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Synthesis of polyesteramide resin from lower purity dimer acid and ethanolamine and its utilization as hardener for epoxy resin

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ABSTRACT

Polyesteramide (PEA) resin was synthesized using lower purity dimer acid (Pripol 1017, composition: 22% trimer acid, 75% dimer acid and 3% linoleic acid) and ethanolamine. Molar ratio of Pripol 1017: ethanolamine was varied as 1:1, 1:1.5 and 1:2. Prepared PEAs were characterized for acid value, amine value, hydroxyl value, Fourier transform infrared spectroscopy, gel permeation chromatography (number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity index (PDI)) and rheological (viscosity vs shear rate) properties. It was determined that amine value and hydroxyl values increased, whereas, acid value, Mn, Mw, PDI and viscosity decreased with increased molar concentration of ethanolamine in the PEA. Prepared PEAs were used as hardener for epoxy resin as a partial replacement for triethylenetetraamine (TETA), to prepare epoxy sheets. PEAs were added as 5% replacement of TETA. Cross-linked epoxy sheets were characterized for mechanical and thermal properties. It was found that tensile strength remained near about constant, Young's modulus and degradation temperature decreased; whereas elongation at break increased with addition of PEA in epoxy as 5% replacement of TETA. Addition of PEA, thus helps in improving the flexibility of epoxy.

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KEYWORDS

Polyesteramide;
Dimer acid;
Ethanolamine;
Gel permeation chromatography;
Epoxy;
TETA.

INTRODUCTION

Polyesteramides (PEA) are polymeric materials synthesized from the reaction of diacid, diamine and diol or diacid and chemical compounds having both amine and alcohol groups present on it. These are copolymers which do not have the regularity of the common polyamides or polyesters^[1]. They have both ester and amide linkages present in their molecular chains. There are many type of PEA described in literature^[2-10]. They

can have varied applications from coating preparation to hot melt adhesive. PEA are also used in applications like hydrogels, scaffolds,

Froehling synthesized hyperbranchedpolyesteramide by reacting cyclic anhydride with diisopropanol amine, yielding a tertiary amide with one COOH and two OH groups^[2]. Ahmad et al. converted oil from *Pongamiaglabra* into *N,N*-bis(2-hydroxyethyl) *P. glabra* fatty amide and further reacted it with phthalic acid to prepare PEA; and prepared anticorrosive coat-

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ing using it^[3]. Castaldo et al. synthesized a range of PEAs using adipoyl dichloride, 1,10-decandiol, and 1,6-diaminohexane; and characterized it for thermal and viscoelastic properties^[4]. Mukherjee et al. prepared jute fibre composite using PEA polyol. PEA polyol was synthesized from the reaction of mixture of alkanolamines, polyethylene glycols, and dicarboxylic acids/anhydrides. Prepared PEA was used as interfacial agent in jute fibre/epoxy composite^[5]. Mohanty et al. prepared jute fibre/biodegradable polyesteramide composite. PEA used was commercially available material named BAK 1095. They investigated the effect of various surface treatments of jute fibre involving bleaching, dewaxing, alkali treatment, cyanoethylation and vinyl grafting on the properties of the prepared composite^[6]. Tuominen and Seppala investigated the effect of temperature and chain extender concentration (2,2'-bis(2-oxazoline)) on the properties of PEA synthesized using lactic acid. The highest molecular weights were achieved with the molar ratio of oxazoline/carboxyl end groups being 1.2/1.0 at 200 °C^[7]. Katsarava et al. synthesized a range of PEAs using nontoxic building blocks like hydrophobic α -amino acids, α,ω -diols, and aliphatic dicarboxylic acids; and examined the effect of molecular structure on the physic-chemical and biochemical properties^[10].

This work is an attempt to understand the effect of molar ratio of ethanolamine and lower purity dimer acid on the properties of PEA. Molar ratio of lower purity dimer acid to ethanolamine was varied from 1:1 (acid to ethanolamine) to 1:1.5 and 1:2. Prepared PEAs were analyzed for acid value, amine value, hydroxyl value, fourier transform infrared spectroscopy, gel permeation chromatography (to get number average molecular weight, weight average molecular weight and polydispersity index) and rheological properties. Then, they were used as 5% replacement of triethylenetetramine (TETA) as a cross-linking material for epoxy.

