

# Aminolysis of Poly(ethylene terephthalate) Wastes Based on Sunlight and Utilization of the End Product [Bis(2-hydroxyethylene) Terephthalamide] as an Ingredient in the Anticorrosive Paints for the Protection of Steel Structures

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**ABSTRACT:** The increasing demand for poly(ethylene terephthalate) (PET) polymer, the simultaneous shortage in landfill disposal spaces, and known problems associated with PET waste specifically (e.g., its nonbiodegradability and huge accumulation) are challenges with which mankind must cope nowadays. In this study, PET post-consumer bottle wastes were cut to very small slides and then subjected to an aminolysis process with ethanol amine as a degradative agent in the presence of one catalyst from three used in this study. These catalysts were dibutyl tin oxide, sodium acetate, and cetyltrimethyl ammonium bromide. The reaction was performed in sunlight: a beneficial, clean, cheap, and renewable source of energy. The end product, which was a white precipitate

of bis(2-hydroxyethylene) terephthalamide, was subjected to spectrophotometric and thermal analyses. The product was characterized to assess its suitability for use in pigments in anticorrosive paint formulations. In general, this process was a green, environmentally friendly degradation based on the utilization of solar energy for the aminolysis reaction using simple, cheap, available chemicals as catalysts. The originality of this study was derived from the use of waste materials to yield a product with beneficial applications in the field of corrosion inhibition. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2842–2855, 2011

**Key words:** degradation; oligomers; recycling; waste

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is a linear semi-aromatic polyester that can be characterized by its superior mechanical, thermal, and chemical advantages. Semi-aromatic polyesters have been used in many industrial fields as engineering plastics (e.g., high-strength fibers, soft drink bottles, photographic films, audio and video tapes, modeling materials, various packages).<sup>1</sup>

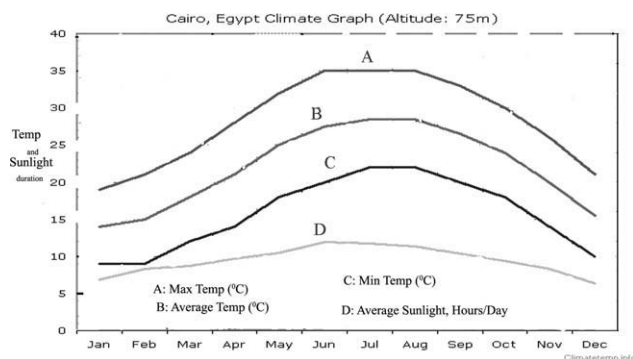
Applications of these synthetic polymers are based on their relative resistance to environmental degradation and biodegradation. The widespread application and nonbiodegradability of this polymer create huge amounts of waste and disposal; what results is a serious environmental problem. The landfilling of plastics is not preferred because of space restrictions and land pollution.<sup>1</sup> In addition, the disposal of

wastes in landfilling will be severely limited or prohibited in many countries in coming years, and hence, suitable action should be taken to solve the uncontrollable problem of increasing volumes of generated wastes.<sup>2</sup> The most important cause for the recycling and reprocessing of PET waste has arisen from the awareness of and concern over environmental pollution.

Several processes for PET depolymerization have been applied either in laboratory research experiments or on an industrial production scale. All of these techniques and processes have their advantages and disadvantages.<sup>3–5</sup> The most sound advantage of the chemical recycling of postconsumer polymer wastes are the availability of a wide spectrum of degradation agents and variable processing conditions that lead to great array of outcomes.<sup>6–9</sup>

Recently, the aminolysis of PET has received extreme attention. The end output of this process is bis(2-hydroxyethylene) terephthalamide (BHETA), which is capable of further reaction; this results in useful products. These materials have the potential for applications such as adhesives and thermal stabilizers in PVC resins and coatings.<sup>10,11</sup>

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**Figure 1** Temperature and average sunlight duration in Cairo, Egypt, in June, July, and August.

In this article, we discuss an alternative green procedure for the aminolysis of PET postconsumer wastes based on the use of sunlight as a renewable clean source of energy for the reaction instead of a conventional heating system and catalytic reagents that were carefully selected to be superior in their role. The chemicals used were commonly available and low in cost [e.g., sodium acetate (SA), cetyltrimethyl ammonium bromide (CAB), and dibutyl tin oxide (DBTO)]. Then, the end product obtained (i.e., BHETA) was subjected to experimental attempts to evaluate its uses as anticorrosive ingredients in corrosion-protection paints.

## EXPERIMENTAL

### Waste materials

Discarded PET postconsumer bottles were obtained from a local market. The bottles, after their caps and labels were removed, were cleaned with a detergent solution, washed, and then dried. Consecutively, they were cut into very small pieces (ca.  $2 \times 2$  mm<sup>2</sup>), and then, they were subjected to subsequent aminolysis experiments.

### Chemicals

The chemicals, including ethanol amine (EA), DBTO, CAB, and SA, were purchased and used without any further purification.

### Chemical recycling of polyester waste

EA was used for the aminolysis of the small pieces of PET waste (1 : 4 PET : EA w/w) in a properly sealed, round-bottom flask. The reaction was carried out in the presence of one of the three catalysts (i.e., DBTO, CAB, or SA) for 21 days of degradation time. The catalyst was added at a ratio 1.5 wt % of the polymer. Flasks filled with PET, EA, and the catalyst were dipped in a sand bath and exposed to sunlight in an open-air area. The aminolytic degradation

process was undertaken during June, July, and August. These months are the summer season in Egypt and record the hottest temperatures over the year. The recorded maximum and minimum temperatures and sun duration through these months are represented in Figure 1.

At the end of the predetermined period, the flask was withdrawn and distilled water was added in excess to the reaction mixture with vigorous agitation to precipitate out the white product. The filtrate mainly contained the white precipitate in addition to the unreacted EA and small quantities of water-soluble PET degradation products. The precipitate obtained was filtered and redissolved in distilled water by boiling for about 30 min. The white crystalline powder of BHETA was obtained through concentration of the filtrate by boiling and chilling. The end product was further purified by recrystallization in water, dried in an oven at 80°C, and then weighed to estimate the yield percentage relative to the unreacted part of the PET waste. This unreacted part of the PET waste was thoroughly washed with water and then dried in a vacuum oven for 2 h at 60°C, and its weight was followed until a constant value was reached.

Similar degradation experiments were performed in the presence of increasing concentrations of DBTO as a catalyst (0.5–2 wt % of the PET waste) for 21 days under the same conditions.

On the basis of the percentage yield obtained, a DBTO concentration of 1.5 wt % of PET was chosen for the processing of the plastic waste under the previously described conditions (i.e., dipping in a sand bath and exposure to sunlight), where the aminolysis reaction was studied for various time periods (7, 14, 21, 30, 45, and 60 days). At the end of each time interval, the white precipitates were separated from the unreacted PET waste, and the weight of the white crystalline BHETA was determined.

### Characterization of the white precipitate end products

Various analytical techniques were used to characterize the obtained white precipitate BHETA.

#### Fourier transform infrared (FTIR) analysis

We examined the white precipitate BHETA by FTIR spectroscopy by pressing with KBr to pellet. The FTIR spectroscopy was performed on a Jasco FTIR-6100 (Tokyo, Japan).

