Indian Journal of Chemical Technology
Vol. 25, November 2018, pp. 539-545

Synthesis of a novel polyetheramide-polyaniline composite anticorrosive coating from PET waste and jatropha oil

Pradnya C Rane, Aarti P More & Shashank T Mhaske*
Department of Polymer and Surface Engineering, Institute Of Chemical Technology, Mumbai, Maharashtra, India
E-mail: st.mhaske@ictmumbai.edu.in

Received 21 April 2016; accepted 5 October 2018

Polyethylene Terephthalate (PET) has been depolymerized by aminolysistechnique using ethanolamine to bis(2-hydroxyethyl) terephthalamide (BHETA). BHETA is a diol along with additional amide linkage as a structural part. It is used as hydroxyl precursor for the synthesis of polyetheramide resin. The conventional polyetheramide resin has been prepared by jatropha oil fatty acid amide and resorcinol. The modification is done in conventional resin with addition of BHETA by replacing fatty amide of oil on 50:50 molar basis. The synthesized resin was characterized by FTIR, ^{1}HNMR and hydroxyl value. The synthesized resins are cured with Melamine Formaldehyde (MF) resin as a hardener and coating is prepared. The coating is evaluated for chemical, mechanical and anticorrosive properties. The anticorrosive performance of BHETA based polyetheramide is further improved by addition of polyaniline at various concentrations in coating system. 3wt% addition of polyaniline in BHETA based polyetheramide resin was shows best anticorrosive properties among all studied formulations.

Keywords: Aminolysis, PET waste, Polyaniline, Polyetheramide, Recycling,

The polymers have not only introduced but also capture the large market area in every industry. The widespread uses also accounts for huge waste of the same. Hence, the recycling of polymer is one of the most attractive zones of research since past few years. It is not only supporting to reduce the environmental threat of accumulation of polymers in nature but also helps to boost up to reduce the use of petroleum resources[1]. The real challenge is to find out the economically viable and sustainable route of recycling which is suitable for the industries as well as easy to peak up for the society. The value addition from the recycling could become the crown for the recycling process[2].

In various polymers which are attractive as well as suitable candidate for the recycling process, one of the important polymers is polyethylene terephthalate (PET). PET is been one of the candidate of recycling since its volume in waste is large which is due its large consumption[3]. PET has occupied the market of water bottles, soft drink bottles which generally used on use and throw basis. Other application area of PET is synthetic fiber and packaging etc. The large consumption and non-biodegradable nature are two key reasons to stand PET as important candidate for recycling[4].

In chemical recycling of PET, the chemistry of ester bond play key role. The ester bond has a reactivity with the various reagents hence different recycling agents were chosen. Each recycling agent opens the door for new product from same PET waste. Few of such recycling route has reach to the industrial scale[5].

There are five major routes for chemical recycling of PET i.e. methanolysis, glycolysis, hydrolysis, aminolysis and ammonolysis. Glycolysis is well explored among all and it reaches to the industrial scale in certain extent[6,7].

Aminolysis of PET is under study from recent few years, and various amines that have explored for depolymerization such as methylamine,and butylamine. Ethylamine, ethanolamine, diethanolamine and triethylenetetramine etc[7-9]. Aminolytic depolymerization of PET with ethanolamine results into bis(2-hydroxyethyl) terephthalamide (BHETA). This depolymerization reaction was studied by varying the catalyst such as glacial acetic acid, sodium acetate and potassium sulphate or by varying the reaction conditions such as sunlight or processing the reaction at reflux temperature[8,10]. Since BHETA has active functional groups it is attractive candidate from synthesis point of view. BHETA can be used as a precursor for synthesis of polyesteramide resin,[7] polyurethane resin, unsaturated polyester resin, adhesive, thermal stabilizer for PVC, hardener for the epoxy resin, non-ionic polymeric surfactant etc[11,12].

