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# Thermoplastic polyester amides derived from oleic acid

## Jiaqing Zuo<sup>a</sup>, Shaojun Li<sup>a</sup>, Laziz Bouzidi<sup>a</sup>, Suresh S. Narine<sup>a,b,\*</sup>

<sup>a</sup> Trent Biomaterials Research Program, Department of Physics & Astronomy, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada <sup>b</sup> Trent Biomaterials Research Program, Department of Chemistry, Trent University, 1600 West Bank Drive, Peterborough, Ontario K9J 7B8, Canada

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## ABSTRACT

Three lipid-based Polyester Amides (PEAs) with varying ratios of ester and amide linkages were synthesized. Oleic acid was used as the starting material to produce the intermediates, characterized by MS and NMR, used for polymerization. PEAs were characterized by FTIR and GPC. The PEAs were constrained to have similar number average molecular weights, in the  $2 \times 10^4$  range, thereby enabling comparison of their physical properties from a structural perspective. The thermal behavior of the polymers was assessed by DSC, DMA and TGA. Thermal degradation was not affected by ester/amide ratios, but  $T_g$  increased non-linearly with decreasing ester/amide ratios and correlated with hydrogenbond density and repeating unit chain length. Crystallinity was studied by XRD and DSC. Degree of crystallization and multiple melting behavior as a function of cooling kinetics were explained well by hydrogen-bond density, repeating unit chain length and density of ester moieties. Mechanical properties were investigated by DMA and Tensile Analysis, with a non-linear increase of storage and tensile moduli recorded as a function of decreasing ester/amide ratios. The findings suggest how approaches to the synthesis of lipid-based PEAs can be targeted to the delivery of specific physical properties.

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## 1. Introduction

Polyester amides (PEAs) have been extensively studied for several years; because they generally demonstrate desired properties of both polyesters and polyamides [1]. PEAs are mainly developed from three building blocks: amino acids, diols and diacvl chlorides [2-5]. Polyamides generally demonstrate preferred mechanical and processing properties, such as thermal stability, tensile strength and biocompatibility, but are generally not biodegradable [6]. Polyesters demonstrate varying degrees of biodegradability; however, lack of the preferred physical properties demonstrated for example by polyamides limits their applications. Therefore when these two different types of linkages are combined in the main chain of one single polymer, the biodegradability caused by the ester linkage and the enhanced thermal and mechanical properties caused by amide-induced intermolecular hydrogen bonds can be combined in one polymer [7], giving rise to a superior material which could be applied in a wide variety of areas.

Biomedical applications is one of the most important areas to which PEAs have generally been applied; this includes absorbable

\* Corresponding author. Trent Biomaterials Research Program, Department of Physics & Astronomy, Trent University, 1600 West Bank Drive, Peterborough, Ontario, Canada, K9J 7B8. Tel.: +1 705 748 1011; fax: +1 705 748 1652.

E-mail address: sureshnarine@trentu.ca (S.S. Narine).

surgical materials, tissue engineering materials as well as carriers in drug delivery systems [4,6]. Most of today's plastics and polymeric materials are made from petroleum-based products. However, in the last few years, environmental issues and concerns have drawn significant attention to petroleum-based products, especially in polymeric materials. Petroleum-based polymers are generally non-degradable, and are implicated in the pollution of the natural environment. Petroleum is also regarded as a finite and dwindling resource. The desire to obtain various products from non-toxic natural resources, and use bio-based renewable products as alternatives for the petroleum-based products is increasing in our society [8–17].

Several investigations have been conducted on producing PEAs from bio-based sustainable resources, such as linseed oil, nahar seed oil and pongamia glabra oil [18–20]. However, the building blocks chosen to connect the lipid-based monomers were not from natural resources, and were mostly toxic. The toxicity of these PEAs limits their applications and motivates the development of alternative building blocks. Several other fatty acid-based PEAs were studied and synthesized from sustainable resources; however, the fatty acid chosen, e.g., gallic acid [21], was much less abundant than oleic acid.