#### NMR spectra

NMR spectroscopy was performed on a JEOL ECA-50 NMR instrument (Akashima, Japan) at 500

**TABLE I**  
**Pigment Characteristics of BHETA Originating from the Aminolysis of PET Wastes and the Main Constituents of the Paint Formulations**

Material	Oil absorption (g/100 g)	Specific gravity	BV (gal/100 b)	pH
BHETA	30	1.50	8.03	8.38
Iron oxide (hematite)	32	4.58	2.63	8.00
TiO <sub>2</sub>	24	4.24	2.84	8.00
Kaolin	35	2.58	4.67	7.00
ZnO	18	5.61	2.15	8.00

BV = bulking volume.

MHz with tetramethylsilane as the internal reference for the <sup>1</sup>H-NMR spectra. The spectra were also obtained in a dimethyl sulfoxide solution.

#### Thermogravimetric analysis (TGA)

TGA was achieved with a TGA7 thermogravimetric analyzer based on a DTG-60H detector (Narwhalk, Connecticut, USA). The analysis was performed in a platinum cell under a nitrogen atmosphere at a flow rate of 20 mL/min, starting from room temperature up to 800°C at a heating rate of 10°C/min.

Although differential scanning calorimetry (DSC) analysis was carried out under a helium atmosphere with a Netzsch STA 409C/CD (Boston, USA). BHETA was also heated from room temperature to 800°C at a heating rate of 10°C/min.

#### Scanning electron microscopy (SEM)

SEM was used in this work to estimate the particle shapes. This was carried out with a Philips XL 30 scanning electron microscope (Pennsylvania, USA) attached to an energy-dispersive X-ray spectroscopy unit with an accelerating voltage of 30 kV, magnifications of 10–400,000×, and a resolution of  $W\lambda$  (3.5 nm). The samples were coated with gold before scanning.

#### Application of the end product as an ingredient in anticorrosive paint formulations

##### BHETA evaluation

The white precipitate originating from the aminolysis degradation of PET wastes was used in anticorrosive paint and evaluated according to the following specifications, which are represented in Table I:

- Specific gravity (ASTM D 5965-96, 2007).
- Oil absorption (ASTM D 281-95, 2007).
- Bulking value (ASTM D 16-62, 1980).
- Hydrogen-ion concentration (pH value; ASTM D 1583-01, 2007).

#### Anticorrosive paint formulations

Fifteen paint formulations containing the tested BHETA and a control formulation free from BHETA were prepared. The paints were divided to three groups on the basis of different pigment/binder (P/B) ratios (1.74, 2.233, and 3). Each group comprised a control and four paints containing increasing concentrations of BHETA ranging from 10 to 40% with a medium oil alkyd resin. The various paint formulations and their characterizations are represented in Tables I and II.

#### Physical and mechanical tests for the painted films

A variety of physical and mechanical evaluations of the paint films were carried out. Relevant methods of sample preparation and evaluations included

- Preparation of glass panels (ASTM D 3891-96, 2007).
- Preparation of steel panels (ASTM D 2201-94, 2007).
- Determination of the viscosity by a Ford cup (ASTM D 1200-94, 2007).
- Determination of the drying time (ASTM D 5909-96a, 2007).
- Determination of the dry paint film thickness (ASTM D 4138-07, 2007).
- Measurement of adhesion with adhesive tape (ASTM D 3359-97, 2001).
- Determination of the film hardness with a pendulum hardness tester (ASTM D 6577- 00, 2007).
- Determination of the ductility with a cupping test machine and evaluation of the resistance of organic coatings to the effect of rapid deformation (impact resistance; ASTM D 5638-00, 2007).

#### Corrosion tests

To evaluate the prepared BHETA characteristics in the various formulations, the following tests were carried out systematically:

- A laboratory corrosion resistance test according to ref. 12.
- Photographic inspection and grading of the paint films according to standard methods at the end of inspection for a filiform corrosion resistance test (ASTM D 2803-93, 2001).
- Evaluation of the degree of rusting (ASTM D 6294-98, 2007).
- Evaluation of the degree of blistering on painted steel surfaces according to ASTM D 714-02 (2007).

TABLE II  
Paint Formulations with BHETA and Medium Oil Alkyd Resin

Group I					
Constituent (wt %)	C1	1	2	3	4
Kaolin	22	20	15	10	5
TiO <sub>2</sub>	12	10	10	8	5
ZnO	10	8	4	4	4
Iron oxide (hematite)	20	16	15	12	10
BHETA	—	10	20	30	40
Total pigment	64	64	64	64	64
Total binder	36	36	36	36	36
P/B	1.77	1.77	1.77	1.77	1.77
Total	100	100	100	100	100
Wetting and dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Group II					
Constituent (wt %)	C2	5	6	7	8
Kaolin	20	15	15	15	15
TiO <sub>2</sub>	12	12	12	7	4
ZnO	10	10	5	5	3
Iron oxide (hematite)	25	20	15	10	5
BHETA	—	10	20	30	40
Total pigment	67	67	67	67	67
Total binder	30	30	30	30	30
P/B	2.233	2.233	2.233	2.233	2.233
Total	100	100	100	100	100
Wetting and dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5
Group III					
Constituent (wt %)	C3	9	10	11	12
Kaolin	30	25	20	12	12
TiO <sub>2</sub>	13	13	10	10	5
ZnO	12	12	10	8	5
Iron oxide (hematite)	20	15	15	15	13
BHETA	—	10	20	30	40
Total pigment	75	75	75	75	75
Total binder	25	25	25	25	25
P/B	3	3	3	3	3
Total	100	100	100	100	100
Wetting and dispersing agent	1	1	1	1	1
Drier	0.5	0.5	0.5	0.5	0.5

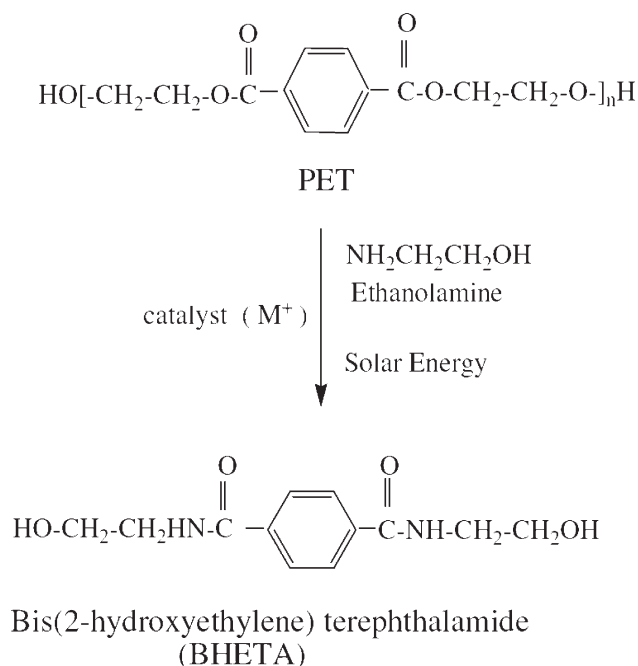
C1–C3 = control formulations free from BHETA.