On the other side, the scarcity of petroleum resources, there increasing prices and the penetration of eco-friendly approach in coating industry results into resin synthesis from renewable resources for coating application. The alternative resources which will give comparable properties is must for upcoming years. Seed oil is most commonly used feedstock for resin synthesis and polyesteramide, alkyd, polyurethane, epoxies were prepared using such renewable resources[7].

Conductive polymers are studied for the anticorrosive application in coating for last few years. Few of the examples of such conductive polymers is polyaniline, polythiophene, polypyrrole etc. Among these polyaniline is most widely studied conductive polymer and its anticorrosive mechanism is explained as when polyaniline based coating is applied on the on ferrous surface, emeraldine salt form of polyaniline gets reduced with iron when contact with water takes place and simultaneously oxidation of metal takes place hence double layers of oxides are formed. In atmospheric conditions, oxygen helps for oxidation of PANI, hence oxide layer can be reconstructed in case of damage of the coating. Apart from this PANI can give the barrier effect increasing the diffusion path for corrosive species hence the anticorrosive properties were enhanced[13,14].

Here in this study, Polyetheramide resin is synthesized and used for coating application which has a presence of ether and amide linkage in alternative manner. BHETA is used as a building block for the synthesis of polyetheramide resin. The evaluation of presence of BHETA on the performance properties of polyetheramide was done by synthesizing firstly the polyetheramide from jatropha oil and resorcinol. In the next part, fatty amide was replaced by BHETA on 50:50 molar basis. Both the resins are cured with MF hardener and their performance properties were compared. Polyaniline was dispersed at 1wt%, 2wt% and 3% wt% in BHETA based polyetheramide coating and its anticorrosive properties are evaluated at various concentration of PANI.

Experimental Section

Materials

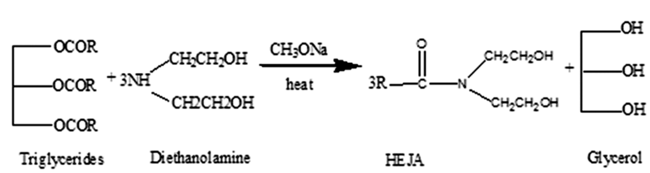
Waste PET bottles obtained from local markets and cut into small flakes. The cleaning of the flakes was carried out by washing first with detergent followed by hot water. Then flakes were dried in oven at 60°C. Ethanolamine, Zinc acetate,sodium acetate, phenol, 1,1,2,2-tetrachloroethane, diethanolamine, sodium methoxide and sodium chloride, anniline, Ammonium persulphate, Methanol, hydrochloric acid (all of analytical grade) were obtained from S. D. Fine Chemical Pvt. Ltd. Mumbai, India. Jatropha oil was obtained from Dahod Mill, India. The fatty acid composition of the oil was oleic acid 40 per cent, linoleic acid 37.3 per cent, palmitic acid 14 per cent, stearic acid 7 per cent and palmitoleic acid 1.3 per cent.Butylated Melamine formaldehyde resin is used for curing purpose.

Synthesis of BHETA

PET was depolymerized using ethanolamine where PET: ethanolamine ratio was taken as 1: 4 (w/w). The catalyst used is zinc acetate and its concentration is taken in reaction mixture as 1.5 wt% of PET. The reaction was carried out in four necked flask with overhead stirrer, condenser, thermocouple and in inert atmosphere. The temperature of the reaction was maintained at 160°C throughout the reaction and duration of the reaction was 3 h. After completion of reaction, the reaction mixture was cooled and filtered. The residue obtained in this case was purified further by recrystallization in hot water. Hence shiny crystals of BHETA are obtained after recrystallization[8].

Synthesis of HEJA

Fatty amide of jathropha oil was prepared by taking oil :diethanolamine in 0.3 : 0.1 (molar basis). Sodium methoxide was used as a catalyst. It's concentration is 0.009 moles in the reaction mixture. The reaction is carried out in same assembly as that for depolymerization of PET. The reaction was carried at 110°C for one and half hour. After completion of the reaction the reaction mixture was cooled. Diethyl ether was added into reaction mixture to dissolve the product. The dissolved product was washed with 15% aqeous NaCl using separating funnel. The obtained product was dried by passing through anhydrous sodium sulphate. The dried solution was collected and rotary evaporator is used to remove the excess solvent. The fatty amide of jathropha oil is obtained as viscous yellow product after rotary evaporator. The reaction scheme for the same was represented in Scheme 1.