MATERIALS AND METHODS

Materials

Ethanolamine and p-toluene sulphonic acid was procured from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. Lower purity dimer acid (Pripol 1017; composi-

tion: 22% trimer acid, 75% dimer acid and 3% linoleic acid) was procured from Soofi Traders Pvt. Ltd., Mumbai, India. Epoxy resin (PER 257 grade, epoxy equivalent weight = 160) and Triethylenetetramine (TETA, PH-111, amine equivalent weight = 24) hardener were obtained from Pliogrip Resins and Chemical Pvt. Ltd., Mumbai, India. All chemicals were used as obtained, without and modification or purification.

Preparation of polyesteramides

Figure 1 shows the molecular structure of the acids present in the lower purity dimer acid (Pripol1017) and ethanolamine; whereas, TABLE 1 lists the molecular weight of the acids and ethanolamine. In the study the molar ratio of lower purity dimer acid to ethanolamine was varied as 1:1, 1:1.5 and 1:2. PEA was prepared by polycondensation technique using p-toluene sulphonic as the catalyst. Prepared formulations and their nomenclature are noted in TABLE 2.

Mentioned method describes the synthesis PEA from lower purity dimer acid and ethanolamine reacted in 1:1 molar ratio i.e. PEA1. Pripol 1017 has acid composition as: 22% trimer acid, 75% dimer acid and 3% linoleic acid. Basis of the reaction was 200 g Pripol

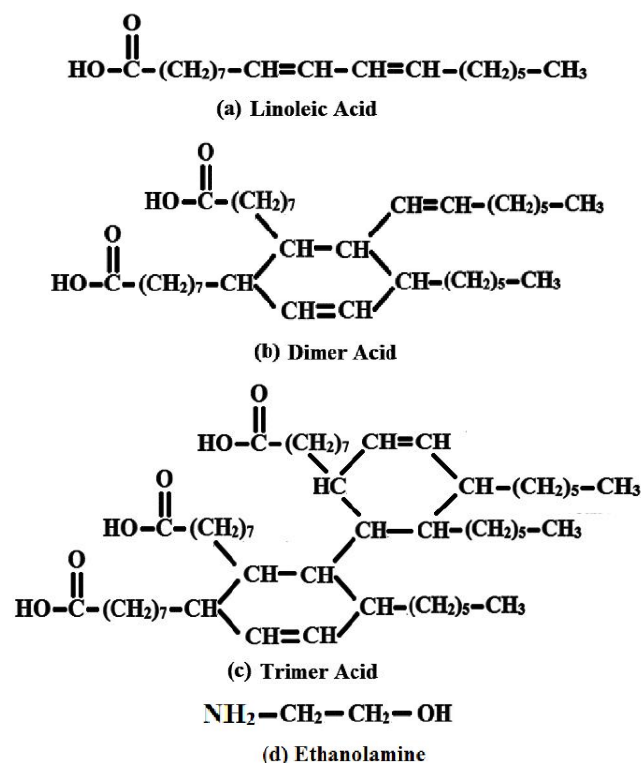


Figure 1 : Molecular structure of the acid present in Pripol 1017 and ethanolamine

1017, which according to the composition will have 44 g trimer acid, 150 g dimer acid and 6 g linoleic acid. Thus, it had 0.05 moles trimer acid, 0.27 moles dimer acid and 0.02 moles linoleic acid. The functionality of trimer acid is 3 while that of ethanolamine is 2, so the number of moles of ethanolamine required as equivalent to trimer acid is higher; and it would be required in

TABLE 1 : Molecular weight of the acids and ethanolamine used in the preparation of PEAs

Sr. No.	Chemical Name	Molecular Weight (g/mol)
1.	Linoleic acid	280
2.	Dimer acid	560
3.	Trimer acid	840
4.	Ethanolamine	61

