Studies in synthesis of polyesteramide resin from lower purity dimer acid and ethanolamine: Effect of ethanolamine content

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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. This PEAs can be successfully used in applications like coatings, foams etc.   © 2013 Trade Science Inc. - INDIA

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[11-14] to hot melt adhesive[15-19]. PEA are also used in applications like hydrogels, scaffolds,

Froehling synthesized hyperbranched polyesteramide by reacting cyclic anhydride with diisopropanol amine, yielding a tertiairy 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 coating using it[3]. Castaldo et al. synthesized a range of PEAs using adipolyl dichloride, 1, 10-decandiol, and 1, 6-diaminohexane; and characterized it for thermal and viscoelastic properties[4]. Mukherjee at al. prepared jute fibre composite using PEA polyol. PEA polyolwas 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

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the effect of various surface treatments of jute fibreinvolving bleaching, dewaxing, alkali treatment, cyanoethylation and vinyl grafting on the properties of the prepared composite[6]. Tuominem 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]. Gast et al. synthesized PEA using linseed oil, diethanolamine and range of acids like azelaic acid, maleic acid, fumaric acid, phthalic anhydride, terephthalic acid, itaconic acid and brassylic acid; and investigated their molecular weight, viscosity and film forming properties[20]. They also prepared hydroxyl-terminated PEAs using soybean oil and linseed oil and prepared coating formulation by reacting it with diisocyanates[21]. Rodriguez-Galan et al. synthesized PEA using metal salts of *N*-chloroacetyl-*β*-alanine and *N*-chloroacetyl-4-aminobutyric acid[22].

This work is an attempt to understand the effect of molar ratio of ethanolamine and lowerpurity 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 chromatograpy (to get number average molecular weight, weight average molecular weight and polydispersity index) and rheological properties.

MATERIALS AND METHODS

Materials

Ethanalamine and p-toluene sulphonic acid was procured from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. Lower purity dimer acid (Pripol 1017; composition: 22% trimer acid, 75% dimer acid and 3% linoleic acid) was procured from Soofi Traders Pvt. Ltd., Mumbai, India. All chemicals were used as obtained, without and modification or purification.

Methods

Figure 1 shows the molecular structure of the acids present in the lower purity dimer acid (Pripol 1017) 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.
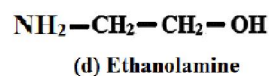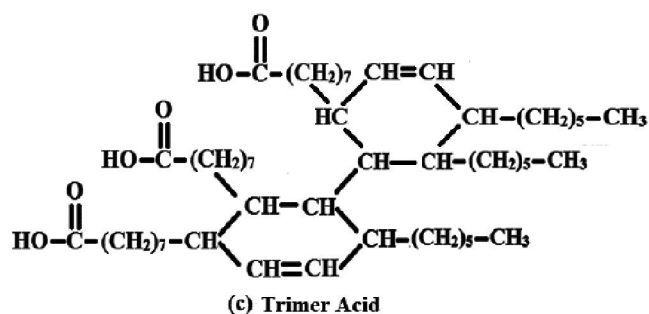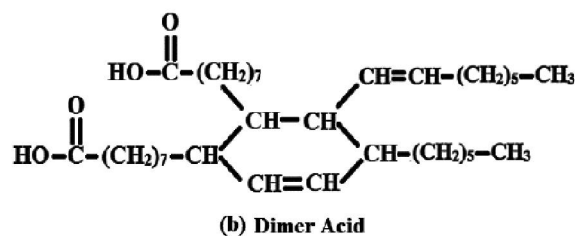

Figure 1 : Structure of the acids and ethanolamine used in the synthesis of PEA

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

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%

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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

linoleic acid. Basis of the reaction was 200 g Pripol 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 the ratio 1:1.5 (trimer acid : 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 teûon blade stirrer attached to the stirring motor), condenser (double walled with water as coolant. Water ûow rate was maintained at 1 l/min), nitrogen gas ûow rate was maintained at 500ml/min) and temperature controller. To the ûask 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 ateûon 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.