Scheme 1 — Synthesis of fatty amide of jatropha oil

Synthesis of Polyetheramide

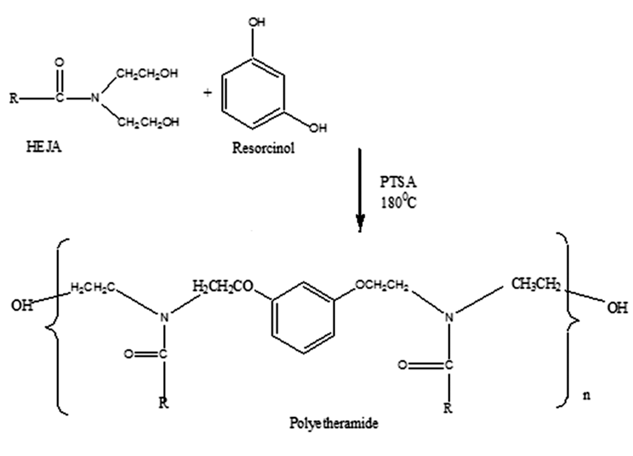
Polyetheramide resin was prepared using jatropha oil amide and resorcinol in mole ratio 0.7:1. BHETA based polyethamide was prepared by replacing fatty amide of jatropha oil with BHETA on 50 : 50 molar basis. The reaction assembly is same as that of depolymerization. Temperature is maintained at 180-190ºC. Extent of reaction monitored by water collected. The reaction scheme for the synthesis of polyetheramide was represented in Scheme 2 and BHETA and synthesized resin was chemically characterized (Table 1).

Synthesis of Polyanniline (PANI)

PANI is prepared using aniline as a monomer, potassium dichromate as an oxidiser and Hydrochloric acid as a dopant. The polymerization is done by chemical oxidation method. The aniline: potassium dichromate ratio was kept as 1:1. Aniline and HCl solution is added to three neck reactor and potassium dichromate is added dropwise at 0-5ºC. Dropwise addition is to be done in 1 h. Then stirring is continued for next 24 h. After completion of the reaction, the reaction mixture was filtered to separate solid PANI particles from rest of the mixture. The water washing is given to the residue followed by ethanol washing to remove unreacted aniline, potassium dichromate etc. The obtained powder was dried at 60°C in vaccum drier.

Application in coating film

The coating was applied to the metal panels i.e. mild steel (MS) having dimension 3 × 5 Inch. The panels were first cleaned to remove any oil, dirt and dust. Panels were first cleaned with detergent followed by water washing and drying. To improve the adhesion of the coating to the metal surface, sanding of the metal surface was done with emery paper no. 800. Then solvent is used to clean the panels and acetone can be used for this purpose. Based on hydroxyl value of polyetheramide resin, ratio of resin to hardener is decided. Solvent used for coating is dimethylformamide. Composite coatings are made with 1wt%, 2wt% and 3wt% PANI in polyetheramide coatings. The flash off time of 30 min was given and then cured at 120°C for 1 h.



Scheme 2 — Synthesis of polyetheramide resin from BHETA, HEJA and resorcinol

Table 1 — Hydroxyl value analysis

Parameter	Value
Hydroxyl value of BHETA	444 mg of KOH/g of sample
Hydroxyl value of polyetheramide resin	110 mg of KOH/g of sample