TABLE 2 : Prepared PEAs with nomenclature

Sr. No.	Nomenclature	Acid: Ethanolamine Ratio	Pripol 1017 g(moles)	Ethanolamine g(moles)	PTSA g(0.05%)
1.	PEA1	1:1	200.00 (0.37)	22.60 (0.37)	0.11
2.	PEA2	1:1.5	200.00 (0.37)	34.16 (0.56)	0.12
3.	PEA3	1:2	200.00 (0.37)	45.14 (0.74)	0.13

the ratio 1:1.5 (trimeracid : amine), so as to equalize the functionality of the two compounds (trimer acid and amines), making all the functional groups undergo reaction. Indirectly, number of moles of trimer acid can be considered 1.5 times its original quantity present, so that calculation becomes easy. Thus instead of 0.05 moles of the trimer acid in the above formulation, it will be considered 0.08 moles of trimer acid. Finally, the molar composition of Pripol 1017 is 0.08 moles trimer acid, 0.27 moles dimer acid and 0.02 moles linoleic acid, making the total moles of acid being 0.37. In this particular PEA composition lower purity dimer acid (Pripol 1017) and ethanolamine were reacted in 1:1 molar ratio. Thus, the moles of ethanolamine required are 0.37, which comes to 22.6 g. Acid value was continuously monitored throughout the reaction process in order to understand the progress of the reaction. Reaction was continued till the acid value felt below 15 mg KOH/g sample. Reactant system was added with 0.05% p-toluene sulphonic acid (catalyst).

The four necked 500 ml reactor was equipped with stirring system (moon shaped teñon blade stirrer attached to the stirring motor), condenser (double walled with water as coolant. Water ðow rate was maintained at 1 l/min), nitrogen gas ðow rate was maintained at 500ml/min) and temperature controller. To the ðask was added 200 g Pripol 1017, 22.6 g ethanolamine and 0.11 g p-toluene sulphonic acid (PTSA). The reactants were heated gradually from 220 to 240 °C; while stirring speed was maintained constant at 1000 rpm. Acid value was continuously noted at an interval of half hour to know the progress of reaction. Time required to reach

the desired acid value was about 4–5 h. Synthesized PEA, in the molten condition, was poured in ateñon mold (having dimension: 15x15x3cm³) and allowed to cool at room temperature. None of the reactants were expected to remain unreacted in the mixture. So, no purification step was thought to be necessary for the final products.

All PEAs were prepared by the same methodology expect the molar ratio between lower purity dimer acid (Pripol 1017) and ethanolamine changed.

Preparation of epoxy sheet using the prepared polyesteramide and TETA

Hardener quantity calculation

Quantity of epoxy was maintained constant at 300g.
Amine required for curing epoxy = $\frac{\text{weight of epoxy resin} * \text{amine equivalent weight of TETA}}{\text{epoxy equivalent weight}}$
 = $\frac{(300*24)}{(160)}$
 = 45 g

This is the theoretical quantity of amine (TETA) required to cross-link Epoxy, reacting them in 1:1 ratio (considering their functionality). But in practice due to thermodynamic and kinetic issues, generally higher quantity of amine is taken. Thus, Epoxy: TETA concentration was maintained at 1:1.5 (considering their functionality). Thus for 300 g of Epoxy, 56.25 g of amine (TETA) was taken for cross-linking. Prepared PEA were added as 5% replacement of the TETA, with the hope to induce flexibility into epoxy. Thus TETA required is 53.43g, while PEA required is 2.81 g Prepared formulations are shown in TABLE 3.

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TABLE 3 : Prepared epoxy compositions

Sr. No.	Nomenclature	Epoxy (g)	TETA (g)	PEA Name	PEA (g)
1.	EP0	300.00	56.25	-	-
2.	EP1	300.00	53.43	PEA1	2.81
3.	EP2	300.00	53.43	PEA2	2.81
4.	EP3	300.00	53.43	PEA3	2.81

Casting

Casting method was used to prepare epoxy sheets. In order to have uniformity and comparability, thickness of the sheet to be casted was maintained constant at 2 mm. 300 g Epoxy was added with required quantity of TETA (53.43 g) and was stirred vigorously with high speed stirrer (1500 rpm) so as to obtain a uniform mix. Stirring was continued for 5 min. Calculated amount of PEA was then added to the mix and the mix was again stirred vigorously for 5 min. Concentration of PEA was maintained constant as 5% replacement of TETA in the epoxy matrix. The mix was then immediately poured into a 20 cm x 20 cm polyethylene terephthalate (PET) mold (See Figure 2). Height of the mold was maintained at 1 cm, in such a way that the mixture attains the height of 2 mm. Casting was then allowed to cross-link at room temperature for 24 hrs. Cross-linked sheet was then post-cured at 80°C for another 4-6 hrs so as to get best possible cross-linked epoxy.