From Table I, we concluded that

1. The oil absorption value of BHETA was low compared to other known pigments [e.g., talc (45 g/100 g) and kaolin (35 g/100 g)], and thus, it is economically feasible. Oil absorption is an indication that BHETA will consume a low binder content when it is used in paints.
2. The specific gravity of BHETA was low compared to other known and commonly used pigments; this means a high dispersability in the vehicle and, consequently, more homogeneous paint films. Also, the paint obtained, containing the BHETA in the role of a pigment, would be characterized by a long storage period in which its constituents would not be easily separated and would take much more time to settle down.
3. The pH of BHETA originating from the aminolysis of PET wastes was alkaline in its nature. The property of alkyds should be taken into account when one chooses pigments for coatings. Alkaline pigments, such as zinc oxide and BHETA, can usefully react with unreacted acid groups in the alkyd; this leads to the strengthening of the film.

## RESULTS AND DISCUSSION

PET wastes create a big disposal problem. The volume of generated waste is so huge that in a short time, it will fill every available dumping space founded for this purpose and, very frequently, necessitates the creation of new disposal sites. These sites are normally created in clusters near populated areas. As a result, most of these points are situated very close to populated cities and towns.



**Scheme 1** Suggested route for the aminolysis of PET waste.

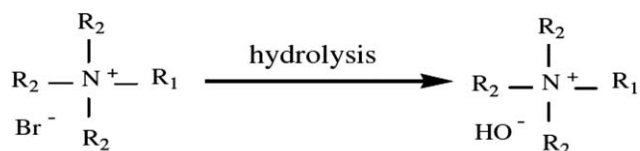
In this study, we carried out the aminolysis process of PET postconsumer drinking bottles by EA in the presence of relatively cheap and available chemicals as catalysts and using solar energy, which is beneficial from a green chemistry perspective and prevents or minimizes insufficient conventional energy consumption.<sup>13</sup> The activation reaction is shown in Scheme 1.

Aliphatic amines are organic bases that are able to cause the cleavage of a polymer's ester bond under mild conditions (e.g., atmospheric pressure, solar energy). In this study, the solvolysis of the PET ester bond caused by EA in the presence of various simple catalysts (i.e., SA, CAB, or DBTO) was carried out. The aminolytic degradation process was performed in a properly sealed container dumped in a sand bath and heated with sunlight for an increasing exposure time. The data obtained for the aminolysis of PET with the three easily available catalysts separately are represented in Table III. It is clear that the use of DBTO resulted in the highest yield after 21 days at a PET : EA ratio of 1 : 4. Although SA

**TABLE III**  
Aminolysis Yield Percentages due to the Degradation of PET in EA with Different Catalyst Types

Catalyst used	Yield (%)
DBTO	60
SA	52
CAB	52

Degradation time = 21 days in sunlight; PET : EA = 1 : 4 w/w; catalyst concentration = 1.5 wt % of PET waste.



Where R<sub>1</sub> = CH<sub>3</sub> (CH<sub>2</sub>)<sub>15</sub> & R<sub>2</sub> = CH<sub>3</sub>

**Scheme 2** Phase transfer of the CAB catalyst.

acted as transesterification catalyst and the CAB was positively charged, independent of the solution pH (Scheme 2), DBTO was the best catalyst candidate for the PET aminolysis under the described conditions.

The yield of BHETA varied between undetectable ranges on optimization of the DBTO catalyst concentration. Increasing the concentration of DBTO from 0.5 to 2% relative to the weight of the PET waste polymer was accompanied with a relative increase in the yield from 59 to 64% after 21 days, as shown in Table IV. This may be explained on the basis that the catalyst formed a complex with the carbonyl group of PET, and increasing its concentration raised the probability of this reaction;<sup>14</sup> consequently, the polarity of the polymer increased, which facilitated its degradation.

The reaction was based on the solar energy for activation of the aminolysis of PET with EA. Figure 2 shows the effect of increasing reaction time on the yield of the aminolysis process. After 60 days at a 1.5% DBTO catalyst concentration and with a PET : EA weight ratio of 1 : 4, complete depolymerization of the polymer took place. On the basis of the obtained data, we concluded that this green process for the aminolysis of PET was performed with a cheap, ecofriendly, simple, and effective catalyst with clean, cheap solar energy under normal pressure and without any requirements for sophisticated arrangements.

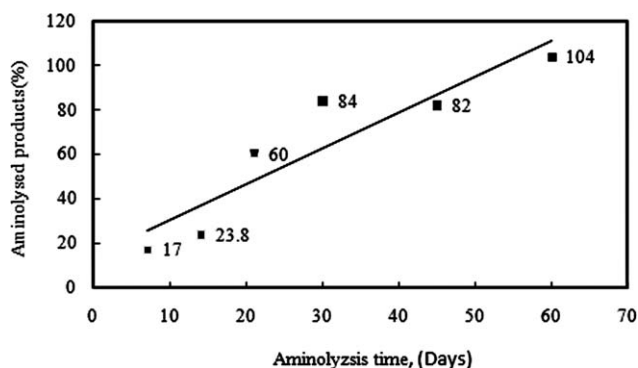
The degradation rate of the accumulated PET postconsumer wastes under the prescribed conditions of EA and catalyst DBTO concentrations are represented in Table V.

Although the degradation rate after 60 days (90 kg/day) was slower than that at 21 days (143 kg/day), the complete degradation (yield ≈ 104%) of PET took place after 60 days. As the process, with

**TABLE IV**  
Aminolysis Yield Percentages due to the Degradation of PET in EA as a Factor of DBTO Concentration After 21 Days of Exposure to Sunlight

Catalyst concentrated (%)	Yield (%)
0.5	59.4
1	60
1.5	60
2	64

PET : EA = 1 : 4 w/w. The catalyst concentration weight is represented as a percentage of the PET waste weight.



**Figure 2** Effect of the reaction time on the yield of the aminolysis of PET waste with 1.5% DBTO as a catalyst.

time, was not accompanied with any energy consumption, it was preferable to let the degradation continue for up to 60 days to reach complete destruction rather than stopping the process after 21 days with an aminolysis yield of only 60%.

#### Spectrophotometric characterization of the degradation products

PET undergoes degradative aminolysis through nucleophilic attack of the nitrogen in EA on the carbonium center of the carbonyl in PET waste polymer. As a result of this aminolytic degradation, numbers of main characteristic peaks representing the white precipitates can be detected clearly through FTIR analysis. The data of processing PET flakes using EA and based on the sunlight energy, under different experimental conditions are represented in Table VI.

It is clear from FTIR analysis that despite the various degradation conditions, that is, catalyst type and/or aminolysis duration, the characteristic peaks representing the white precipitate had identical

**TABLE V**  
Degradation Rate of PET Wastes in EA at a Ratio of 1 : 4 w/w with the DBTO Catalyst at a Concentration of 1.5 wt % of PET with Solar Energy as a Heating Source

Aminolysis time (days)	Degradation rate (kg/day)
7	120
14	85
21	143
30	140
45	91
60	90

assignments. This could be explained through an endwise homolytic mechanism for the aminolytic degradation of PET wastes. In addition, the route supposed for the processing of PET postconsumer wastes could be claimed through the solvolysis attack of the peripheral-end ester bond in the PET polymer by EA, and this process was repeated successively. Finally, on the basis of the FTIR results, we affirmed that the end product of the aminolysis of PET was BHETA.