Characterisation

The functional group in the synthesized resin and polyaniline was characterized by ATR-FTIR. The ^{1}HNMR is done to determine the structure of the synthesized resin and to compare the structure of both the resin to confirm the incorporation of BHETA in the polyetheramide structure. X-ray diffraction analysis (XRD) analysis is donewith the help of RigakuMiniflexwith the scanning speed of 2º/min to determine the characteristic peak and crystallinity of PANI, which supports for the confirmation of POA synthesis. Mechanical properties of the coating was determined by measuring its cross hatch adhesion test (ASTM D-3359), Impact resistance (ASTM D-2794), Pencil hardness (ASTM D-3363), flexibility (ASTM D-522) and scratch resistance (ISO-104) of the coating. The impact resistance which is determined by falling dart impact test and flexibility determined by conical mandrel gives the idea about load distribution capacity and flexible nature of the coating respectively. The pencil hardness and scratch hardness was done to get the idea about the hardness nature of the coating. The chemical resistance of the coating was determine by measuring its resistance against solvent (ASTM D-4752) and acid and alkali (ASTM D-1308). The solvent rub method is used to determine the solvent resistance, and solvent used for the study is xylene and Methyl ethyl ketone (MEK). The to and fro 500 cycles of solvents are done and evaluated for the results. The acid resistance is done with 5% HCl solution and alkali resistance is done with 5% NaOH solution and spot test is carried out for 24. The salt spray method is used to evaluate the corrosion resistance of the coating (ASTM B-117). The salt solution used for the testing is 5% NaCl solution and test was carried out for 500 h.

Result and Discussion

Here in this study, polyetheramide resin is made and used for coating application. The polyetheramide resin is upcoming technology in coating industry from last few days and has structural benefit of ether and amide linkage. The C-O-C ether linkage is aliphatic and proving flexibility on the other hand –CONH linkage of amide will provide the stiffness to the resin hence the coating system has proper balance of flexibility and stiffness. These both ether and amide linkage will helps to improve the adhesion of the coating to the metal surface. The polyetheramide resin was synthesized firstly from resorcinol and fatty amide of jatropha oil. In the next part, BHETA was used as replacement for the fatty amide of oil on 50 : 50 molar basis. The coating is prepared by curing both synthesized polyetheramide resin with MF hardener and compared for its performance properties. The 50 : 50 molar ratio of BHETA and fatty amide helps to get the structural benefit of both at the same time at equivalent quantity. When the fatty amide of oil helps to incorporate flexibility to the coating due to its aliphatic linkage, BHETA helps for improving hardness hence coating of the same resin rich in both ends i.e. in flexibility as well as in hardness properties. In the final part of the study PANI was added at three different concentrations in the BHETA based polyetheramide coating. It is observed that with addition of PANI anticorrosive properties were significantly improved.Hence the anticorrosive coating system was made in this study which is based on PANI-polyetheramide composite. The polyetheramide synthesized here is eco-friendly in nature since it is synthesized from firstly from fatty amide of oil and resorcinol. As compared to conventional polyetheramide which are bisphenol A based here resorcinol based polyetheramide itself proves its eco-friendly nature since it avoids the presence of carcinogenic bisphenol A. With incorporation of BHETA it further enhances its eco-friendly nature since waste aggregation problem is solved by such incorporation. Presence of PANI helps to enhance the performance further and enhances the anticorrosive properties of the coating. Hence here in this study, anticorrosive coating was synthesized which is eco-friendly in nature.

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 represents the FTIR analysis of synthesized polyetheramide resin. The asymmetrical andsymmetrical stretching of C-O-C which is for aryl alkyl ether is observed at 1284-1177 cm^{-1} and 1055 cm^{-1}. The characteristic peak of fatty amide which corresponds to asymmetrical stretching of aliphatic CH_2 linkage is appeared at 2854 cm^{-1} whereas symmetrical stretching of the same appeared at 2925 cm^{-1}. The –C=O stretching is appeared at 1612 cm^{-1} which corresponds to amide linkage. The –C-N stretching observed at 1464 cm^{-1}. The hydroxyl group is observed at 3308 cm^{-1}. The peak appeared at 3011 cm^{-1} is represents –C-H stretching of unsaturation in polymeric chain. The band appear in the range of 904-743 cm^{-1} corresponds to C-H vibrational frequencies which are from aromatic rings of resorcinol[15].