This present study is targeted at the development of lipid-based polymers that would be tough, thermally stable and biodegradable, yet be safe to use in a wide variety of areas. In particular, introducing amide units to enhance the material's cohesion thorough



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hydrogen bonding is proposed. In order to understand the structure—property relationship and assess any underlying trend, three PEAs with different ratios of ester to amide groups, i.e., 1:1 (PEA (I)), 1:2 (PEA (II)) and 1:3 (PEA (III)) were prepared. The lipid-based, non-toxic components, oleic acid-derived diol, amino acid and azelaoyl chloride (also derived from oleic acid) were chosen as the building blocks of the new polymeric materials. Furthermore, the synthesis procedures were simple and performed under mild conditions. The PEA samples were synthesized with similar number average molecular weights, in the  $2.08 \times 10^4$  to  $2.26 \times 10^4$ range, to enable comparison of their physical properties. Wide angle X-ray diffraction (WAXD), DSC, TGA, DMA and tensile techniques were used to investigate the crystal structure, and thermal and mechanical properties of the polymers.

## 2. Experimental

#### 2.1. Materials

All reagents, Oleic Acid (90% purity), Potassium hydroxide (KOH), Potassium permanganate (KMnO<sub>4</sub>), Lithium aluminum hydride (LiAlH<sub>4</sub>), 1,3-propane diol, 4-(Dimethylamino) pyridine (DMAP), N, N'-Dicyclohexylcarbodiimide (DCC), sodium borohydride (NaBH<sub>4</sub>), Boc-Ala-OH (N-tert-butoxycarbonyl protected alanine), Trifluoroacetic acid (TFA), Azelaoyl chloride, N-methyl-2-pyrrolidone (NMP), and propylene oxide, were purchased from Sigma–Aldrich.

## 2.2. Synthesis of diols from oleic acid

#### 2.2.1. 1,9-Nonanediol

1,9-Nonanediol was synthesized by a two-step procedure, starting from oleic acid (Scheme 1). First KMnO<sub>4</sub> was used to oxidize the double bonds of the oleic acid, forming azelaic acid, following procedures in the literature [22] (Yield: 80%). 1,9-Nonanediol was then prepared according to the literature by reducing the azelaic acid with LiAlH<sub>4</sub> [23] (Yield: 88%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 3.67–3.62 (t, 4H, C<u>H</u><sub>2</sub>OH), 1.59–1.55 (m, 4H, C<u>H</u><sub>2</sub>CH<sub>2</sub>OH), 1.32 (m, 10H, C<u>H</u><sub>2</sub>). MS (ESI): calcd for C<sub>9</sub>H<sub>20</sub>O<sub>2</sub> 160.15, found *m*/*z* 183.0 ([M + Na]<sup>+</sup>).

## 2.2.2. Di-ester diol

Di-ester diol was synthesized by a two-step procedure as shown in Scheme 2.

Step 1. 1, 3-propane diol (7.6 g, 0.1 mol) and oleic acid (69 g, 90% purity, 0.22 mol) were dissolved in 200 mL of dichloromethane (DCM) in a round bottom flask. The reaction mixture was kept at 0 °C using an ice bath. DMAP (3.6 g,



Scheme 1. 1, 9-Nonanediol from oleic acid.

0.03 mol) was added, followed by adding DCC (49.4 g, 0.24 mol) slowly to the reaction mixture. The ice bath was removed and the reaction was stirred at room temperature for 24 h. The resulting mixture was filtered to remove the solid. The crude products were collected by evaporating DCM under vacuum. Column chromatography was used to purify the product (hexane/ethyl acetate 30:1) (Yield: 88%).

Step 2. Di-ester 3 (30.2 g, 0.05 mol) was dissolved in 300 mL of anhydrous ethanol in a three-necked round bottom flask and cooled to -20 °C using an ice salt bath. Ozone was bubbled into the solution with a flow rate of 5 L/min. The reaction was monitored by thin layer chromatography (TLC) until the starting material was gone. After the reaction, nitrogen was purged through the mixture for 20 min to remove the extra ozone in the flask. Next, 3.8 g NaBH<sub>4</sub> (0.1 mol) was slowly added into the ozonolysis mixture. The reaction was stopped after 4 h, and then water and dilute hydrochloride acid were added into the reaction mixture to eliminate the extra NaBH<sub>4</sub>. The resulting mixture was extracted by 2  $\times$  200 mL of ethyl acetate. The ethyl acetate phase was washed by brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude products were collected by removing the solvent under vacuum. The desired product was purified by recrystallization using ethyl acetate and hexanes with a ratio around 1:3 (Yield: 72%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 4.16–4.12 (t, 4H, C<u>H</u><sub>2</sub>OCOR), 3.64–3.61 (t, 4H, C<u>H</u><sub>2</sub>OH), 2.31–2.27 (t, 4H, C<u>H</u><sub>2</sub>COOR), 1.99–1.93 (m, 2H, C<u>H</u><sub>2</sub>CH<sub>2</sub>OCOR), 1.63–1.52 (m, 8H, C<u>H</u><sub>2</sub>CH<sub>2</sub>COOR and C<u>H</u><sub>2</sub>CH<sub>2</sub>OH), 1.36–1.27 (m, 16H, C<u>H</u><sub>2</sub>). MS (ESI): calcd for C<sub>21</sub>H<sub>40</sub>O<sub>6</sub> 388.28, found *m/z* 411.3 ([M + Na]<sup>+</sup>).