To confirm the FTIR data,  $^1\text{H-NMR}$  analysis was carried out for the white precipitate obtained from degradation of the PET waste in the presence of 1.5% DBTO as the catalyst and with solar energy for 60 days. The spectrum obtained showed that four distinct absorption peaks were detected, as shown in Figure 3. A slightly broad, low-hump peak appeared at  $8.53 \delta$ , and this peak was attributed to the  $\text{CO-NH}$  proton. A sharp singlet signal appeared at  $7.88 \delta$ , which accounted for the four phenyl H protons. Another sharp singlet, which was associated with a hydroxyl group, appeared at  $4.724 \delta$ . The protons bonded to the amide and hydroxyl groups underwent exchange with deuterium in the  $\text{D}_2\text{O}$ -dimethyl sulfoxide solvent, and this confirmed the postulated described characterization for the two

**TABLE VI**  
Some Peaks of Interest Characterizing the White Product Generated from the Degradative Aminolysis of PET Wastes with Different Catalysts at a Concentration of 1.5 wt % of PET<sup>9,10,14-16</sup>

Peak assignment ( $\text{cm}^{-1}$ )	Characteristic	Degradation conditions			
		CAB		SA	
		21 days	21 days	21 days	60 days
3364	—NH— in hydrogen bonding	3365	3365	3364	3365
3289	Amide NH— plane bending	3288	3289	3289	3289
1627	—C=O bending	1627	1628	1627	1628
1553	Secondary amide stretching	1556	1555	1555	1555
1498	Aromatic C—C bending	1497	1498	1498	1498
1460	Methylene —C—H bending	1459	1461	1460	1461
1314	—C—N stretching	1312	1314	1314	1314
1159	—C—N stretching	1159	1159	1159	1159
1053	Primary alcohol stretching	1053	1055	1056	1054
837	Para disubstituted benzene-ring stretching	837	837	837	837

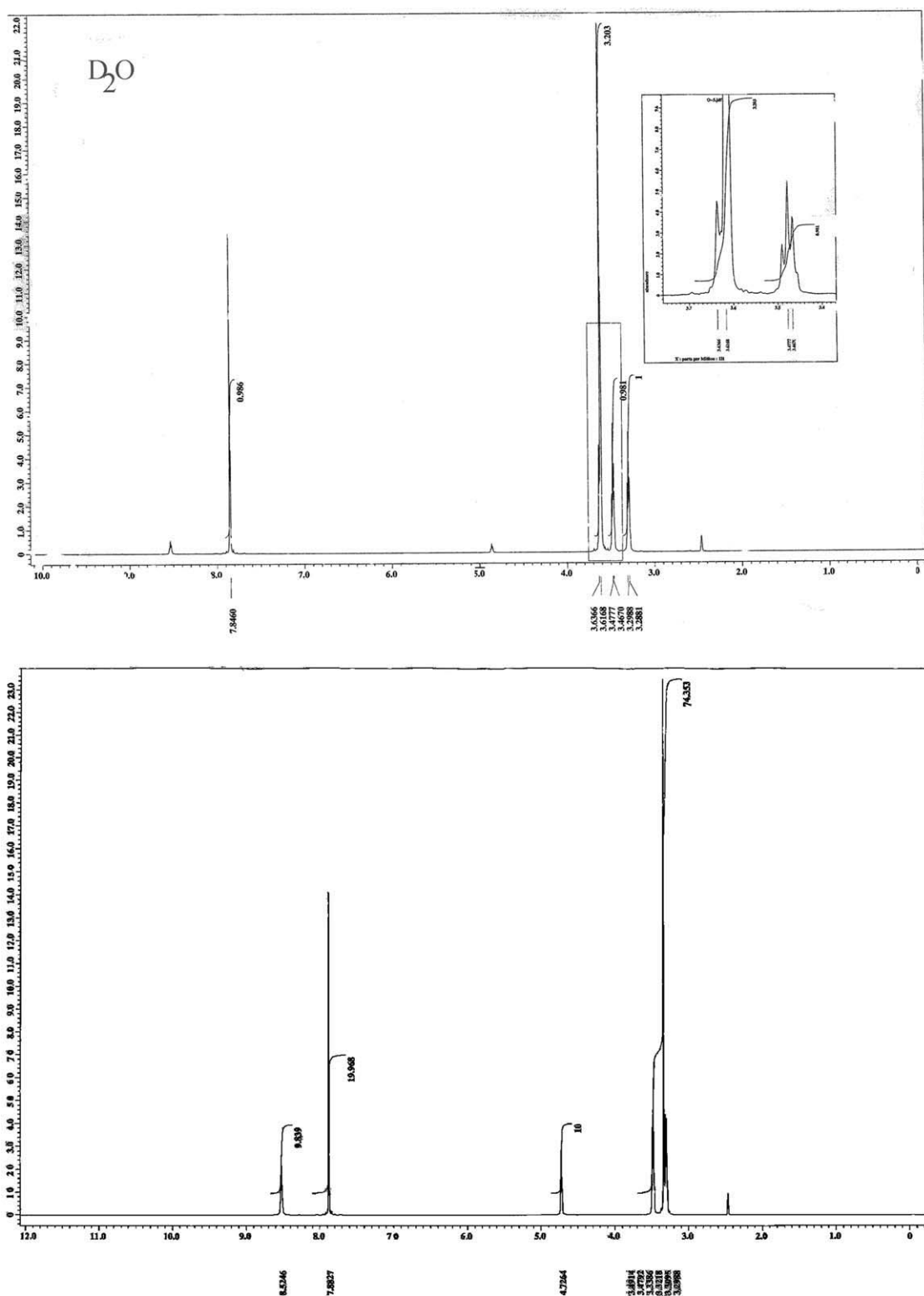


Figure 3  $\text{NMR}$  spectra of BHETA.

peaks.<sup>17</sup> Both peaks could not be detected in Figure 3; the two deshielded methylene protons appeared as a triplet between 3.5 and 3.3  $\delta$  and adjacent to the two electronegative atoms oxygen and nitrogen. This is shown clearly in Figure 3. Thus, the major

structural features that stood clear were those representing  $\text{C}_6\text{H}_4$ , OH, secondary amide, and duplicate methylene groups. This verified the FTIR data and fortified the postulated mechanism for the aminolysis process of PET wastes. All of the

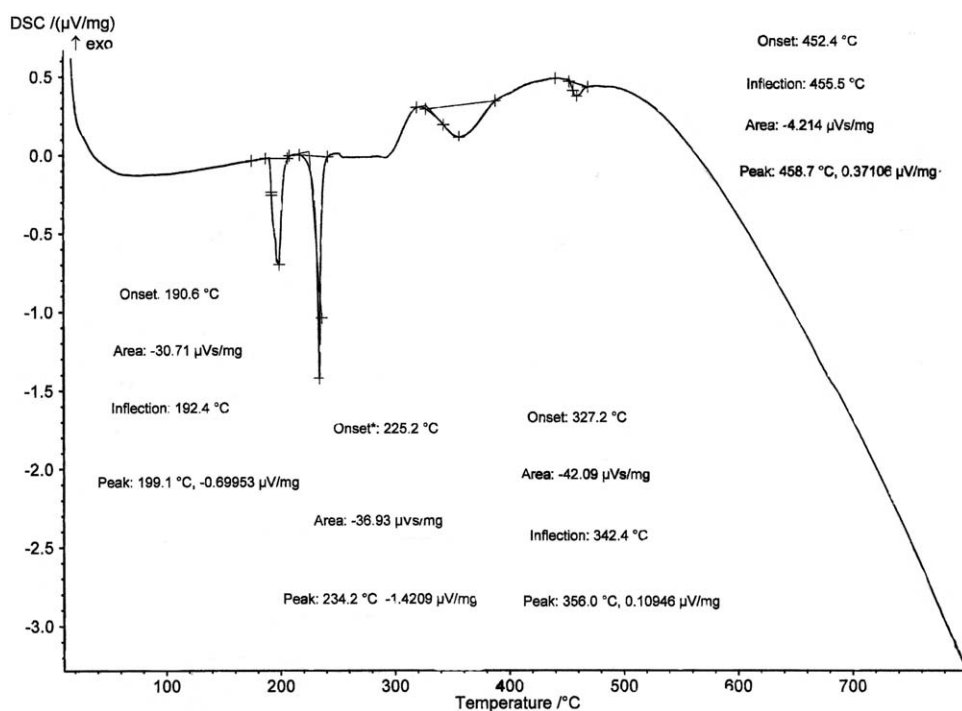


Figure 4 DSC thermogram of BHETA.

previous results were in high accordance and confirmed that the end product was BHETA.