The FTIR characterization of polyaniline is represented in Fig. 2. The peak occurs at 1590 cm^{-1} corresponds to C=N in the quinoidal units. The in-plane bending vibrations of –C-H bonds was appeared at ~1385, ~1136 and ~614 cm−1. The peaks at 1485 cm^{-1} and 3470 cm^{-1} correspond to stretching of benzenoid and –N-H bonds. The peak of –NH– of polyaniline is appeared at 1447 cm^{-1}.

^{1}H NMR characterization of resin

The ^{1}H-NMR spectra of the synthesized resin was plotted. The peak appeared at δ 6.98-7.2 ppm corresponds to aromatic ring of resorcinol. The peak appeared at δ 4.1-4.2 pm represents the –CH_2 groups attached to -O- aromatic and it represents ether

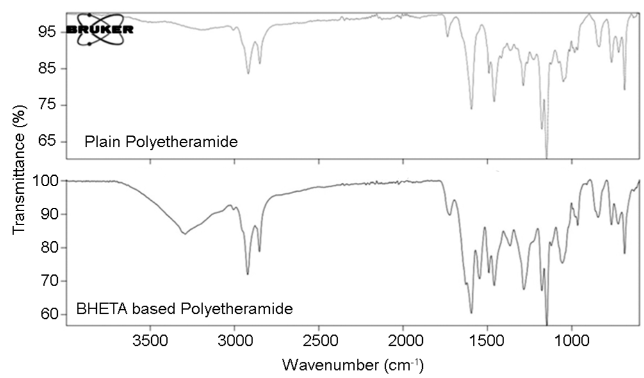


Figure 1 — FTIR analysis of Polyetheramide resins

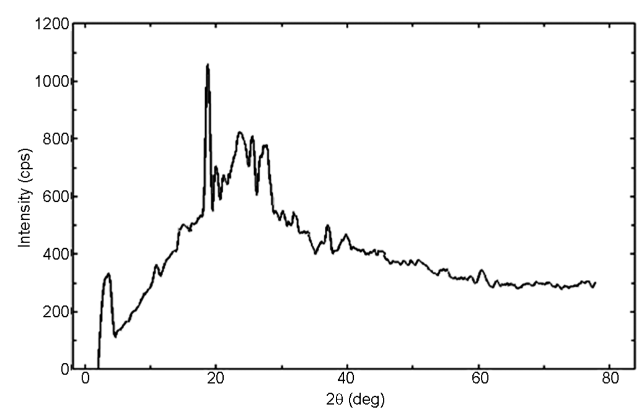


Figure 2 — XRD analysis of Polyaniline

linkage. This peak is appeared in both the resin system hence it confirms the ether linkage is present in both which is formed through the reaction of fatty amide and resorcinol in first case. In BHETA based resin BHETA also reacts with resorcinol to form ether linkage. The olefinic unsaturation appears at δ 5.2-5.4 ppm. The peak appeared at δ 3.5-3.6 ppm corresponds to $–CH_2$ groups linked to the amide nitrogen and peak at δ 3.3-3.5 ppm corresponds to $–CH_2$ groups linked to the hydroxyl group. The $–CH_2$ groups attached to the amide carbonyl were appeared at δ 2.3-2.5ppm. The presence of proton due to olefin unsaturation was observed at δ 5.2-5.3 ppm. The internal $–CH_2$ groups of fatty amide appeared at δ 1.1-1.2 ppm whereas $–CH_3$ of fatty amide chain appeared at δ 0.95-0.98 ppm. The spectrum in the range of δ 3.2-3.5 ppm is broad in the BHETA based polyetheramide resin because $–CH_2$ of BHETA also giving the peak in this area. The characteristic of BHETA based polyetheramide which differentiate it from plain polyetheramide is sharp singlet at δ 7.9 ppm which corresponds to aromatic linkage of BHETA.