## 2.2.3. Tetra-ester diol

Tetra-ester diol was synthesized by a two-step procedure as shown in Scheme 3. First, tetra-ester 5 was synthesized by reacting the di-ester diol and oleic acid (Yield: 86%); the esterification reaction between diol and oleic acid has been described in the synthesis procedure of di-ester 3. Then tetra-ester diol was synthesized by breaking the double bonds and changing them to hydroxide groups, using ozonolysis and NaBH<sub>4</sub>. This reaction has been described in the synthesis of di-ester diol 4 (Yield: 50%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 4.17–4.03 (m, 8H, CH<sub>2</sub>OCOR), 3.66–3.61 (t, 4H, CH<sub>2</sub>OH), 2.32–2.26 (t, 8H, CH<sub>2</sub>COOR), 1.99–1.94 (m, 2H, ROCOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCOR), 1.61–1.53 (m, 24H, CH<sub>2</sub>CH<sub>2</sub>COOR and CH<sub>2</sub>CH<sub>2</sub>OH), 1.32–1.28 (m, 24H, CH<sub>2</sub>). MS (ESI): calcd for C<sub>39</sub>H<sub>72</sub>O<sub>10</sub> 700.51, found *m*/*z* 723.8 ([M + Na]<sup>+</sup>).

## 2.3. Polymerization

## 2.3.1. Syntheis of diamines

Because three polymers were synthesized in this study, a general synthesis procedure to prepare polymers is shown in Scheme 4 and described as follows. First, a selected diol (10 mmol) and Boc-Ala-OH (22 mmol) were dissolved in DCM in a round bottom flask. The flask was kept at 0 °C in an ice bath. DMAP (3 mmol) was then added to the mixture. DCC (24 mmol) was slowly added over 30 min. The ice bath was removed and the reaction was stirred at room temperature for 24 h, and the resulting mixture was then filtered. The crude products were collected by removing DCM under vacuum. Column chromatography was used to purify the product.

TFA was added drop wise to this product in DCM in a round bottom flask. The reaction was stirred at room temperature until the starting materials had all reacted; the reaction was monitored by TLC. After the reaction, DCM was evaporated by rotary



Di-ester diol 4

Scheme 2. Di-ester diol synthesized from oleic acid.

evaporation, and the residue was neutralized by a saturated sodium bicarbonate (NaHCO<sub>3</sub>) solution to a pH value of 8 or 9. The diamine was extracted by chloroform (CHCl<sub>3</sub>) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated by reduced pressure and the residue was purified by column chromatography with ethyl acetate, methanol and ammonium hydroxide (100/10/1).

HO

Diamine (I) was synthesized from 1,9-Nonanediol (Yield: 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 4.13–4.06 (m, 4H, CH<sub>2</sub>OCOR), 3.63–3.53 (m, 2H, NH2CHCOOR), 2.13–2.06 (m, 4H, CH<sub>2</sub>), 1.65–1.58 (m, 4H, CH<sub>2</sub>), 1.38–1.23 (m, 12H, CH<sub>2</sub>, CH<sub>3</sub>).

Diamine (II) was synthesized from di-ester diol (Yield: 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 4.12–4.03 (m, 8H, CH<sub>2</sub>OCOR), 3.53–3.47 (m, 2H, NH2CHCOOR), 2.28–2.24 (t, 4H, CH<sub>2</sub>COOR), 1.97–1.89 (m, 2H, ROCOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCOR), 1.61–1.56 (m, 12H, CH<sub>2</sub>), 1.32–1.28 (m, 18H, CH<sub>2</sub>, CH<sub>3</sub>).

Diamine (III) was synthesized from tetra-ester diol (Yield: 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 4.15–4.01 (m, 12H, CH<sub>2</sub>OCOR), 3.61 (m, 2H, NHCHCOOR), 2.29–2.25 (m, 8H, CH<sub>2</sub>COOR), 1.96–1.93 (m, 2H, ROCOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OCOR), 1.60–1.54 (m, 24H, CH<sub>2</sub>), 1.37–1.22 (m, 30H, CH<sub>2</sub>, CH<sub>3</sub>).