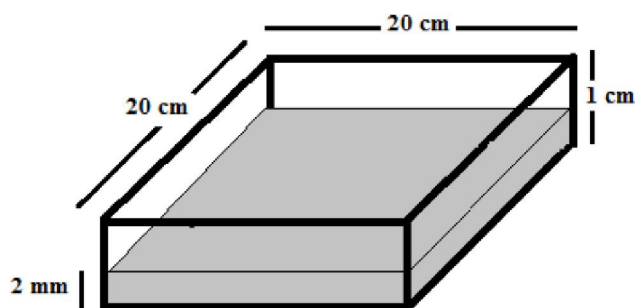


Figure 2 : Diagrammatic representation of PET mold used for preparing the cast

Characterization and testing

Acid value determination

50 ml neutralized benzene-alcohol mixture was added to dissolve 2 g sample in 125 ml Erlenmeyer flask, warming in water bath if necessary. Solution was cooled (if necessary) and added a few drops of phenolphthalein indicator. The solution was titrated against 0.5 N alcoholic potassium hydroxide solution, to a faint

pink color which remains for 30 seconds or more. The calculation of acid value is shown below:

$$\text{Acid Value} = \frac{(56.1 \times \text{Volume of alc. KOH} \times \text{Normality of alc. KOH})}{(\text{Weight of sample})}$$

Amine value determination

50 ml neutralized iso-propyl alcohol was added to dissolve 2 g sample in 125 ml Erlenmeyer flask, warming on a heat source if necessary. Solution was cooled (if necessary) and added a few drops of bromocresol green indicator. The solution was titrated against, 0.5 N standardized hydrochloric acid (HCl), to a yellowish green color which remains for 30 seconds or more. The calculation of amine value is shown in below:

$$\text{Amine Value} = \frac{(56.1 \times \text{Volume of HCl} \times \text{Normality of HCl})}{(\text{Weight of sample})}$$

Hydroxyl value determination

5 g sample was accurately weighed in a 250 ml Erlenmeyer flask; whereas other Erlenmeyer flask was not added with sample to obtain blank reading. Both the flasks were then added 20 ml of acetic anhydride – pyridine reagent (1:4 volume ratio) and attached with air condenser. Flasks were then immersed up to the liquid level in an oil bath maintained at 95 – 100 °C. Flasks were swirled vigorously to bring about complete dissolution of the sample in the reagent. Flasks were heated continuously for 1 hour to insure uniform reaction. Flasks were cooled to room temperature. Then, 10 ml water was added to the flasks through the air condenser. Flasks were again heated on oil bath for 15 min to hydrolyze the excess acetic anhydride reagent. Flasks were then cooled to room temperature and added with 25 ml neutralized alcohol (half through the condenser, which was removed afterwards). Prepared mixture was stirred rigorously. Mixture was made ready for titration on addition of 1 ml phenolphthalein indicator and was titrated against 0.5 N alcoholic potassium hydroxide to a faint pink color, which remains for 30 seconds or more. The calculation of acid value is shown below:

$$\text{Hydroxyl Value} = \frac{[56.1 \times \text{Normality of alc. KOH} \times (\text{ml KOH blank} - \text{ml KOH sample})]}{[\text{Weight of Sample}] - \text{Acid Value}}$$

The FTIR spectra were recorded with a PerkinElmer, Spectrum GX equipment. 1-2 wt% solution of PEA was dissolved in chloroform and was scanned with a resolution of 2cm⁻¹ in the scan range of 450–4000 cm⁻¹.

FTIR of pure solvent was run prior to running the FTIR of the samples, to use its peaks as baseline, to automatically subtract it from the samples peak.

The viscosity vs shear rate was determined at the temperature of 30°C up to maximum shear rate of 100 s⁻¹. Rheological characterization was performed on MCR101 Rheometer (Anton Paar, Germany) using Rheoplus data analysis software.

PEA samples were dissolved in THF. The solution was injected into Gel permeation chromatography column (Waters, model no. 2690). The flow rate of eluent was maintained at 0.5ml/min. Molecular weight was determined by using polystyrene standard.

Tensile properties (tensile strength, tensile modulus and elongation at break) and flexural properties (flexural strength and flexural modulus) were measured at ambient condition using a Universal Testing Machine (LR-50K, Lloyds Instrument, UK), according to ASTM procedures D638 and D790; at a crosshead speed of 5 mm/min and 0.8 mm/min respectively. Charpy Impact Strength was determined at ambient condition according to ASTM D256, using Impact Tester (Avery Denison, UK) employing a 2.7 J striker having striking velocity of 3.46 m/s.