X-Ray diffraction Analysis of polyaniline (XRD)

The X-ray diffraction pattern of the synthesised PANI was represented in Fig. 3 and crystallinity of the same was found out as 66% and hence it is proved as PANI is semi-crystalline in nature. The peak at $2\theta \sim 26^{o}$ corresponds to emeraldine salt of PANI. The peaks observed are sharp in nature which proves its semicrystalline behaviour.

Mechanical properties of the coating

The DFT of all coatings was shown 80-90 micron. All the coatings passed cross hatch adhesion test successfully. It is the indication that all coating formulation has good adhesion to the metal surface. In polyetheramide, the BHETA or fatty amide of oil having amide linkage which contains lone pair of electron on nitrogen atom. So when coating was applied on the ferrous metal which contains vacant d orbital, chemisorption takes place. Ether linkage present in the coating also help to improve the adhesion. Hence coating films shows good adhesion to the metal surface. This is proved by even though filler added the coating passes adhesion test successfully. The pencil hardness of the BHETA-polyetheramide was higher than plain polyetheramide resin. The scratch resistance also shows the same trend. Iin plain polyetheramide resin presence of resorcinol and melamine incorporates aromaticity into the resin structure hence toughness of the film increases which is further improved in BHETA based resin. The reason is BHETA again having aromatic structure which helps to improve the hardness properties further. As the PANI is added into coating formulation, hardness properties further improved. PANI is acting as a filler material here and improving