2.3.2. Polymerization

OH

PEA was synthesized by conventional low-temperature solution polymerization, and propylene oxide was used as a hydrogen chloride acceptor in this reaction [24]. The polymerization procedure is described here only for PEA (I). Diamine (I) (4.00 g, 7.55 mmol) was added in a round bottomed flask with 24 mL of NMP under nitrogen gas; the reaction mixture was cooled at 0 °C using an ice bath. Propylene oxide (2.8 mL) and 1.70 g (7.55 mmol) dichloride (Azelaoyl chloride) was added to the solution successively. The solution was stirred at 0 °C for half an hour, and then the ice bath was removed. After reacting at room temperature for 28 h, the reaction mixture was precipitated into 200 mL of aqueous methanol (CH<sub>3</sub>OH:H<sub>2</sub>O = 3:1 v/v). The polymer was settled for 12 h. PEA was then collected by vacuum filtration, washed with water and dried in a vacuum oven at 50 °C for 2 days.

2.3.2.1. PEA (I). IR (cm<sup>-1</sup>): 3306 (N–H stretching), 2926, 2852 (C–H stretching), 1736 (ester carbonyl stretching), 1643 (amide carbonyl stretching), 1539 (C–N–H deformation). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.37 (d, NH), 4.59–4.52 (m, NHCHCOOR), 4.15–4.02 (m,



Tetra-ester diol 6

Scheme 3. Tetra-ester diol synthesized from di-ester diol.





 $\begin{array}{l} CH_2OCOR), 2.21-2.18 \ (m, CH_2COOR), 1.61-1.60 \ (m, CH_2), 1.38-1.29 \\ (m, CH_2 \ and CH_3). \ ^{13}C \ NMR \ (CDCl_3, 300 \ MHz) \ \delta \ (ppm): \ 173.5 \ (O-C=0), 173.0 \ (NH-C=0), \ 65.8 \ (COOCH_2), \ 48.2 \ (NHCHCOOR), \ 36.5 \\ (CH_2C=0), \ 29.5, \ 29.4, \ 29.2, \ 29.1, \ 28.7, \ 25.9, \ 25.7 \ (CH_2), \ 18.8 \ (CH_3). \\ Yield: \ 81\%. \end{array}$ 

2.3.2.2. *PEA* (*II*). IR (cm<sup>-1</sup>): 3311, 2928, 2852, 1738, 1647, 1537. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.15–6.13 (d, N<u>H</u>), 4.55–4.48 (m, NHC<u>H</u>COOR), 4.11–4.01 (m, C<u>H</u><sub>2</sub>OCOR), 2.28–2.12 (t, C<u>H</u><sub>2</sub>COOR), 1.93–1.87 (m, C<u>H</u><sub>2</sub>), 1.56–1.48 (m, C<u>H</u><sub>2</sub>), 1.34–1.24 (m, C<u>H</u><sub>2</sub> and C<u>H</u><sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 173.9, 173.5 (O–<u>C</u>=O), 172.9 (NH–<u>C</u>=O), 65.8, 61.0 (COOC<u>H</u><sub>2</sub>), 48.2 (NHCHCOOR), 36.6, 34.4 (CH<sub>2</sub>C=O), 29.3, 29.2, 29.1, 28.7, 28.2, 25.9, 25.6, 25.1 (CH<sub>2</sub>), 18.9 (CH<sub>3</sub>). Yield: 78%.

2.3.2.3. *PEA* (*III*). IR (cm<sup>-1</sup>): 3311, 2928, 2854, 1732, 1645, 1537. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 6.13–6.12 (d, N<u>H</u>), 4.58–4.54 (m, NHC<u>H</u>COOR), 4.14–4.01 (m, C<u>H</u><sub>2</sub>OCOR), 2.29–2.16 (t, C<u>H</u><sub>2</sub>COOR), 1.97–1.91 (m, C<u>H</u><sub>2</sub>), 1.60–1.55 (m, C<u>H</u><sub>2</sub>), 1.38–1.28 (m, C<u>H</u><sub>2</sub> and C<u>H</u><sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 174.1, 173.9, 173.6 (O–<u>C</u>=O), 172.9 (NH–<u>C</u>=O), 65.8, 64.6, 61.0 (COOC<u>H</u><sub>2</sub>), 48.2 (NHCHCOOR), 36.6, 34.5, 34.4 (CH<sub>2</sub>C=O), 29.4, 29.3, 29.2, 29.1, 28.8, 28.7, 28.2, 26.1, 26.0, 25.6, 25.1 (<u>C</u>H<sub>2</sub>), 18.9 (<u>C</u>H<sub>3</sub>). Yield: 76%.

