

STUDIES IN PREPARATION AND CHARACTERIZATION OF POLYESTERAMIDE BASED HOT MELT ADHESIVE FROM DIMER ACID, ETHANOLAMINE AND ETHYLENEDIAMINE: EFFECT OF ETHANOLAMINE CONCENTRATION

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ABSTRACT

Polyesteramide based hot melt adhesives were synthesized from high purity dimer acid (composition: ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid), ethylenediamine and ethanolamine. The effect of ethanolamine content on the properties of polyesteramide, such as thermal properties: glass transition temperature (T_g), melting temperature (T_m), enthalpy of melting (H_m), crystallization temperature (T_c), enthalpy of crystallization (H_c) and softening point (T_s); mechanical properties: tensile strength, elongation at break and °Shore hardness; adhesion properties: lap shear strength (LSS) and T-Peel strength (TPS); crystallinity and rheological properties were investigated. Ethanolamine was added as a partial replacement of ethylenediamine. Ethylenediamine was replaced by 10, 20 and 30% (molar basis) of ethanolamine. It was found that T_g , T_m , H_m , T_c , H_c , T_s , LSS, TPS, tensile strength, °Shore D hardness, crystallinity and viscosity, all decreased with increased concentration of ethanolamine. This was due to the decrease in the crystallinity of the polyesteramide caused by conversion of certain amide linkages to ester linkages, which increased with increased concentration of ethanolamine, decreasing crystallinity and thus the above-mentioned properties.

Keywords: Hot melt, Lap shear, Peel, Rheology.

1. INTRODUCTION

Hot-melt adhesives (HMA) are solid adhesives which when heated are converted to a molten liquid state for application to substrates; whereas on cooling quickly sets up the bond. [1] The substrates must be joined immediately on application of the HMA. [2]

When hardened, HMA can have various degrees of tackiness depending on the formulation. Conventional HMAs cool to harden and do not chemically cross-link. Such systems have an open time from few seconds to few minutes. [1]

Materials that are primarily used as HMAs include ethylene and vinyl acetate copolymers (EVA), polyvinyl acetates (PVAc), polyethylene (PE), amorphous polypropylene (PP), block copolymers (styrene butadiene rubber, SBR), polyamides (PA) and polyester (PEster). HMAs are solid at temperatures below 80°C. Typical application temperatures are 150-200°C. [2]

The most important advantage of HMA is the ability of being able to pre-apply e.g. as powder or adhesive spheres, in melt liquid form, as dispersion or as an adhesive foil. The joining procedure does not have to take place directly after applying the adhesive to the substrate; this can happen at any time later on. [3] The market for HMA is mainly in the manufacture of durable goods. Examples are shoe assembly, kitchen and bathroom cabinets, telecommunication cable repair sleeves, and window assembly. [4]

First PEA based HMA was reported by Martins and Ashley in 1972. They prepared PEA HMA from dimer acid, sebacic acid, hexamethylenediamine and ethylene glycol; and had bond strength of about 13.8 MPa. PEA synthesized from dimer acid, diols and diamines have low crystallinity and wide range of melting temperatures, which make them particularly suitable to be used as a HMA. [5] Krieger et al. synthesized hot melt pressure sensitive adhesive by reacting dimer acid with ethanolamine; and dimer acid with mix of ethylenediamine and dimethyl terephthalate. Prepared adhesives were found to have adhesion strength of 0.34 and 0.47 MPa respectively; and were used for sticking polystyrene labels to glass. [6] Martins and Donermeyer prepared spherical metal particles filled PEA HMAs for cavity filling applications. PEA consisted of 60 percent by weight of polyethylene terephthalate and 40 percent by weight of polyamide prepared from dimer acid and hexamethylenediamine with a minor amount of anti-oxidant. This PEA was filled with spherical alumina, iron, mild steel, stainless steel and zinc particles of varied particle size and concentration. [7, 8] Veazey investigated the PEA HMA for joining vinyl based substrates. He synthesized PEA HMA by reacting 0.201 equivalents (eq.) of dimer acid with 1.82 eq. of sebacic acid, 1.95 eq. ethylenediamine, 0.21 eq. 1,4-cyclohexane dimethanol and 0.06 eq. stearic acid. Dimer acid used was of 95.6 % purity. Viscosity of the polymer was determined to be 59000 cps, softening point of 162 °C and had T-Peel strength of 7.6 MPa. [9] Frihart and Veazey prepared PEA HMA by reacting 0.92 eq. dimer acid with 0.4 eq. sebacic acid, 0.41 eq. ethylenediamine, 0.97 eq. N-(2-hydroxyethyl) piperazine and 0.02 eq. stearic acid. Prepared HMA had viscosity of 15,500 cps at 195 °C and a softening point of 115 °C. It had improved adhesion strength at low temperature (3.6 MPa at 0°C) compared to ambient temperature (1.9 MPa at 22 °C) for vinyl based substrates. [10] They synthesized many such PEA HMAs for vinyl substrates. [11, 12] Hayes et al. synthesized PEA HMA from dimer acid (70 %), sebacic acid (30 %), ethylenediamine (45 %) and 1,6-hexamethylenediamine (55 %). Prepared HMA was found to have viscosity of 6,000 cps at 195 °C and lap shear strength of 5.7 MPa. [13] Swan and Hansen developed PEA based HMA suitable for bonding polyester and polycarbonate substrates by reacting dimer acid, adipic acid, hexamethylenediamine and ethylene glycol in varied proportion. [14] Chen et al. synthesized PEA of different