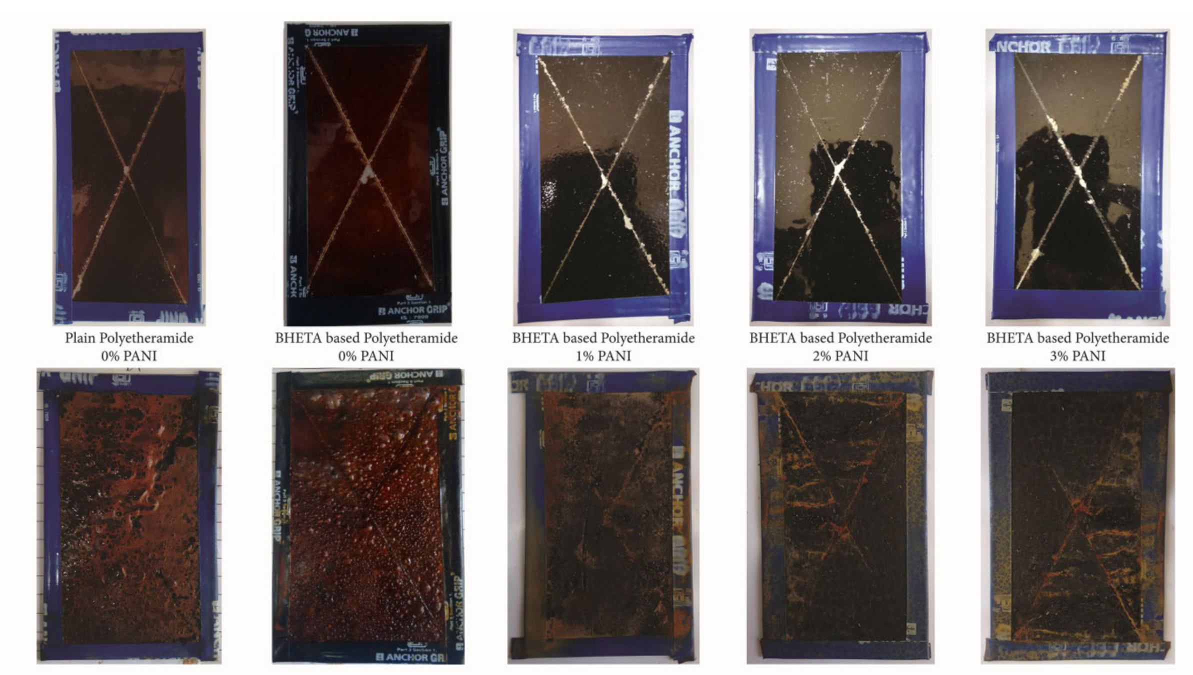


Figure 3 — Salt spray test of Polyetheramide coating

the strength of the film hence hardness and scratch resistance improves. Impact resistance of the coating also improved after addition of PANI as explained earlier strength of the film increases after addition of PANI hence impact resistance improved. All the coating formulations passing flexibility test successfully. Presence of fatty amide of oil having aliphatic linkage which helps to take care of flexibility as well as ether linkage also improves the flexibility of the film hence all the formulations passed conical mandrel test successfully without any crack formation (Table 2).

Chemical properties of the coating

The chemical properties of the coating were evaluated by measuring its resistance against acid, alkali and solvent (Table 3). As shown in table, all the formulations passing acid resistance successfully where film remain unaffected. Alkali resistance was slightly poor where loss of gloss is observed. But for all the formulations adhesion remain unaffected after acid and alkali exposure also. The solvent resistance is also excellent for all the formulations. The probable reason is better adhesion of the coating to metal surface due to above mention mechanism, the excellent curing of all formulations with MF resin

Salt spray results

The coated steel panels were exposed to salt spray and its anticorrosive nature was determined. Figure 4 shows the photographic references of panels before test and after the test. As seen from the figure, comparative results are obtained for plain polyetheramide and BHETA based polyetheramide. BHETA contain aromatic moiety hence shows better water repellence as compared to plain polyetheramide. Both the formulations show better adhesion to the metal surface as explained earlier by chemisorption mechanism. Hence the after salt spray also adhesion of the coating was not affected. But both plain polyetheramide and BHETA based polyetheramide coating formulations shows blistering after salt spray exposure. Hence it is proved that replacement of fatty amide by BHETA was shows comparative results with plain polyetheramide. The anticorrosive performance was enhanced by addition of PANI. PANI acting as filler, increases the diffusion path for corrosive species hence anticorrosive performance enhances. As well as PANI also works by electrochemical interaction as explained earlier to improve the anticorrosive properties. Hence as the concentration of PANI increase hence anticorrosive performance also increases in same trend. So as shown in Figure 3% concentration of PANI shows best anticorrosive performance.

TGA analysis

The TGA analysis was carried out for plain polyetheramide resin, BHETA based polyetheramide and 3wt% of BHETA based polyetheramide. The result for the same was represented in Figure 6. As seen from the figure the onset of degradation for plain

Table 2 — Mechanical properties of polyetheramide coating

Sr. No	Property	Reading									
		Plain Polyetheramide 0% PANI		BHETA based Polyetheramide 0% PANI		BHETA based Polyetheramide 1% PANI		BHETA based Polyetheramide 2% PANI		BHETA based Polyetheramide 3% PANI	
1.	DFT (µm)	80-90		80-90		80-90		80-90		80-90	
2.	Cross hatch Adhesion	5B		5B		5B		5B		5B	
3.	Gloss (60º)	90		91		92		93		85	
4.	Pencil Hardness	H		H		2H		3H		3H	
5.	Scratch Hardness (Kg)	1.0		1.25		1.5		1.7		1.8	
6.	Impact Resistance (Kg-cm)	F.I.	B.I.	F.I.	B.I.	F.I.	B.I.	F.I.	B.I.	F.I.	B.I.
		50	50	50	50	55	55	55	55	60	60
7.	Flexibility (mm)	0		0		0		0		0	

Table 3 — Chemical properties of polyetheramide coating

Sr. No	Property	Reading				
		Plain Polyetheramide 0% PANI	BHETA based Polyetheramide 0% PANI	BHETA based Polyetheramide 1% PANI	BHETA based Polyetheramide 2% PANI	BHETA based Polyetheramide 3% PANI
1.	Acid Resistance	A	A	A	A	A
2.	Alkali Resistance	B	B	B	B	B
3.	Solvent Resistance	A	A	A	A	A