#### Thermal characterization of BHETA

DSC thermogram recording was performed from room temperature to 800°C at a heating rate of 10°C/min with Al<sub>2</sub>O<sub>3</sub> as a reference material and is shown in Figure 4 for the white end-product precipitate obtained. The thermogram showed four distinct exothermic peaks, starting from 199.1°C due to the melting of BHETA followed by three successive peaks at 234, 356, and 458.7°C, respectively. These described the destruction of the inter-chain hydrogen bonding, chain scission, and pyrolysis reaction, respectively, during the BHETA turnout.

In parallel, the TGA and differential TGA graphs, shown in Figure 5, of BHETA accounted for the following peaks:<sup>7,9,14</sup>

- Weight reduction started at about 196.6°C.
- A four-step degradation process with weight reductions of 21.61, 43.31, 16.6, and 18.5%, corresponding to the four exothermic peaks, were recorded in the differential TGA thermogram (Fig. 5).
- The char residue constituted about 0.34% on the basis of the thermal analysis data.
- The slightly high melting-point characterizing the BHETA (199.1°C) may have been due to

the presence of an aromatic ring that caused retardation of the product degradation. These results were in high agreement with the literature.<sup>7,9,14</sup>

- Generally, the obtained white precipitate end-product BHETA was characterized by an acceptable thermal stability; this would allow it to be used in various applications, especially those requiring products that could withstand a relatively high temperature.

#### Application of BHETA as an anticorrosive ingredient for the protection of steel structures

Organic coatings are an efficient way of protecting metallic substrates from corrosion. For reliable, long-term performance, pigments that release corrosion-inhibiting substances are usually added to organic coatings. However, nearly all powerful corrosion inhibitors may have detrimental effects on both the environment and human health due to their toxic and carcinogenic natures. Thus, to ensure the protective properties over years, the coatings need to be highly pigmented. Because of corrosion inhibitors are constantly released into the environment, a number of novel approaches are being sought by companies to replace anticorrosive inorganic pigments.

On the basis of the data in Table VII representing the physical, mechanical, and corrosion test results after the incorporation of BHETA in anticorrosive paint formulations, we detected that generally, the



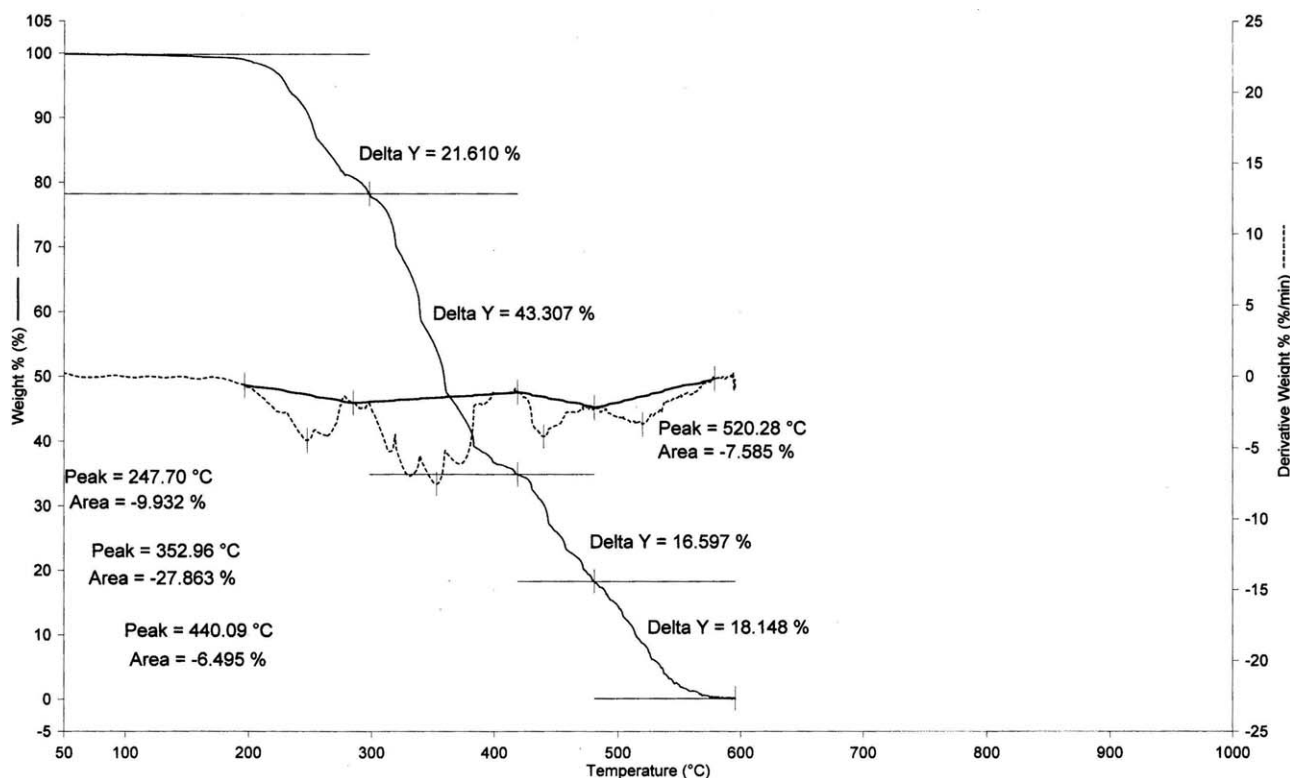


Figure 5 TGA thermogram of BHETA.

adhesion of paint formulations, we detected that generally, the adhesion of paint films to the metal surface were highly strict and very strong for the three prepared formulations. This is denoted in the table by the symbol Gt0.

#### Physical and mechanical properties

1. For the three groups, the control formula exhibited the lowest hardness, impact, and ductility values, but as BHETA was added, the stated properties were enhanced.
2. Paint films containing 10% of the BHETA pigment (paints 1, 5, and 9) showed results that were very comparable to the control. An increase in the percentage of BHETA in the paint formulations was accompanied with manifested improvements in the physical and mechanical characteristics.
3. Undetectable enhancements in the physical and mechanical properties of the paint films were recorded when the BHETA content was increased in the paint formulations from 30% (paints 3, 7, and 11) to 40% (paints 4, 8, and 12); that is, increasing the percentage of BHETA did not impart better physical and mechanical properties to the paint films.