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viscosities using dimer acid, sebacic acid, ethylenediamine and diethylene glycolamine. They determined improvement in mechanical and adhesion properties with increase in inherent viscosity of the PEA. [15] They also investigated the effect of PEA addition on the properties of EVA based HMA; and found that PEA/EVA blend composition containing about 20 % PEA showed highest miscibility and best possible improvement in adhesion properties. [16] Broos et al. synthesized biodegradable PEA HMA using 1.2 kg ethylenediamine, 4.56 kg ϵ -caprolactone, 2.62 kg dimethyl adipate and 1.35 kg 1,4-butanediol [17]. Appleman et al. synthesized PEA HMAs using 258 g dimer acid, 44.4 g ethylenediamine and 24.6 g dimer diol. Prepared HMA had softening point of 95 °C, glass transition temperature of - 46 °C and lap shear strength of 28 J/mm² [18].

Current study deals with PEAs synthesized from high purity dimer acid (composition: ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid), ethanolamine and ethylenediamine. The effect of the content of ethanolamine on the properties such as lap shear strength, T-peel strength, tensile strength, elongation at break, glass transition temperature, softening point, melting temperature, enthalpy of melting, crystallization temperature, enthalpy of crystallization, crystallinity and viscosity was investigated.

2. EXPERIMENTAL

2.1. Materials

Arizona Chemicals, Mumbai, India, supplied high purity dimer acid (Unidyme 18, composition: linoleic acid ~1%, dimer acid ~98%, trimer acid ~1%), with an acid value of 198 mg potassium hydroxide (KOH) /g sample. Ethylenediamine was obtained from Ankita Chemicals, Mumbai, India. Ethanolamine was obtained from S.D. Fine Chemicals Pvt. Ltd., Mumbai, India. All chemicals were used as obtained without any purification or modification.

2.2. Preparation of Polyesteramides

Fig. 1 (a-e) show the molecular structures of the reactants used in the study; while their molecular weights are listed in Table 1. In order to obtain high molecular weight polymer with molecular uniformity, the ratio of total acid equivalent present in Unidyme 18 to total amine equivalents present in ethylenediamine and, hydroxyl and amine equivalents present in ethanolamine was kept at, approximately, 1. Unidyme 18 consists of ~1% trimer acid, ~98% dimer acid and ~1% linoleic acid. Basis of the reaction was 200 g Unidyme 18, which according to its composition had 2 g of trimer acid, 196 g of dimer acid and 2 g of linoleic acid. This means it had 0.002 mol of trimer acid, 0.35 mol of dimer acid and 0.007 mol of linoleic acid. Trimer acid and linoleic acid were present in a very negligible amount. So, their quantities were not considered in calculating the required quantities of ethylenediamine and ethanolamine. Accordingly, 200 g of Unidyme 18 was supposed to consist of 200 g dimer acid. Thus, Unidyme 18 provided about 0.36 mol of dimer acid. Unidyme 18 was reacted with ethylenediamine and ethanolamine in 1:1 molar ratio. 0.36 mol of Unidyme 18 were thus, reacted with 0.36 mol of ethylenediamine and ethanolamine (both combined). Number of moles of ethylenediamine and ethanolamine required will vary according to the formulation, taken

based on Unidyme 18. Formulations for preparing PEA HMA using Unidyme 18 and their nomenclatures are listed in Table 2.

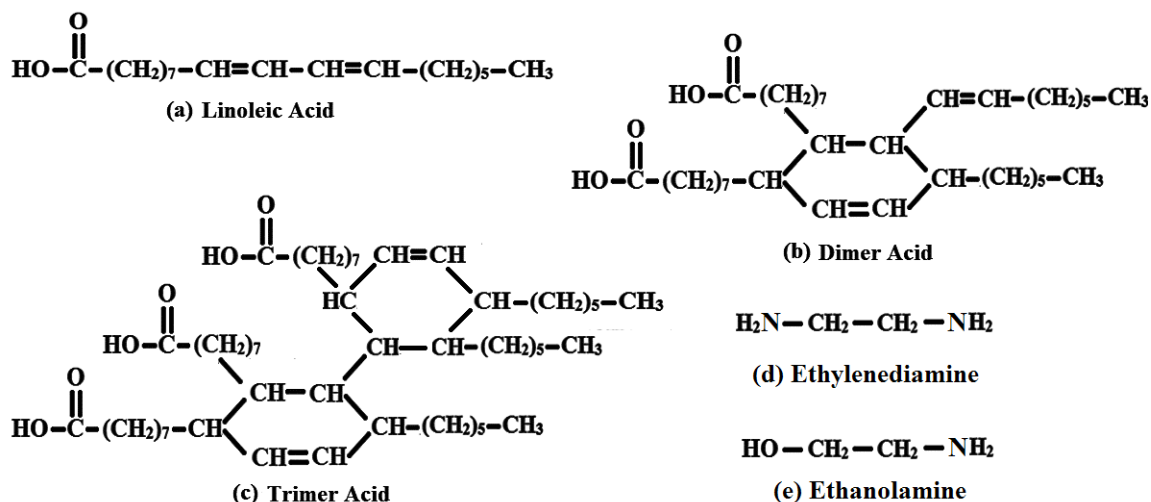


Figure 1: Molecular structures of (a) linoleic acid, (b) dimer acid, (c) trimer acid, (d) ethylenediamine (e) ethanolamine

