Acetone    dof       2149.6
file            exp    dm           nnn
      ACQUISITION      dmm            c
sfrq        299.951    dmf          200
tn               H1        PROCESSING
at            2.002    fn      not used
np            23980
sw           5988.0    werr
fb         not used    wexp
bs                2    wbs
pw              3.0    wnt
pw              3.0          DISPLAY
tpwr             60    sp         -50.3
d1                0    wp        3635.1
tof           900.0    vs           100
nt             1600    sc             0
ct             1600    wc           250
alock             n    hzmm        9.85
gain              6    is       7846.31
        FLAGS          rfl        643.1
il                n    rfp            0
in                n    th             2
dp                y    ins        2.000
                       nm      ph
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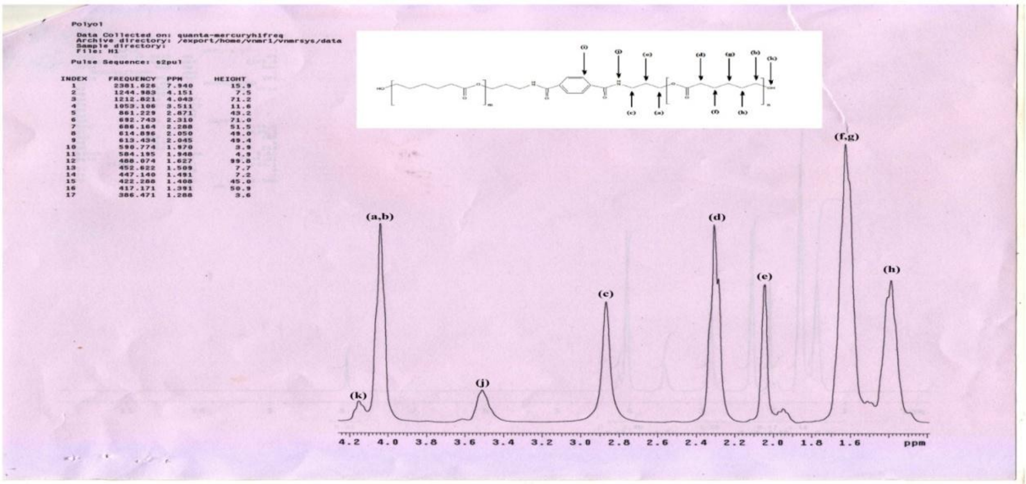
Figure 8: ^{1}H NMR of Polyol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Polyol
 Data Collected on: quanta-mercuryh1freq
 Archive directory: /export/home/vnmr1/vnmrsys/data
 Sample directory:
 File: H1

Pulse Sequence: s2pul

INDEX     FREQUENCY  PPM      HEIGHT
   1       2381.626  7.940      15.9
   2       1244.983  4.151       7.5
   3       1212.821  4.043      71.2
   4       1053.106  3.511      11.6
   5        861.229  2.871      43.2
   6        692.743  2.310      71.0
   7        686.164  2.288      51.5
   8        614.896  2.050      49.0
   9        613.434  2.045      49.4
  10        590.774  1.970       3.9
  11        584.195  1.948       4.9
  12        488.074  1.627      99.8
  13        452.622  1.509       7.7
  14        447.140  1.491       7.2
  15        422.288  1.408      45.0
  16        417.171  1.391      50.9
  17        386.471  1.288       3.6
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Figure 9: ^{1}H NMR of Polyol

Conclusion

Waste PET bottles were subjected to aminolytic depolymerization to obtain pure BHPTA with yield of 84%. BHPTA was successfully used to synthesize polyol using ε-caprolactone through ring opening polymerization. Polyurethane surface coating material formulated using this polyol was found to possess excellent coating properties. Thus, a novel environment friendly and sustainable approach of chemical recycling of PET waste has been explored successfully.

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