#### Corrosion properties

1. In the first group, with a P/B ratio of 1.77, blistering varied among the entire group, but better results were recorded for paint films containing 40% BHETA (Fig. 6). Rust under the film also varied; it was clean and bright under the control and also for the paint films containing 10% BHETA pigment, although some rust began to appear under the paint films and could be found as spot under the paint films containing 20% BHETA. When the pigment ratio was elevated to 40%, general rusting under the paint films manifested. Blistering is sometimes an indication of a change in pH under paint films; this leads to a higher osmotic pressure, which is the main cause of detachment of this part of the paint film, which causes these blisters.
2. In the second group, with a P/B ratio of 2.233, the control shows no blistering or rust under the film; this indicated a high-built film. Paint films containing 10% BHETA showed high blistering and no rust under the film; this indicated high corrosion protection. As the percentage of BHETA increased in the paint formulations, less corrosion protection was exhibited but to a very low extent, although

**TABLE VII**  
**Physicomechanical and Corrosion Characteristics of Dry Paint Films with Various Paint Formulations**

Paint number					
Group I (P/B = 1.77)					
Test	C1	1	2	3	4
Drying time (h)					
Surface dry			1–2		
Through dry			3–4		
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness (s; 70 $\mu$ )	98	118	120	123	126
Ductility (Mm)	3.5	3.8	4.5	4.6	4.6
Impact resistance (kg m)	62.5	62.5	67.5	67.5	67.5
Corrosion resistance					
Degree of blistering	2MD	4F	2F	6F	8F
Degree of rusting	10	10	7S	5G	5G
Filiform corrosion			Figure 1: FA		
Group II (P/B = 2.233)					
Test	C2	5	6	7	8
Drying time (h)					
Surface dry			1–2		
Through dry			3–4		
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness (s; 70 $\mu$ )	107	123	124	125	125
Ductility (Mm)	4.2	5.2	5.3	5.3	5.4
Impact resistance (kg m)	60	62.5	62.5	67.5	67.5
Corrosion resistance					
Degree of blistering	10	8MD	8D	2F	6F
Degree of rusting	10	10	6S	8G	8G
Filiform corrosion			Figure 1: FA		
Group III (P/B = 3)					
Test	C3	9	10	11	12
Drying time (h)					
Surface dry			1–2		
Through dry			3–4		
Adhesion	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness (s; 70 $\mu$ )	110	112	112	117	117
Ductility (Mm)	4.5	4.7	4.7	5.4	5.4
Impact resistance (kg m)	57.5	57.5	60	60	62.5
Corrosion resistance					
Degree of blistering	6F	10	10	10	10
Degree of rusting	10	10	7S	5G	5G
Filiform corrosion			Figure 1: FA		

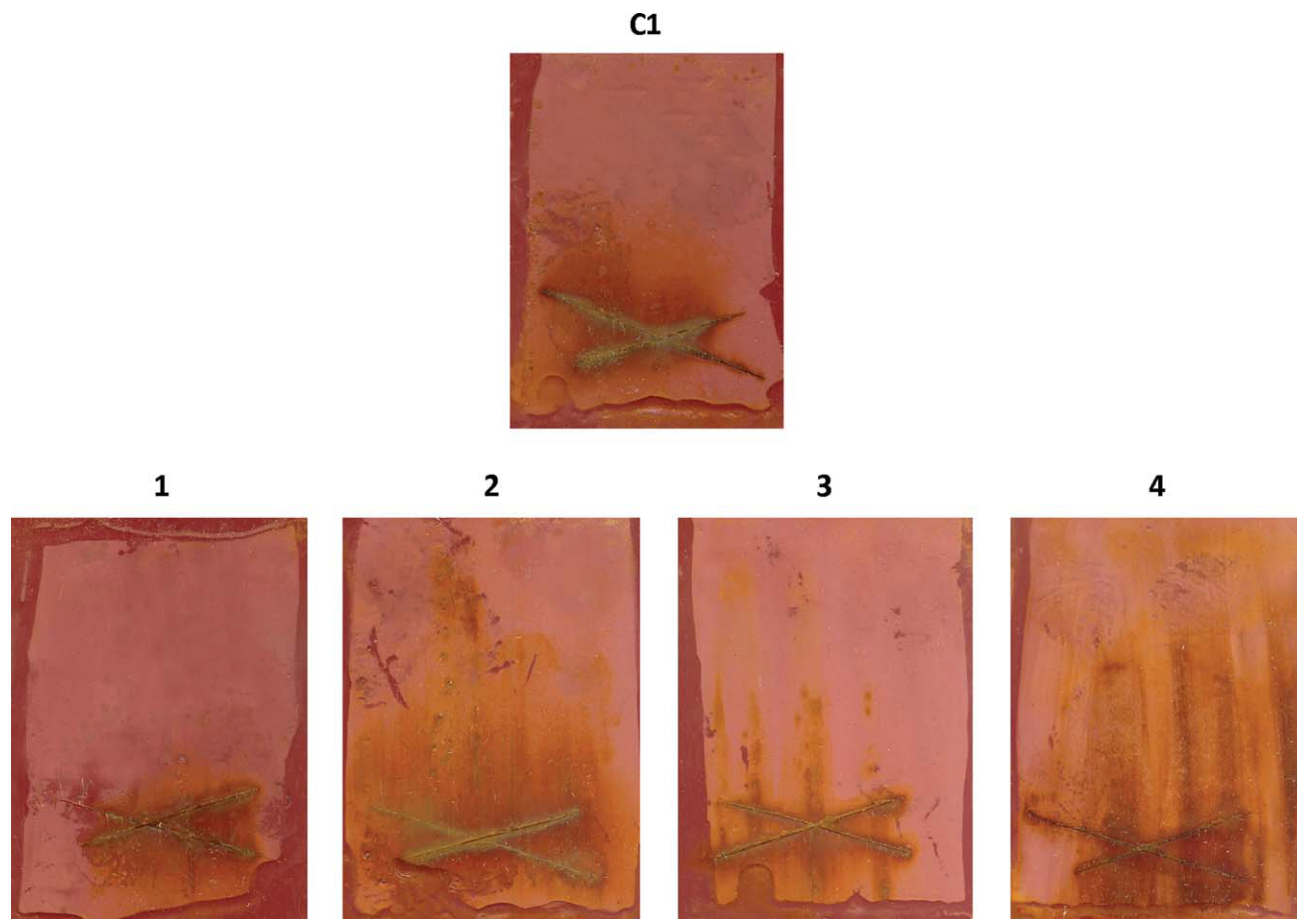
NB = notations; 7S = 0.3% spots rusted; 5G = 3% general rusting; 6S = 0.1% spot rusting; 8G = 0.1% general rusting; 2F = two few; 6F = six few; 8MD = eight medium dense; Gt0 = nothing was chipped off the paint film; 8D = eight dense. Numbers 2, 4, 6, and 8 in blistering are related to the blister volume, with 2 being the biggest and 8 being the smallest.

this group still had better results compared to group I; this indicated that at this P/B ratio, the paint formulation showed a higher performance than the previous ones (Fig. 7).

- For the third group, with a P/B ratio of 3, the control and paint film containing 10% BHETA showed the best results among the paint films of the group, with no rust under film and, therefore, exhibited high corrosion protection, but as the BHETA content increased, less protection was detected, and data were recorded that were similar to those of the group I paint formulations (Fig. 8).