Table 1: Molecular weight of the reactants used in preparing PEA HMA

Sr. No.	Reactant	Molecular weight (g/mol)
1.	Trimer acid	840
2.	Dimer acid	560
3.	Linoleic acid	280
4.	Ethylenediamine	60
5.	Ethanolamine	61

2.3. Experimental Procedure

The four necked 500 ml flask was equipped with stirring system (moon shaped teflon blade stirrer attached to stirring motor), condenser (double walled with water as coolant. Flow rate of water was maintained at 1 l/min), nitrogen gas inlet (flow rate of nitrogen was maintained at 500 ml/min) and temperature controller. To the flask was added 200.0 g of Unidyme 18 and the calculated amounts of ethylenediamine and ethanolamine. Order of addition of reactants is: Unidyme 18, ethanolamine and ethylenediamine. The reactants were heated gradually from 230 to 250 °C while stirring speed was maintained constant at 1500 rpm. Acid value was continuously determined at an interval of half hour to know the progress of reaction. Product was removed from the reactor when the acid

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value of the PEA reached approximately 5 or below. Time required to reach the desired acid value is about 5 to 6 h. Finally, the reaction was conducted under constant vacuum (pressure < 1 mmHg) at 250°C. Synthesized PEA, in the molten condition, was poured in the teflon mold (having dimension: 15×15×3 cm³) and allowed to cool at room temperature.

Table 2: Formulations and nomenclature of PEA HMAs prepared using Unidyme 18

Sr. No.	Nomenclature	Unidyme 18 mole (g)	Ethylenediamine (EDA) mole (g)	Ethanolamine mole (g)
1.	UEE0	0.36 (200)	0.36 (21.6)	-
2.	UEE10	0.36 (200)	0.32 (19.2)	0.04 (2.4)
3.	UEE20	0.36 (200)	0.28 (16.8)	0.08 (4.9)
4.	UEE30	0.36 (200)	0.24 (14.4)	0.12 (7.3)

Ethanolamine was added as a partial replacement of ethylenediamine. Ethanolamine was added as 10, 20 and 30 % as partial replacement of ethylenediamine in the PEAs prepared using Unidyme 18.

3. CHARACTERIZATION AND TESTING

3.1. Acid Value Determination

50 ml 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 remained for 30 seconds or more. The calculation of acid value was performed as per Equation 1.

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

Equation 1

3.2. Amine Value Determination

50 ml 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 remained for 30 seconds or more. The calculation of amine value was performed as per Equation 2.

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

Equation 2

3.3. Hydroxyl Value Determination

5 g sample was accurately weighed in a 250 ml Erlenmeyer flask; whereas other Erlenmeyer flask had no added 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 hydroxyl value was performed as per Equation 3.

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

Equation 3

3.4. FTIR Analysis

The FTIR spectra were recorded with a PerkinElmer, Spectrum GX equipment. 1-2 wt % solution of HMA was dissolved in chloroform and was scanned with a resolution of 2cm^{-1} in the scan range of $450\text{--}4000\text{ cm}^{-1}$. 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.

3.5. Mechanical Properties

Tensile test of the compression-molded sheet was measured in accordance with ASTM D638. Crosshead speed, for testing, was maintained at 50 mm/min. Shore D hardness was determined in accordance with ASTM D2240. Both the tests were performed at ambient conditions of 25 °C and 75% relative humidity.

3.6. Thermal Properties

Differential scanning calorimetry (Q100 DSC, TA Instruments) was used to investigate the crystallization and melting behaviour of the prepared HMAs. Two consecutive scans were obtained to minimize the influence of possible residual stresses in the material due to any specific thermal history. A scanning rate of the $10^\circ\text{C} / \text{minute}$ was used for both the exo- and endo- thermal cycle with the nitrogen purge at 50 ml/min. The glass transition temperature (T_g) and enthalpy of melting (H_m) were determined from the second heating scan, while the enthalpy of crystallization (H_c) was determined from first cooling scan. The area under the melting or crystallization peak represents the amount of energy required to melt the polymer (H_f) and the amount of energy released during crystallization (H_c) respectively. The peak area calculation is used with the limits of the calculation on the flat portion of the baseline before and after the melting or crystallization peak. Peak temperatures were noted as the melting (T_m) and crystallization (T_c) temperatures.

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3.7. Rheological Properties

The viscosity vs shear rate was determined at the temperature of 200°C up to maximum shear rate of 100 s⁻¹; whereas, viscosity vs time was determined at the temperature of 200°C at a constant shear rate of 1 s⁻¹ for 400 seconds using MCR101 rheometer (Anton Paar, Germany).

3.8. Adhesion Properties

PEA adhesive films were also obtained by compression molding. The adhesive joint was then obtained by pressing the film between two pieces of surface treated aluminum adherent at a temperature of 200°C and at a pressure of 30 KPa for 20 min, followed by cooling at room temperature for 24 h. Lap shear strength was determined according to ASTM D1002-72 at a crosshead speed of 1.3 mm/min. T-peel strength was measured in accordance with ASTM D1876 with a crosshead speed of 254 mm/min. Average thickness of adhesive layer in the lap and T-peel joints was kept within 0.035 ± 10 % mm (0.001 inch). Lap shear strength and T-Peel strength were measured using a Universal Testing Machine (LR 50K, Lloyds Instruments, UK).

3.9. X-ray Diffraction Analysis

XRD analysis was carried out to determine the percentage crystallinity of the prepared samples. A normal focus copper X-ray tube was operated at 30 kV and 15 mA. Sample scanning was done from 10° to 60° at the rate of 3°/min. The data processing was done using the Jade 6.0 software.