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:

Acid Value = (56.1 x Volume of alc. KOH x Normality of alc. KOH)/(Weight of sample)

Amine Value Determination: 50 ml neutralized isopropyl 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:

Amine Value = (56.1 x Volume of HCl x Normality of HCl)/(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 obtained 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

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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:

Hydroxyl Value = [56.1 x Normality of alc. KOH x (ml KOH blank – ml KOH sample)]/[Weight of Sample] – 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 ûow rate of eluent was maintained at 0.5ml/min. Molecularweightwas determined by using polystyrene standard.

RESULTS AND DISCUSSION

Acid values, amine value and hydroxyl value

Acid value, amine value and hydroxyl value obtained for the prepared PEAs are listed in TABLE 3. It was determined that acid value decreased while amine value and hydroxyl value increased with increase in molar

TABLE 3 : 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

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 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 2. 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 ($-NH_2$ 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 (C=O). The carbonyl peak ($-CONH_2$) was at around 1639 cm^{-1} (steep peak). Amide II band/CH_2 asymmetric deformation was indicated by the peak of wavenumber 1559 cm^{-1}. The peak at 1225 cm^{-1} was corresponded to C–N stretching vibration bond. Small peak at 760 cm^{-1} showed C-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 3; whereas, the values of number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity index (PDI) are listed in TABLE 4.

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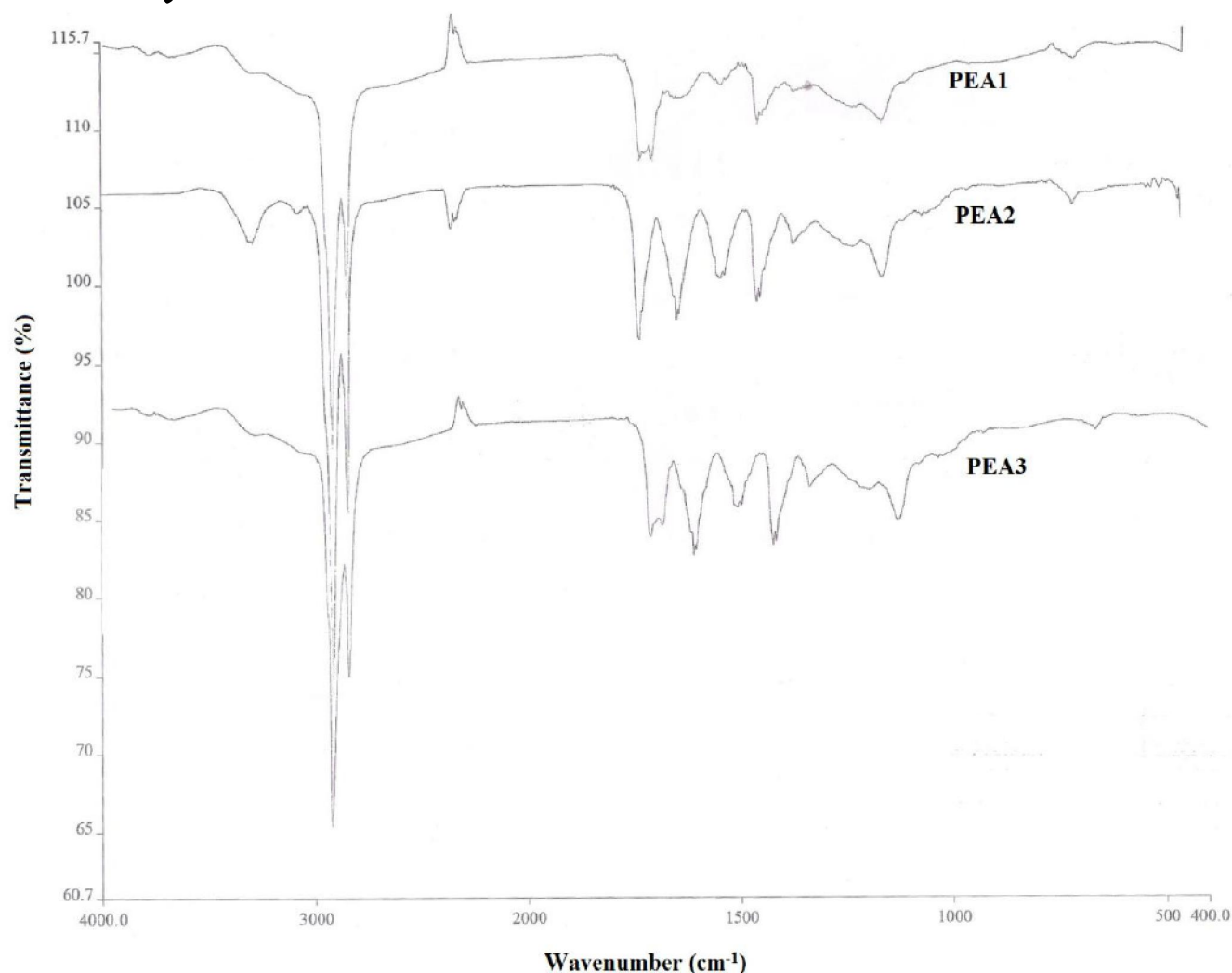Polymer