Therefore, as exemplified in Table VII, we concluded that

- The best group among the three formulations was group II, with a P/B ratio of 2.233, which showed the least rust under the film and lower blistering and was characterized by acceptable corrosion-protection efficiency.
- The best paint films of the three groups, exhibiting optimal corrosion-protection behavior, were paint films containing 10% BHETA and showed comparable results to that of the high-built control.



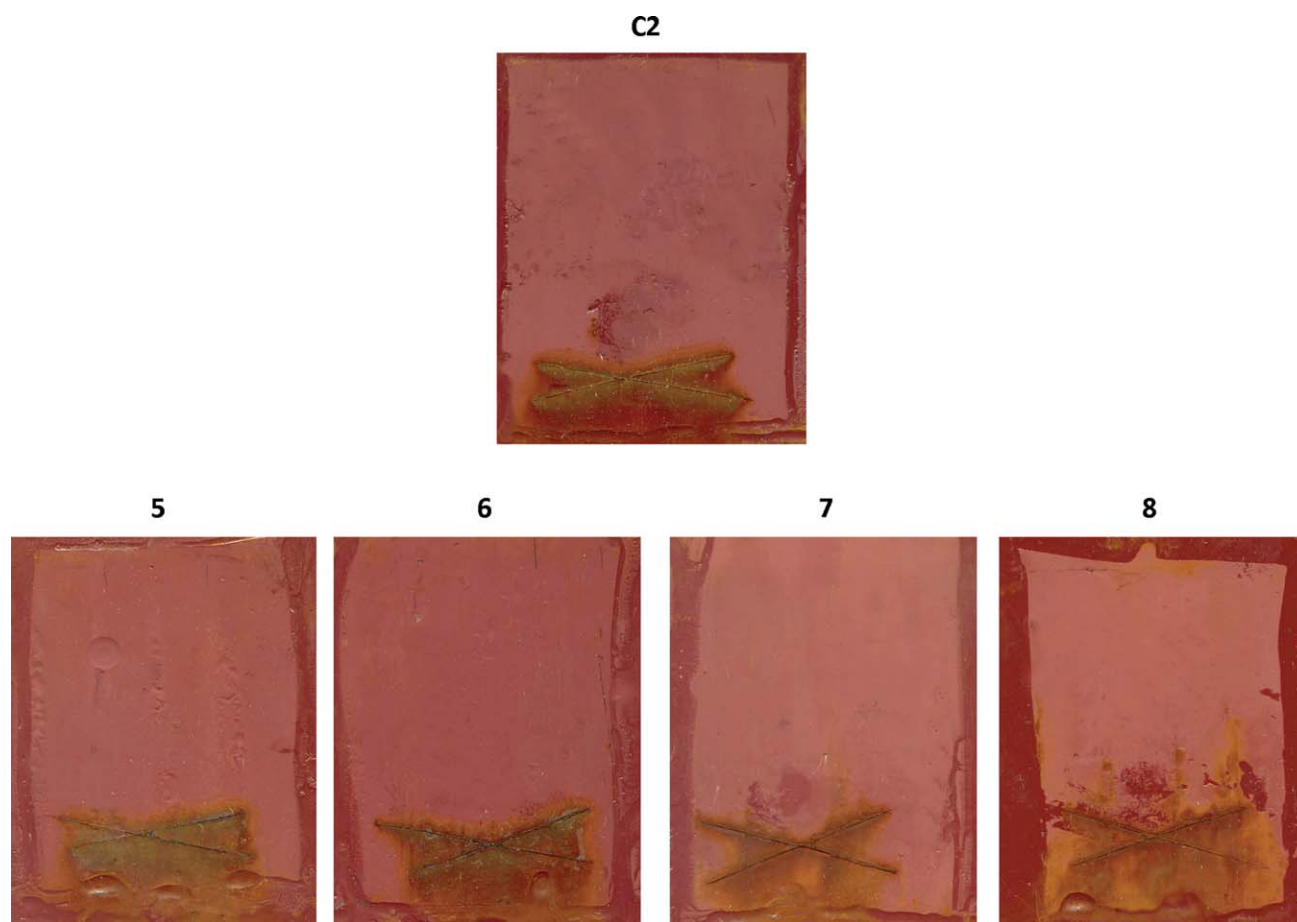
**Figure 6** Paint films of group I after immersion for 28 days in 3.5% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

- As the percentage of BHETA increased, less protection behavior was detected, and for paint films containing 30 and 40% BHETA, the results were almost the same; this indicated that an increase in the BHETA content could have led to undetectable effects on the paint film properties.

#### Proposed mechanism for BHETA's role in protecting steel:<sup>18–25</sup>

- Most well-known corrosion-inhibiting compounds that contain nitrogen and/or oxygen are adsorbed on the metal surface in the corrosion media. The adsorption of these compounds proceeds through the nitrogen, triple-conjugated double bonds or an aromatic ring in their molecular structure.
- BHETA contains in its empirical formula nitrogen, both in its secondary amide and also in its aromatic ring (Scheme 1). Hence, the role of BHETA can be summarized on the basis of this fact as follows:

1. The secondary amide adsorbed as a layer all over the metal surface rather than at specific cathodic or anodic sites.
2. The adsorption of BHETA on the metal surface could take place on the basis of donor–acceptor interactions between the lone unshared pair of electrons of secondary amide nitrogen and the vacant *d* orbitals of the metal surface atoms. Thus, the adsorption of inhibitor on the metal surface could occur by the displacement of water from the carbon steel surface and could offer the unsaturated electron of nitrogen-forming chemisorption bonds. Moreover, the remaining part of the molecules, including the aromatic ring, may have oriented themselves away from the metal surface toward the paint bulk, forming an additional protective layer, which seemed to be hydrophobic in nature, and in this way, water and aggressive gases could have been excluded from the carbon steel surface.
3. The optimal value of BHETA in anticorrosive paint formulations can be better explained by the permission of complete chelation to the



**Figure 7** Paint films of group II after immersion for 28 days in 3.5% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

metal surface. It has been reported that a small thickness in the protection layer smoothly and uniformly covering the metal surface is more efficient in inhibiting corrosion.

4. The excess BHETA in the paint formulation may have competed with itself for the active sites on the metal surface, and consequently, a random distribution in the bulk of the protective film could have taken place. These unarranged polar molecules may have acted to attract more water from the surroundings through the hydrophilic  $-\text{NH}-$  group, which counteracted the role of the protecting film, especially in the case of long-range exposure to corrosive media. This finding could explain the lower values of inhibitor efficiency in the case of increasing BHETA content in the tested paint formulations. However, the addition of organic BHETA into the paint formulation hardly affected the physical and mechanical properties of the films.
5. SEM micrographs showed that the BHETA crystals possessed platelet shapes (Fig. 9).