4. RESULTS AND DISCUSSION

Reaction product formed by the reaction between Unidyme 18, ethylenediamine and ethanolamine is shown in Figure 2.

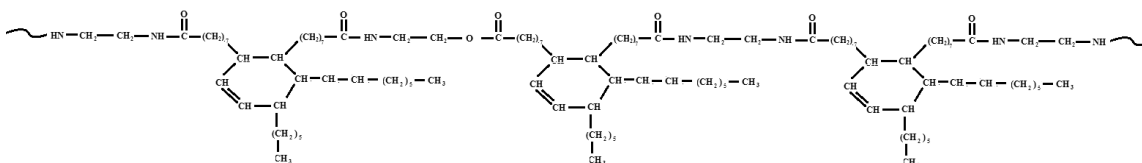


Figure 2: Molecular structure of the product formed by reaction between Unidyme 18, ethylenediamine and ethanolamine

4.1. Acid, Amine and Hydroxyl Value

Acid, amine and hydroxyl values obtained for the prepared PEA HMAs are reported in Table 3. Acid value was found to be nearly constant for the prepared PEAs; however, amine value decreased and hydroxyl value increased with increased concentration of ethanolamine in the formulations. Ethanolamine was added as a partial replacement of ethylenediamine, replacing certain amide linkages by ester linkages and certain amine end groups to hydroxyl end groups. Higher the replacement of ethylenediamine by ethanolamine, more of amine end groups will be replaced by hydroxyl end groups, acid

value being maintained nearly constant. Thus, hydroxyl value increased whereas, amine value decreased with increase in concentration of ethanolamine in the PEA.

4.2. FTIR Analysis

FTIR spectras obtained for the prepared PEA HMAs UEE0 and UEE20 are shown in Figure 3.

Table 3: Acid, amine and hydroxyl values obtained for the prepared PEA HMAs

Sample Name	Acid Value (mg KOH/g)	Amine Value (mg KOH/g)	Hydroxyl Value (mg KOH/g)
UEE0	4.3	4.1	-
UEE10	4.7	3.8	2.7
UEE20	4.0	3.2	3.4
UEE30	4.8	2.5	4.7

Small band of amide I ($-\text{NH}_2$ in primary amides) appeared at 3300 cm^{-1} . Peaks at around 2900 cm^{-1} were due to asymmetric and symmetric stretching of $-\text{CH}_2$ group. A small peak at around 1725 cm^{-1} corresponded to the ester linkage ($\text{C}=\text{O}$). This peak is present only in UEE20, but absent in UEE0 as no ethanolamine was used in it, forming no ester linkage. Carbonyl peak ($-\text{CONH}_2$) of polyamide was seen at around 1640 cm^{-1} (steep peak). Amide II band/ CH_2 asymmetric deformation was indicated by the peak at 1560 cm^{-1} . Peak at 1225 cm^{-1} corresponded to $\text{C}-\text{N}$ stretching vibration. A small peak at 750 cm^{-1} was due to the $\text{C}-\text{C}$ deformation. FTIR analysis thus proves that compound formed was an amide. However, with the addition of ethanolamine, polyamide got converted to PEA, proven through the presence of ester linkage peak in the FTIR curves at 1725 cm^{-1} . UEE10 and UEE30 were also prepared using ethanolamine as one of its reactant, thus they are also PEAs.

4.3 Mechanical Properties

Mechanical properties – °Shore D hardness, tensile strength (MPa) and percentage strain at break (%), obtained for the prepared PEA HMAs are shown in Table 4.

HMA prepared using Unidyme 18 and ethylenediamine was found to have tensile strength of 7.8 ± 0.5 MPa and percentage elongation at break of 10.7 ± 0.4 %. It was determined that tensile strength decreased, while percentage elongation at break increased with increase in concentration of ethanolamine (by partial replacement of ethylenediamine). Replacement of ethylenediamine with ethanolamine led to the replacement of amide linkages by ester linkages. Due to the unavailability of hydrogen atom on the ester linkage it was not able to form intermolecular hydrogen bonding as strong as that made by the amide linkage. Decrease in intermolecular forces of attraction led to decrease in the molecular packing per unit area, decreasing crystallinity of the HMA. Diminished crystallinity resulted in lower tensile strength and °Shore. Tensile strength and °Shore hardness decreased with increased concentration of ethanolamine in

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the HMA. Decrease in crystallinity allowed better molecular movement, making it easier for them to pass over each other, increasing the elongational property. This was the reason for the increase in percentage elongation at break with increase in concentration of ethanolamine in the HMA.