Thermogravimetric Analysis (Q 500 DSC, TA instruments Ltd., India) characterization was done to in-

vestigate the change in degradation temperature and enthalpy of degradation of the prepared epoxy formulations. 4-5 mg samples were heated from 40°C to 600°C at a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

Analysis of the prepared polyesteramides

Acid values, amine value and hydroxyl value

Acid value, amine value and hydroxyl value obtained for the prepared PEAs are listed in TABLE 4. It was determined that acid value decreased while amine value and hydroxyl value increased with increase in molar concentration of ethanolamine in the PEA.

Ethanolamine contains both amine and hydroxyl group onto its molecular structure. Increasing the molar concentration of it with respect to Pripol 1017 (lower purity dimer acid) increased the amine and hydroxyl

TABLE 4 : Acid values, amine value and hydroxyl value obtained for the prepared PEAs

Sr. No.	Sample Name	Acid Value (mg KOH/g sample)	Amine Value (mg KOH/g sample)	Hydroxyl Value (mg KOH/g sample)
1.	PEA1	12.2	7.1	7.9
2.	PEA2	9.5	7.8	8.7
3.	PEA3	8.7	8.4	9.8

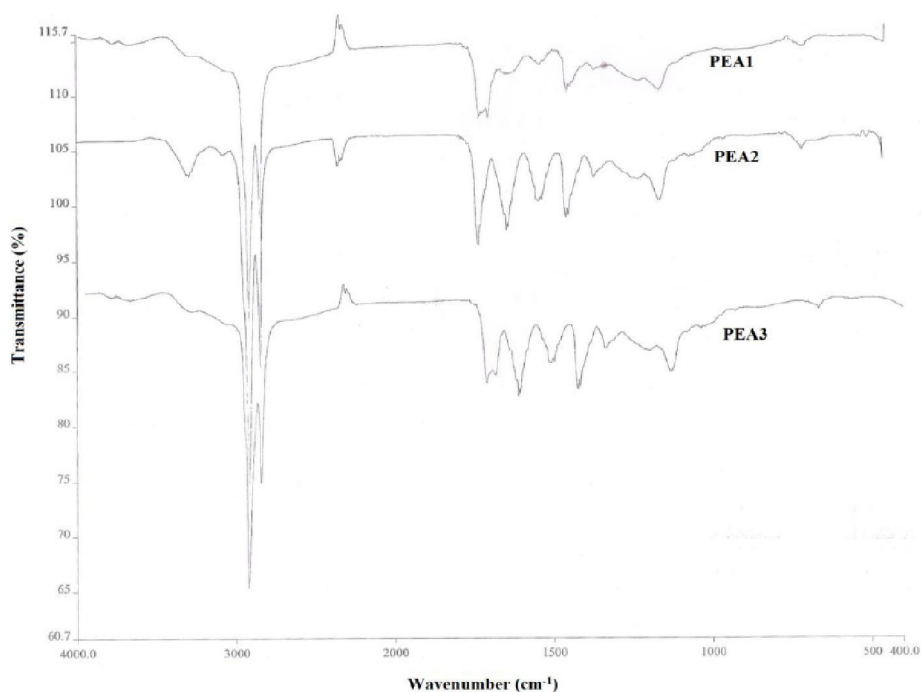


Figure 3 : FTIR spectrographs obtained for the prepared PEAs

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group in number more than required with the available acid groups. This increased amine and hydroxyl groups demanded more acid groups and eventually consumed more of it decreasing the acid value with increase in the molar concentration of ethanolamine. After consuming the additional acid groups PEA was left with increased number of amine and hydroxyl end groups increasing their respective values.

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectrographs obtained for the prepared PEAs are shown in Figure 3. It can be seen that there is no appreciable difference in the shape of the peaks or the positioning of the peaks in the FTIRs.

A small band of the amide I ($-\text{NH}_2$ in primary amides) groups appeared at about 3294 cm^{-1} . Peaks at about 2925 cm^{-1} were due to asymmetric and symmetric stretching of CH_2 , respectively. Small peak at around 1725 cm^{-1} correspond to the ester linkage ($\text{C}=\text{O}$). The carbonyl peak ($-\text{CONH}_2$) was at around

1639 cm^{-1} (steep peak). Amide II band/ CH_2 asymmetric deformation was indicated by the peak of wave-number 1559 cm^{-1} . The peak at 1225 cm^{-1} was corresponded to $\text{C}-\text{N}$ stretching vibration bond. Small peak at 760 cm^{-1} showed $\text{C}-\text{C}$ deformation. FTIR analysis thus proves that compound formed was a PEA.