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Figure 2 : FTIR spectrographs obtained for the prepared PEAs

TABLE 4 : Values of Mn, Mw and PDI obtained for the prepared PEAs

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

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 form the PDI analysis.

Rheological analysis

Figure 4 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).

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
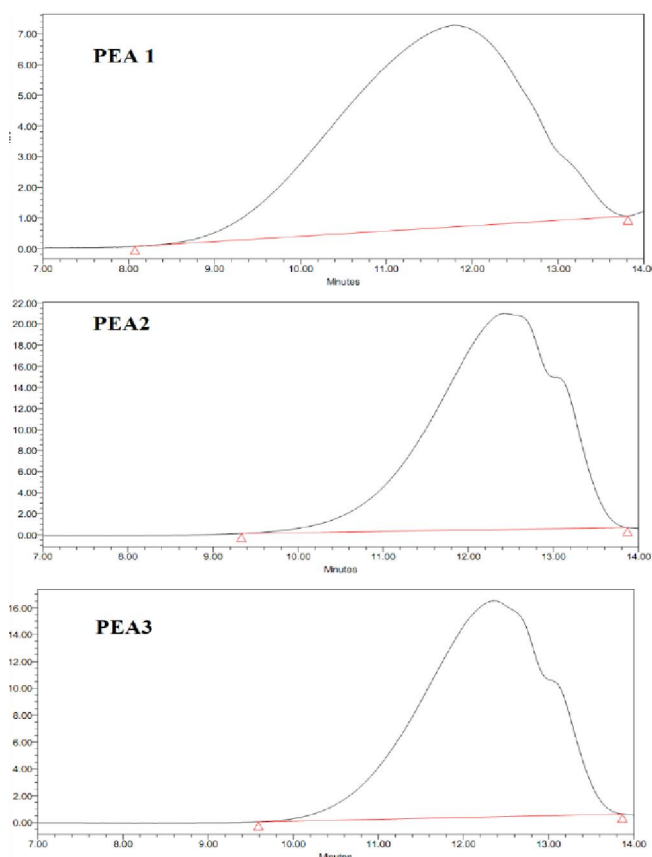
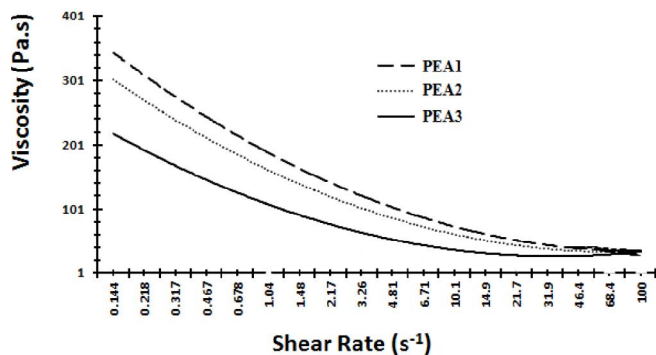**Figure 3 : GPC graphs obtained for the prepared PEAs**

Figure 4 : Plot of viscosity vs shear rate obtained for the prepared PEAs

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 concentration of ethanolamine.

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.

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