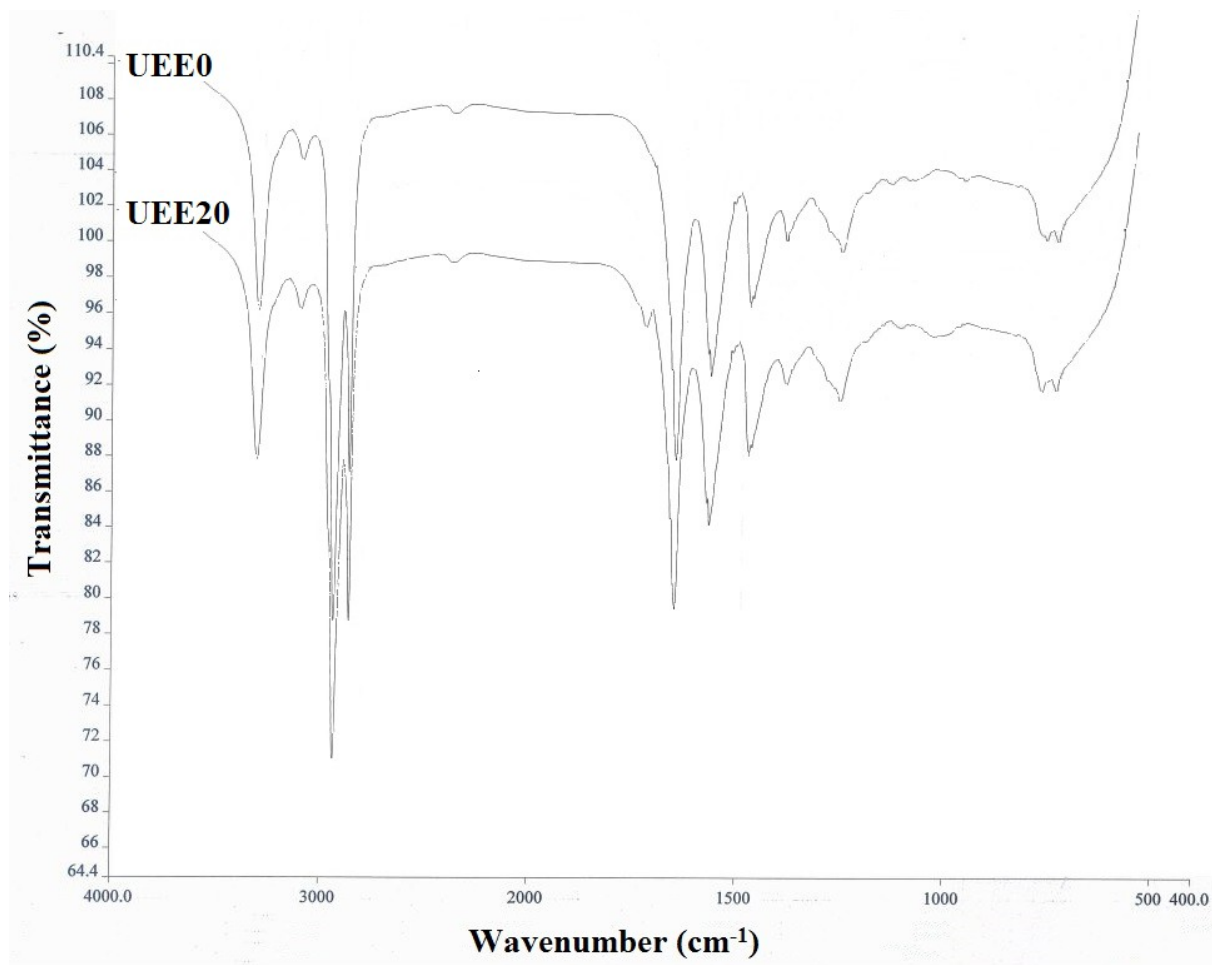


Figure 3: FTIR spectra obtained for UEE0 and UEE20

Table 4: Mechanical properties obtained for the prepared PEA HMAs

Sample Name	Tensile Strength (MPa)	Percentage Strain at Break (%)	°Shore D Hardness
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UEE0	7.8 ± 0.5	10.7 ± 0.4	65 ± 3
UEE10	5.7 ± 0.4	15.8 ± 2.1	58 ± 2
UEE20	4.6 ± 0.3	24.9 ± 1.9	52 ± 3
UEE30	2.8 ± 0.5	27.9 ± 2.7	47 ± 3

4.4. Thermal Properties

Graphs of thermal properties like glass transition temperature (T_g), heating and cooling curves are shown in Figures 4 to 6; and the values of softening temperature (T_s), glass transition temperature (T_g), melting temperature (T_m), enthalpy of melting (H_m), crystallization temperature (T_c) and enthalpy of crystallization (H_c) are shown in Table-5.