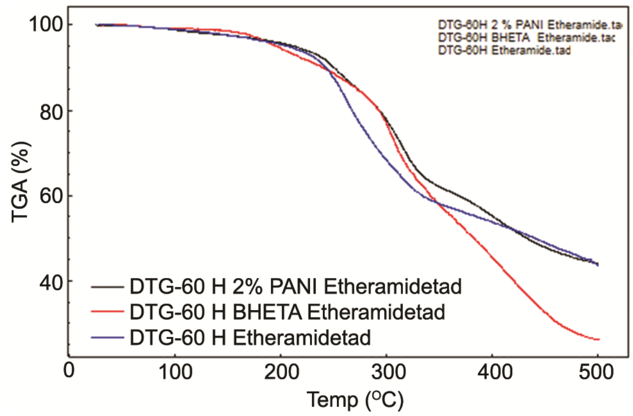


Figure 4 — TGA analysis of the coating

polyetheramide resin, BHETA based polyetheramide was comparable, i.e. at 259ºC and 204ºC respectively. But as the polyaniline was added into the coating, its thermal stability increases and onset has been found out at 290ºC. The probable reason is polyaniline providing strength to the coating, increase its compactness. Hence polyaniline based coating not only give better anticorrosive properties but also shows the best thermal stability hence successfully can be used in area where anticorrosive properties of the coating play major role.

Conclusion

Here in this study, novel polyetheramide resin has been synthesized by combination of renewable resources and waste material. HEJA is obtained from jatropha oil and BHETA is obtained from aminolysis of PET waste, both having hydroxyl functionality as well as amide linkage present in their structure. Due to their hydroxyl functionality, by reacting them with Resorcinol, they converted into polyetheramide. Addition of polyaniline to the coating has increased its corrosion resistance. The aromatic linkage of BHETA Resorcinol, amide linkage of HEJA and BHETA, acid and proper curing of resin with melamine formaldehyde help to improve mechanical and anticorrosion properties of final coating.

Acknowledgement

We would like to thanks TEQIP Grant Fellowship and DST INSPIRE fellowship to provide the support.

References

1 Maeda Y, Mor H, Maeda T, Itoh O, Yamaguch K, Kubota S, Nakayama A, Kawasaki N, Yamamoto N & Aiba S, *J Appl Polym Sci,* 84 (2002) 1838.
2 Farahat M S, Nikles D E, Macromol *Mater Eng,* 287 (2002) 353.
3 Desai S D, Patel J V, Patel M R & Sinha V K, *Indian J Chem Technol,* 12 (2005) 82.
4 Tawfik M E,Ahmed N M & Eskander S B, *J Appl Polym Sci*, 120 (2011) 2842.
5 Colomine G, Robin J & Tersac G, *Polymer,* 46 (2005) 3230.
6 Goje A S & Mishra S, *Macromol Mater Eng,* 288 (2003) 326.
7 More A P, Kute R A & Mhaske S T, *Iran Polym J,* 23 (2014) 59.
8 More A P, Kute R A & Mhaske S T, *Pigm Resin Technol,* 43 (2014) 285.
9 Spychaj T, Fabrycy E, Spychaj S & Kacperski M, *J Mater Cycles Waste Manag*, 3 (2001) 24.
10 Sadeghi G M M, Sayaf M & Shams R, *J Polym Environ,* 19 (2011) 522.
11 Tawfik M E, Ahmed N M & Eskander S B, *J Appl Polym Sci,* 120 (2011) 2842.
12 Achilias D S, Tsintzou G P, Nikolaidis A K, Bikiaris D N & Karayannidis G P, *Polym Int,* 60 (2011) 500.
13 Rajasekharan V, Stalin T, Viswanathan S & Manisankar P, *Int J Electrochem Sci*, 8 (2013) 11327.
14 Talo A, Passiniemi P, Forsén O & Yläsaari S, *Synt Met*, 85 (1997) 1333.
15 Akintayo Cecilia O, Akintayo Emmanuel T & Ziegler T, *Am J Sci Ind Res*, 2 (2011) 78.