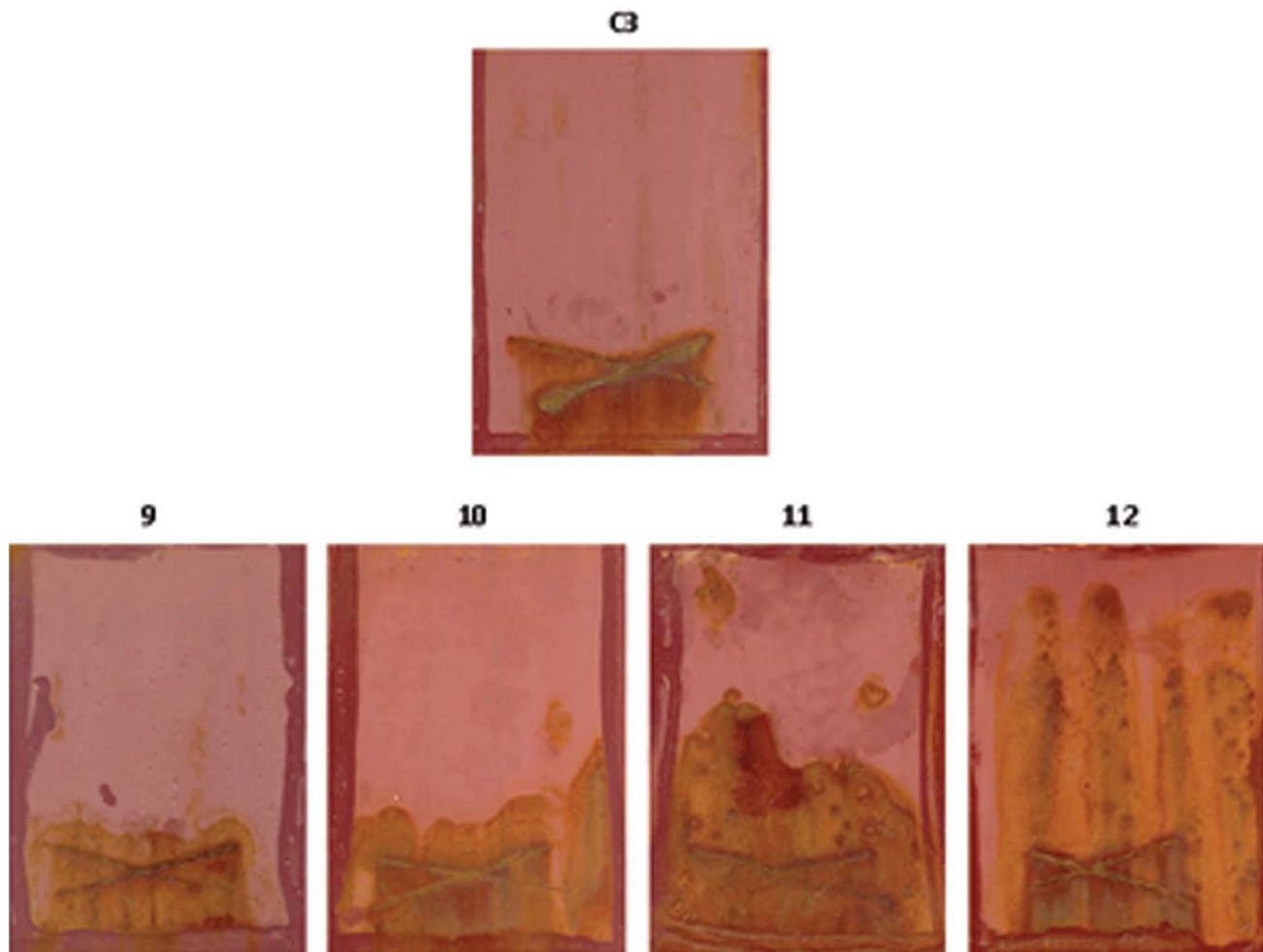
These plates provided a reinforcing effect and reduced the water and gas permeability and, thus, imparted good anticorrosive properties and a special appearance to the paint film when they were used in the paint formulations.<sup>26</sup>

6. The presence of BHETA in the films improved their adhesion and provided various levels of moisture-ingress protection.<sup>27</sup>
7. BHETA possesses high hardness and stiffness, good resistance to weathering, creep strength, and high dimensional stability. This may be the reason for the high adherence of the paint film to the steel substrate, which helped to improve the performance of the paint films.<sup>28</sup>

## CONCLUSIONS

The reported study shed light on

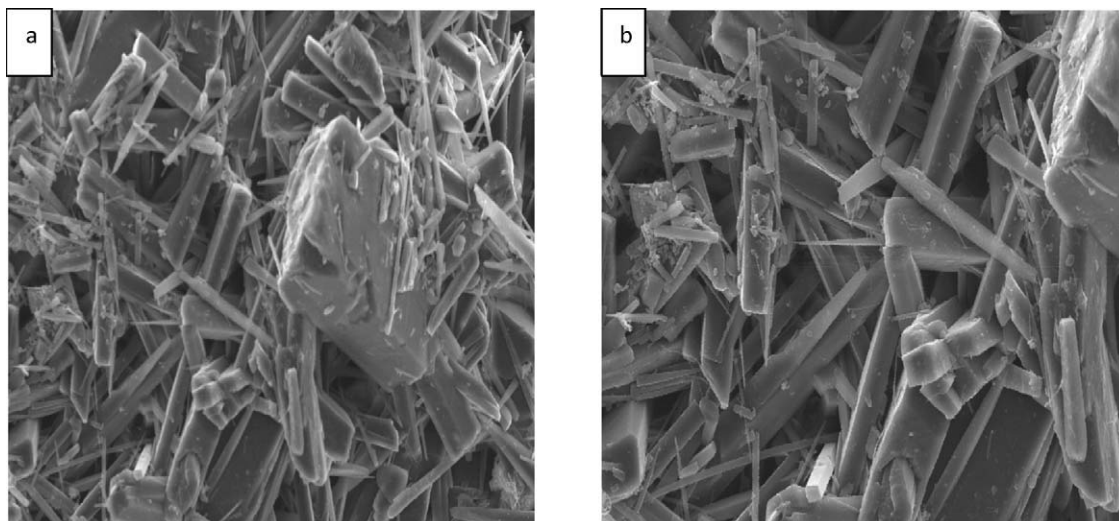
- The recycling of one of the most nonbiodegradable, most problematic plastics, hugely accumulated PET wastes, with simple,



**Figure 8** Paint films of group III after immersion for 28 days in 3.5% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

available chemicals as catalysts and on the basis of sunlight as a renewable source of energy. The white precipitate end product

(BHETA) was obtained at a yield of about 100% from the aminolyzed PET postconsumer bottle wastes.



**Figure 9** SEM micrographs of BHETA at magnifications of 15 and  $25 \times 10^2$ .

- The originality of this part in the study, derived from the use of waste material, that is, PET wastes, to obtain a product that could work efficiently in protecting steel structures.
- The study of the role of recycled white precipitate in anticorrosive paint formulations for the protection of steel structures. This article highlights a novel application for recycled PET postconsumer bottles in addition to those that can be compared to commonly used pigments.
- Green procedures for the aminolysis of PET polymer wastes, which should upload our limited conventional energy resources for other more vital applications, in addition to protecting the biosphere throughout the application of the clean, unconventional renewable energy source for degradation processes. In addition, in this article, we put forward the basis for one of the most promising solutions for controlling the diverse effects of PET waste on the environment due to their accumulation in huge amounts and/or the use of conventional energy resources for their treatment with other methods.
- Concomitant saving that could be generated in anticorrosive paint formulations by a lowering of the weight percentages of the used pigments and compensation of their presence by the addition of these waste degradation products.

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