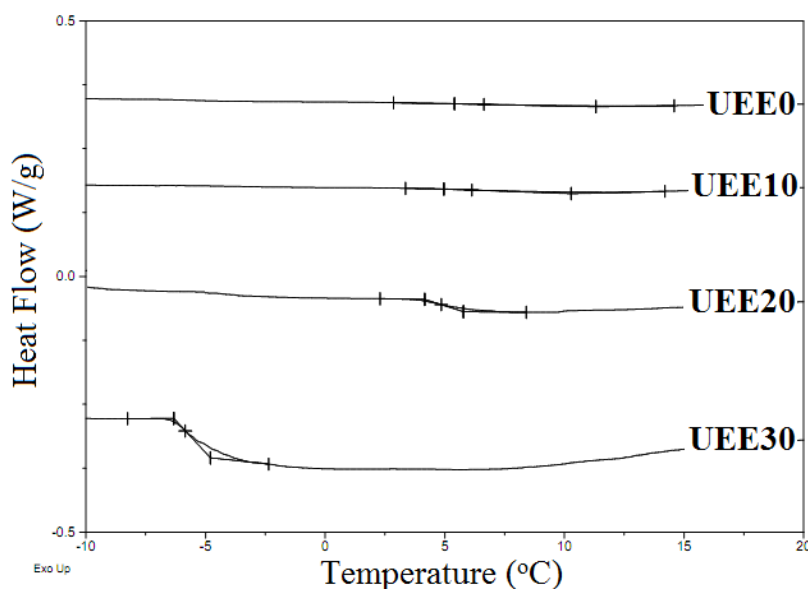


Figure 4: Glass transition curves obtained for the prepared PEA HMAs

HMA prepared using Unidyme 18 and ethylenediamine was found to have T_s , T_g , T_m , H_m , T_c and H_c of $113.00\text{ }^\circ\text{C}$, $6.64\text{ }^\circ\text{C}$, $93.78\text{ }^\circ\text{C}$, 18.07 J/g , $84.98\text{ }^\circ\text{C}$ and 9.27 J/g respectively. T_s , T_g , T_m , H_m , T_c and H_c decreased with replacement of ethylenediamine by ethanolamine. Addition of ethanolamine as a replacement of ethylenediamine, replaced certain amide linkages by ester linkages. Ester linkages (formed by the reaction between ethanolamine and dimer acid) were not able to form hydrogen bonding (intermolecular forces of attraction) as efficient as that formed by the amide linkage, due to the presence of $-H$ atom in the primary amide linkage; which was absent on the ester linkage. This led to the decrease in the crystallinity of the PEA HMA. Crystallinity of the HMA prepared using dimer acid, ethylenediamine and ethanolamine decreased with

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increase in concentration of ethanolamine. Decrease in T_s , T_g , T_m , H_m , T_c and H_c proves the occurrence of the above mentioned phenomena on addition of ethanolamine; as this properties are directly proportional to crystallinity of the material. However, lower T_g indicates a better low temperature flexibility for the HMAs prepared using dimer acid, ethylenediamine and ethanolamine. Low temperature flexibility would increase with increase in concentration of ethanolamine in the PEA HMA.

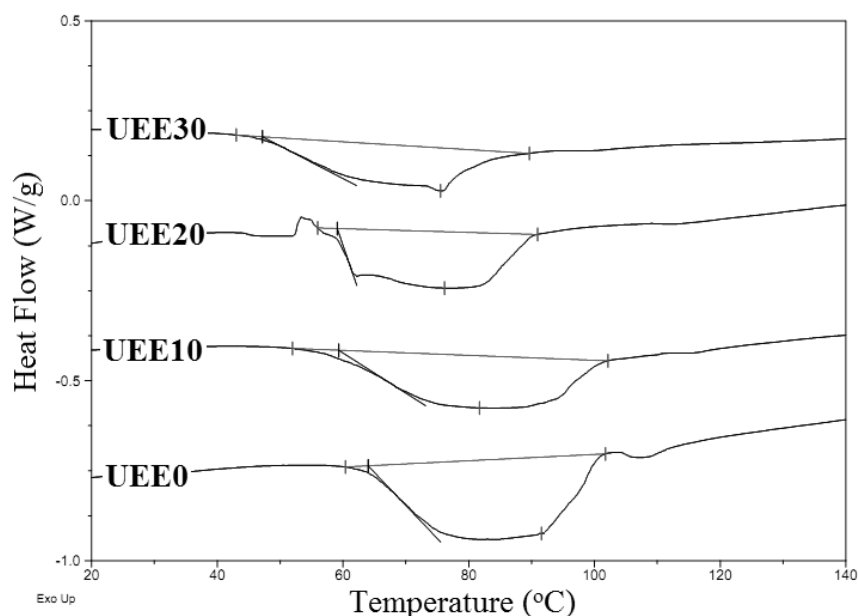


Figure 5: Melting curves obtained for the prepared PEA HMAs

4.5. Adhesion Properties

Adhesion properties like lap shear strength (MPa) and T-peel strength (N/mm) obtained for the prepared HMAs are listed in Table 6.

HMA prepared from Unidyme 18 and ethylenediamine were found to have lap shear strength of 7.1 ± 0.4 MPa and T-peel strength of 11.5 ± 0.8 N/mm. Lap shear strength and T-peel strength decreased with increased replacement of ethylenediamine with ethanolamine. As the concentration of ethanolamine increased, intermolecular forces of attraction decreased, mainly due to the replacement of amide linkages by ester linkages. Decrease in intermolecular forces of attraction allowed the PEA molecules to flow past each other more easily on application of force in lap shear or T-peel joint, decreasing the adhesion strength of the prepared HMAs.

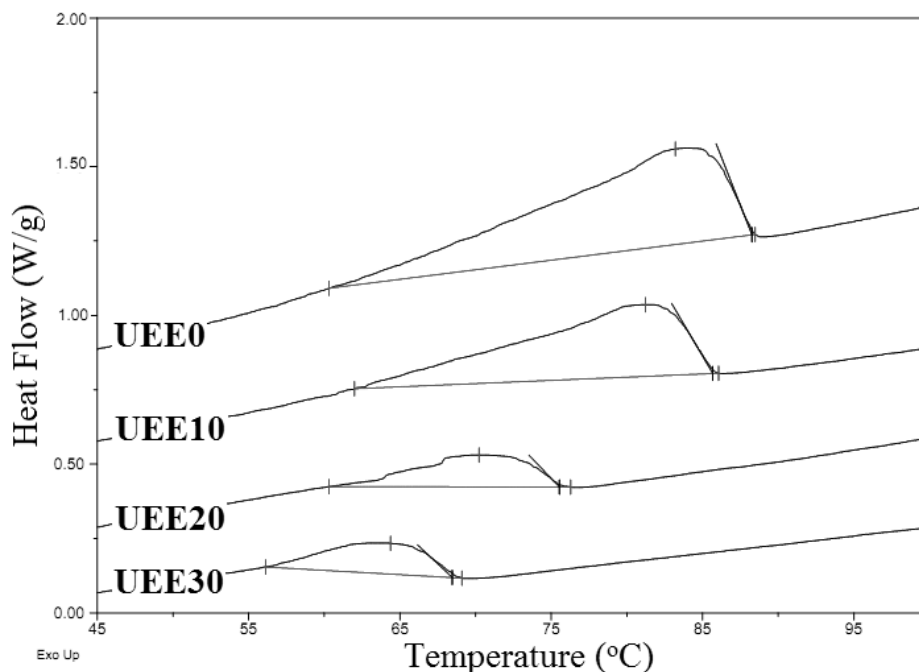


Figure 6: Crystallization curves obtained for the prepared PEA HMAs.