Gel permeation chromatography (GPC)

GPC curves obtained for the prepared PEAs are shown in Figure 4; whereas, the values of number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) are listed in TABLE 5.

TABLE 5 : Values of M_n , M_w and PDI obtained for the prepared PEAs

Sr. No.	Sample Name	M_n	M_w	PDI
1.	PEA1	6831	13214	1.9
2.	PEA2	4244	5980	1.4
3.	PEA3	4064	5821	1.4

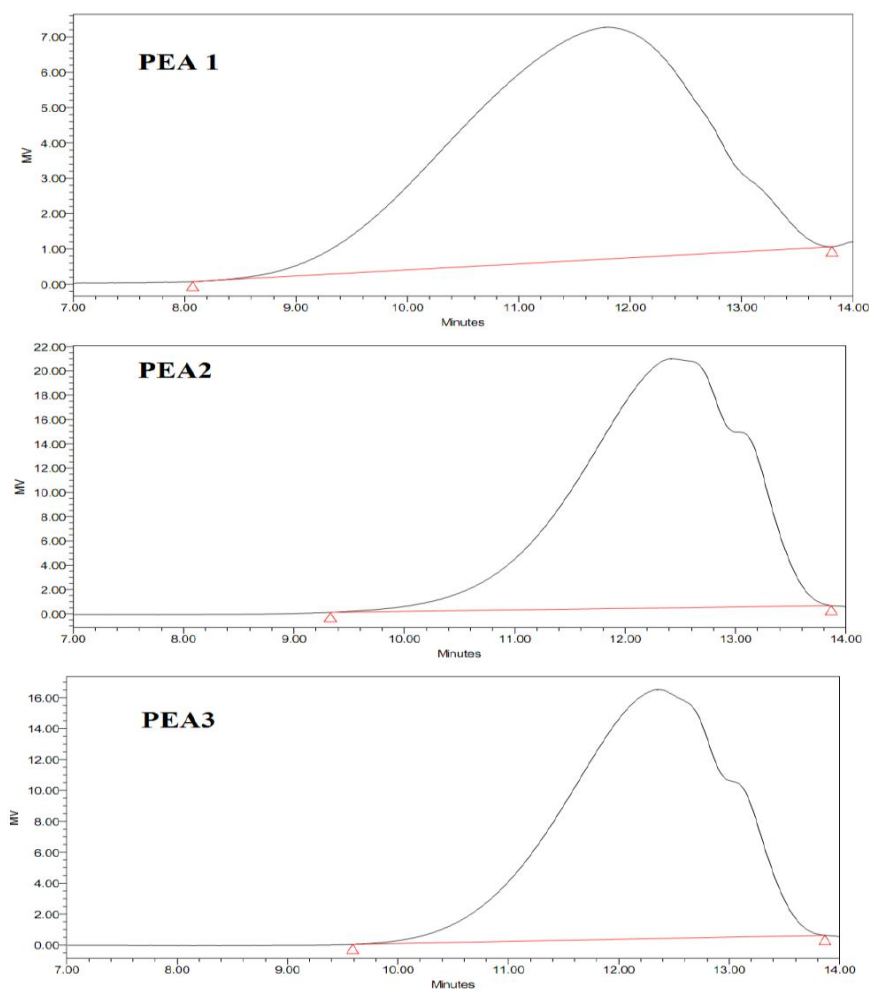


Figure 4 : GPC graphs obtained for the prepared PEAs

It was observed that Mn, Mw and PDI decreased with increase in the molar ratio between lower purity dimer acid (Pripol 1017) and ethanolamine. Reacting them in 1:1 molar ratio gave both the molecules an equal probability to undergo reaction with each other making the obtained PEA to have about equal number of acid and amine functional groups. But, as the concentration of the ethanolamine increased as compared to lower purity dimer acid (Pripol 1017) reaction ability of the Pripol 1017 acids got restricted, as the molecules of ethanolamine acted as the chain stoppers. This is clearly evident from the GPC analysis. Also it can be seen that

uniformity in the chain growth increased with increase in the molar concentration of ethanolamine as compared to Pripol 1017, which is evident from the PDI analysis.