Table 5: Thermal properties obtained for the prepared PEA HMAs

Sample Name	T _g (°C)	T _m (°C)	H _m (J/g)	T _c (°C)	H _c (J/g)	T _s (°C)
UEE0	6.64	93.78	18.07	84.98	9.27	113.0
UEE10	6.13	81.85	16.23	80.05	6.70	103.9
UEE20	4.82	74.72	15.89	73.21	4.21	98.8
UEE30	-5.88	75.48	10.71	67.52	4.04	87.4

Table 6: Adhesion properties obtained for the prepared PEA HMAs

Sample Name	Lap Shear Strength (MPa)	T-Peel Strength (N/mm)
UEE0	7.1 ± 0.4	11.5 ± 0.8
UEE10	6.9 ± 0.4	9.2 ± 0.4
UEE20	5.6 ± 0.7	7.8 ± 0.5
UEE30	2.8 ± 0.7	5.1 ± 0.4

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4.6. Rheological Properties

Figure 7 is a plot of viscosity (Pa.s) vs shear rate (s^{-1}) obtained for the prepared PEA HMAs at 200°C. It can be seen that viscosity decreased with increase in shear rate. Thus, the prepared HMAs showed shear thinning behaviour. In addition, the viscosity of the prepared PEA HMAs decreased with increased replacement of ethylenediamine by ethanolamine, at same shear rate. Partial replacement of the amide linkage by the ester linkages, decreased the hydrogen bond formation capacity of the HMA prepared using ethanolamine. This led to the decrease in the intermolecular forces of attraction and thus the crystallinity of the HMA. Thus PEA HMAs containing higher quantity of ethanolamine, showed lower resistance to the rotating rheometer spindle, showing lower viscosity. These results strongly correlate with the observed mechanical and thermal properties.

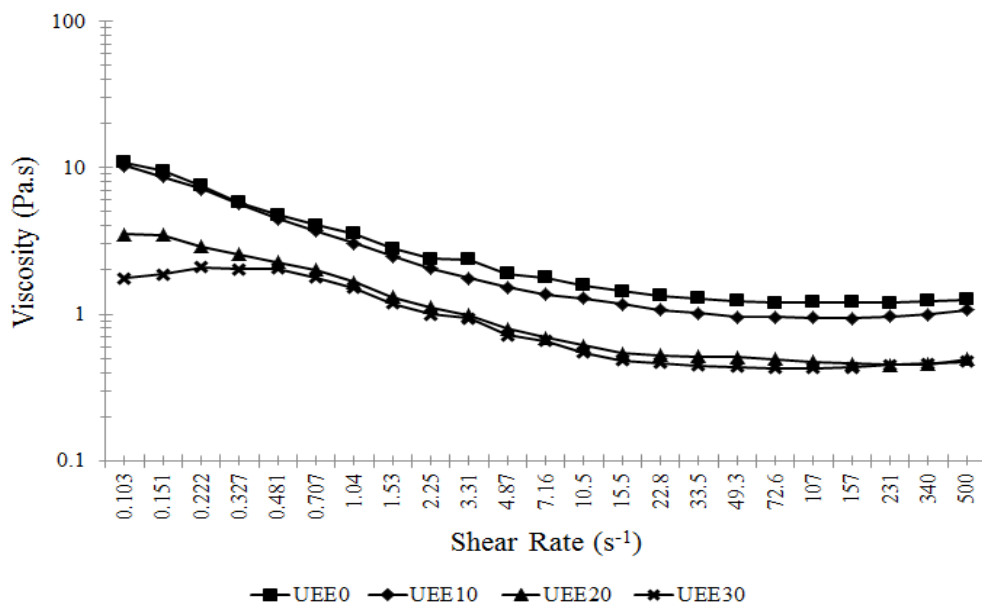


Figure 7: Graph of viscosity (Pa.s) vs shear rate (s^{-1}) of the prepared PEA HMAs at constant temperature of 200 °C

Figure 8 is a plot of viscosity (Pa.s) vs time (s) obtained for the prepared PEA HMAs at 200°C. It was determined to understand the effect of time on the viscosity of the prepared HMAs. In general, viscosity decreased with increase in time at constant temperature. Thus, the prepared HMAs showed thixotropic behaviour. Decrease in viscosities of UEE0 and UEE10 with time was very less as compared to UEE20 and UEE30. Viscosity of UEE20 and UEE30 decreased drastically with time. This can be due to the decrease in crystallinity of HMA caused by ethanolamine replacing ethylenediamine; which caused decrease in intermolecular forces of attraction. Intermolecular forces of attraction decreased due to the replacement of amide linkages by ester linkages.

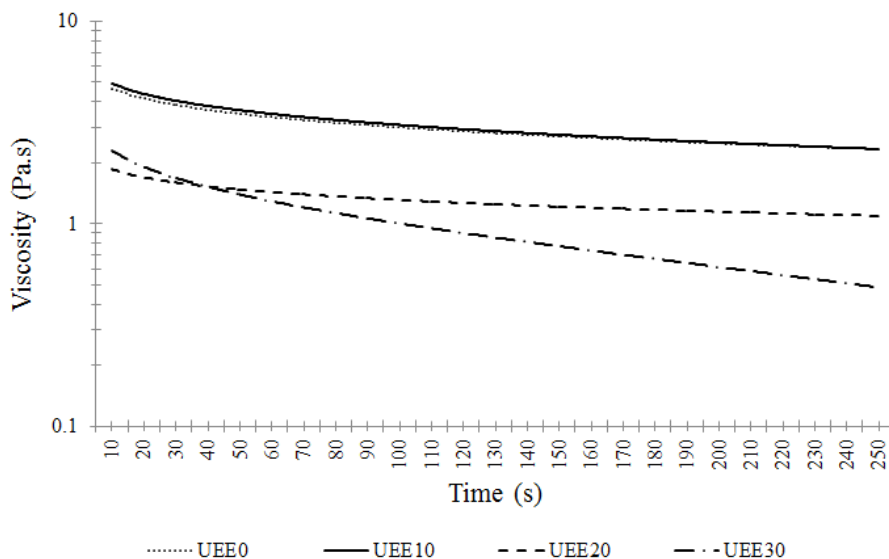


Figure 8: Graph of viscosity (Pa.s) vs time (s) of the prepared PEA HMAs at constant temperature of 200 °C

4.7. X-ray Diffraction Analysis

Figure 9 shows the x-ray diffractograms obtained for the prepared PEA HMAs, while the percentage crystallinity values are reported in Table 7. It was determined that crystallinity decreased with increased replacement of ethylenediamine by ethanolamine.

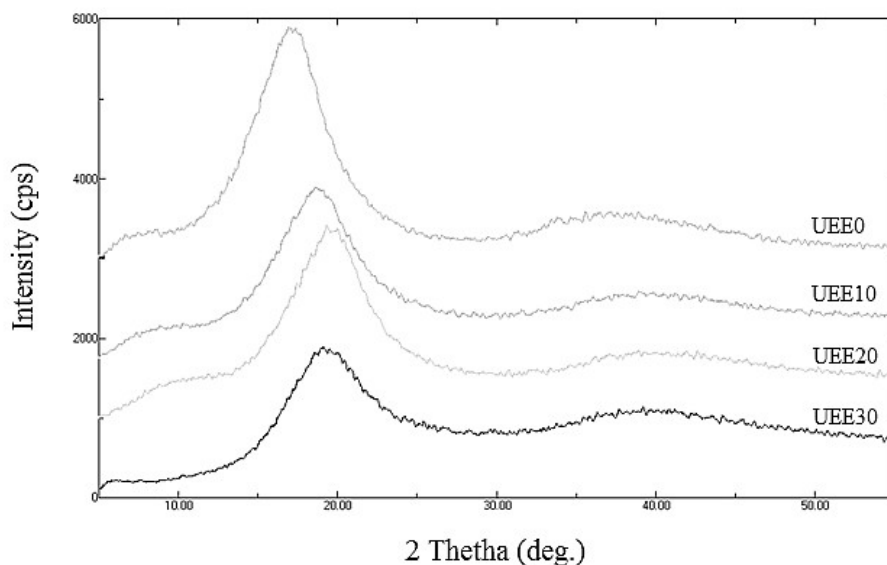


Figure 9: X-ray diffraction curves obtained for the prepared PEA HMAs

**STUDIES IN PREPARATION AND CHARACTERIZATION OF POLYESTERAMIDE BASED
HOT MELT ADHESIVE FROM DIMER ACID, ETHANOLAMINE AND ETHYLENEDIAMINE:
EFFECT OF ETHANOLAMINE CONCENTRATION**

Table 7: Crystallinity values obtained for the prepared PEA HMAs

Sample Name	Crystallinity (%)
UEE0	7.94
UEE10	5.55
UEE20	4.33
UEE30	2.05

Addition of ethanolamine as a partial replacement of ethylenediamine, replaced certain amide linkages by ester linkages. Ester linkages were not able to form hydrogen bonding as efficient as that formed by the amide linkage, due to the presence of –H atom in the primary amide linkage; which was absent on the ester linkage. This led to the decrease in the crystallinity of the PEA HMA, and thus proves the above-mentioned phenomenon.

5. CONCLUSION

Polyesteramide (PEA) based hot melt adhesives (HMA) were successfully synthesized using ethanolamine as a partial replacement of ethylenediamine to react with the high purity dimer acid (Unidyme 18). In the formulations, ethylenediamine was partially replaced by 10-30% (on molar basis) of ethanolamine. Prepared PEA HMAs were characterized for mechanical, thermal, rheological and adhesion properties. Crystallinity and thus the inter-molecular forces of attraction played an important role in affecting the above said properties. It was found that tensile strength, melting temperature, enthalpy of melting, crystallization temperature, enthalpy of crystallization, glass transition temperature, lap shear strength, T-peel strength, crystallinity and viscosity decreased with increased replacement of ethylenediamine by ethanolamine. This was attributed to the diminished hydrogen bond formation capacity of ester linkage as compared to the amide linkage. However, lower glass transition temperature indicates better low temperature flexibility for the HMAs prepared using ethanolamine and would also have better adhesion process due to lower viscosity and melting temperature.

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