Rheological analysis

Figure 5 is a plot of viscosity vs shear rate for the prepared PEA resins. It can be seen that the viscosity of the PEAs decreased with increase in shear rate. Decrease in viscosity is gradual yet continuous with increase in shear rate. Thus, they all show shear thinning behavior; however, viscosity decreased with increase in the molar concentration of ethanolamine as compared to lower purity dimer acid (Pripol 1017).

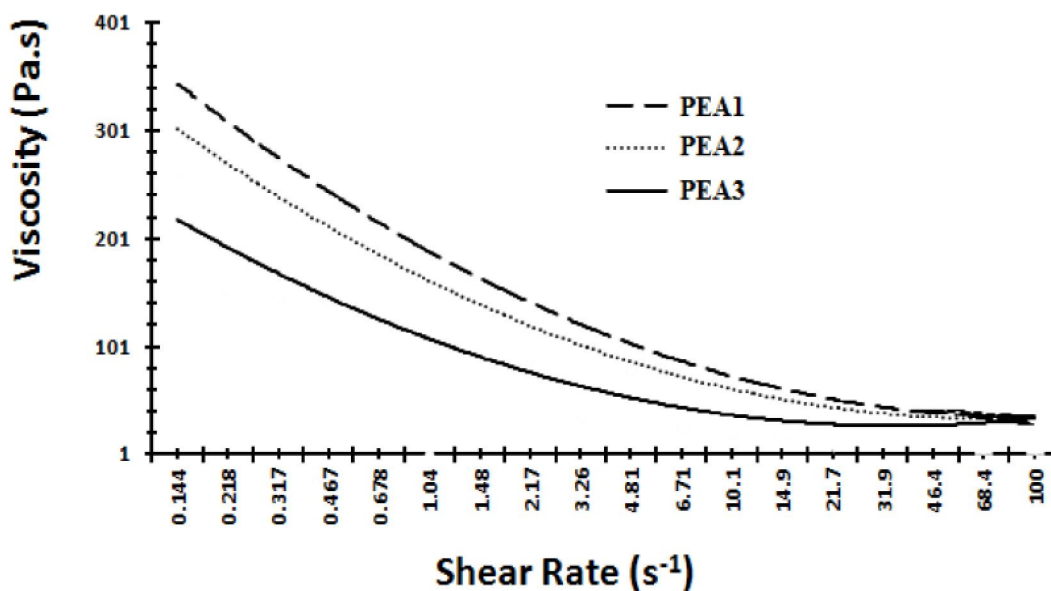


Figure 5 : Plot of viscosity vs shear rate obtained for the prepared PEAs

This can be clearly attributed to the molecular weight of the material. It was determined from the GPC analysis that the molecular weight of the PEA decreased with increase in concentration of ethanolamine as compared to lower purity dimer acid (Pripol 1017). This led to decreased intermingling of the PEA polymer chains also the decreased interaction between them, ultimately decreasing the intermolecular forces of attraction. Thus, viscosity of the PEA decreased with increased concen-

tration of ethanolamine.

Analysis of the prepared epoxy formulations

Mechanical property

Mechanical properties like tensile strength, Youngs modulus, elongation at break (%), flexural strength, flexural modulus and impact strength, obtained for the prepared epoxy formulations are shown in TABLE 6.

TABLE 6 : Mechanical properties obtained for the prepared epoxy formulations

Sr. No.	Sample Name	Tensile Strength (MPa)	Youngs Modulus (MPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
1.	EP0	33.2	78.3	90.2	45.7	1833.1	861.7
2.	EP1	22.7	54.4	79.7	22.8	921.7	598.2
3.	EP2	26.1	68.25	121.7	13.7	406.1	1023.3
4.	EP3	28.5	70.8	117.4	111.3	269.4	982.5

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Tensile strength of the epoxy formulation decreased drastically on addition of 5% of PEA1, but then increased steadily on addition of PEA2 and PEA3. PEA1 was prepared by 1:1 reaction of Pripol 1017 and ethanolamine, giving polymer of highest molecular weight, thus having maximum separated end groups. Thus it may have happened that the PEAs of PEA1 might not have underwent complete reaction with the epoxy. Whereas, PEA2 and PEA3 are low molecular weight PEAs having sufficient quantity of end groups to react with the epoxy chains. Also, PEA1 and PEA2 are long enough to induce flexibility into the formulation. Similar trend was observed for Young's modulus. However, flexural strength and flexural modulus decreased continuously. Being flexible in nature, the prepared formulations, might not have got enough strength to resist the flex load. But, the most important thing is the increase in the elongational and the impact properties. Maximum improvement in the elongational and impact properties were obtained for EP2 containf 5% PEA2. Increase is about 35%, which is highly appreciable compared to the quantity added.

Thermal property

TABLE 7 lists the onset degradation temperature, while Figure 6 shows the thermogravimetric plot obtained for the prepared epoxy formulations. It can be seen that the onset degradation temperature decreased from EP0 to EP3. This can be attributed to the flexibility induced by the PEAs added into the epoxy. Addition of PEA induced flexibility, making the polymer molecules to be placed apart. This makes them more susceptible to the temperature. Thus, the addition of PEA affects the thermal stability of the material. But, if we compare this trend to the obtained increase in the elongational and impact property, then it's not that appreciable.

TABLE 7 : Onset degradation temperature values obtained for the prepared epoxy formulations

Sr. No.	Sample Name	Onset degradation temperature (°C)
1.	EP0	284.9
2.	EP1	269.7
3.	EP2	265.2
4.	EP3	259.8

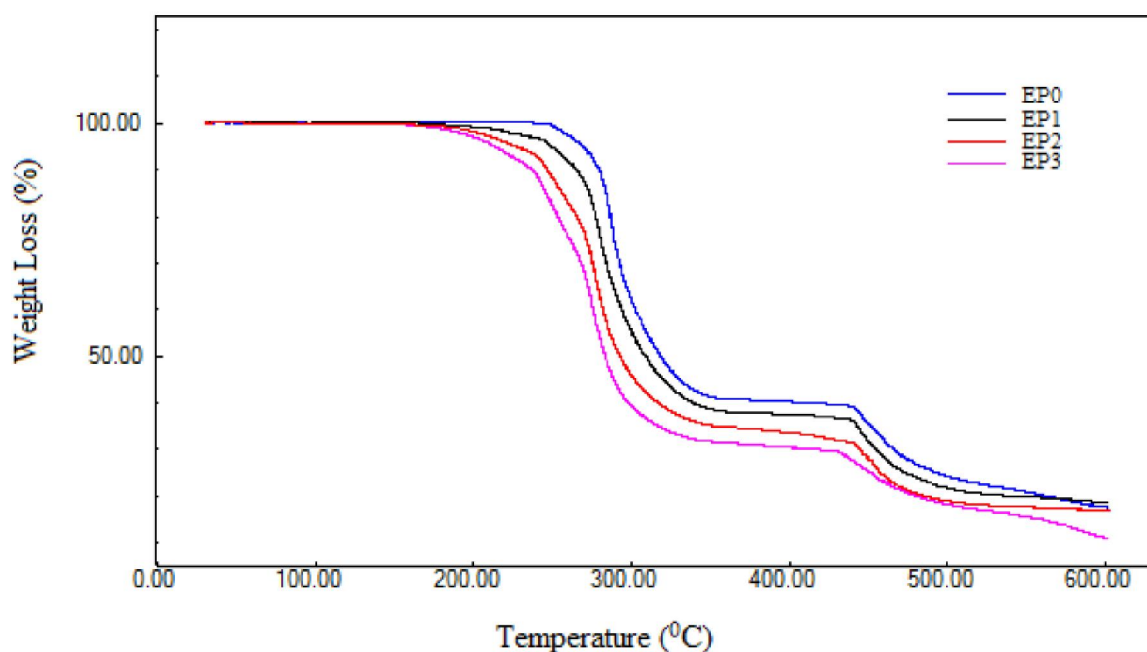


Figure 6 : Plot of thermogravimetric analysis obtained for the prepared epoxy formulations

CONCLUSION

Polyesteramide (PEA) was successfully prepared using lower purity dimer acid (Pripol 1017) and etha-

nolamine. It was found the molar ratio between them had significant effect on the obtained properties. Mw, Mn, PDI and viscosity decreased appreciably with increased molar concentration of ethanolamine. This was attributed to the endcapping of the PEA by the

excess ethanolamine making it unable to react further, as no significant amount of acid chains become available to react with the ethanolamine. Addition of this PEAs into epoxy as a partial replacement of TETA induced flexibility, but at the expense of strength and thermal stability.

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