## 2.4. Characterization techniques

<sup>1</sup>H NMR was used to qualitatively analyze the products, and was recorded at a larmor frequency of 400 MHz, using a Varian Unity

400 NMR spectrometer (Varian, Inc., Walnut Creek, U.S.A.). Mass spectra were acquired on a Quattro LC (Micromass) electrospray ionization (ESI) mass spectrometer with a syringe pump (Harvard). FTIR spectra were measured with a Thermo Scientific Nicolet 380 FTIR spectrometer (Thermo Electron Scientific Instruments LLC, U.S.A.) fitted with a PIKE MIRacle<sup>TM</sup> attenuated total reflectance (ATR) system (PIKE Technologies, Madison, WI, U.S.A.). The samples for FTIR testing were made into 0.5 mm thick films and placed onto the ATR crystal area and held in place by the pressure arm. The molecular weight and distribution were determined by Gel Permeation Chromatography (GPC) (Waters, MA). The test was carried out with a Waters e2695 pump, Waters 2414 refractive index detector and a Styragel HR5E column (5 um). Chloroform was used as eluent with a flow rate of 1 mL/min. The sample was made with a concentration of 4 mg/mL, and the injection volume was 30 µl for each sample. Polystyrene (PS) Standards were used to calibrate the curve.

Thermogravimetric Analysis (TGA) was carried out using a Q500 (TA instrument, New Castle, DE, U.S.A.) following the ASTM D3850-94 standard to test the thermal stability of the synthesized PEAs. The polymer samples were loaded in the form of powders. Samples were heated from room temperature to 700 °C under dry nitrogen at a constant heating rate of 10 °C/min.

The DSC measurements have been carried out on a temperature modulated DSC Q200 model (TA Instruments, New Castle, DE) equipped with a refrigerated cooling system. During the heating process, measurements were performed with a modulation amplitude of 1 °C/min and a modulation period of 60 s. The measurements were performed at least in triplicate following the ASTM E1356-03 standard procedure. Approximately 5.0–10.0 ( $\pm$ 0.1) mg of sample was placed and sealed in an aluminum DSC pan. An empty aluminum pan was used as a reference and the experiments were performed under a nitrogen flow of 50 mL/min. The "TA Universal Analysis" software coupled with a method developed by our group [25] was used to analyze the data and extract the main characteristics, i.e.,  $T_{g}$ ,  $T_{On}$ ,  $T_{Off}$  and  $T_{m}$  (glass transition, onset, offset, and peak maximum temperature, respectively) and enthalpy,  $\Delta H$ . The characteristics of the non-resolved individual peaks and shoulder signals were estimated using the first and second derivatives of the signal and a simple decomposition of the signal into its obvious main components.

A first DSC heating cycle was performed on the preformed PEA. In this experiment, the sample which was ambient cooled was heated from room temperature (10 °C/min) to 140 °C to record the development of the phases preformed. In a second set of experiments, the sample was equilibrated at 140 °C, and held at that temperature for 5 min to erase the thermal history; then cooled down to  $-60^{\circ}$  with a cooling rate of 5 °C/min. In the heating cycle, the sample was heated with a constant heating rate of 3 °C/min from  $-60^{\circ}$ C to 140 °C.

The viscoelastic properties of PEAs were tested by a dynamic mechanical analyzer (DMA), model Q800 (TA Instruments, New Castle, DA,) equipped with a liquid nitrogen cooling system. The samples were into cut а rectangular shape (17.5 mm  $\times$  10 mm  $\times$  0.5 mm) and were analyzed in a single cantilever mode. The samples were heated under a constant rate of 2 °C/min over a temperature range of -60 °C to 40 °C. The measurements were performed following the ASTM E1640-99 standard at a frequency of 1 Hz and fixed oscillation displacement of 15 µm.

The measurements of tensile strength and tensile strain were obtained using a Texture Analyser (TA HD, Texture Technologies Corp, NJ, U.S.A.) equipped with a 2 kg load cell. Tensile tests were performed on PEAs processed into films using a simple hot-press technique. The samples were die cut by an ASTM D638 type V cutter to determine the mechanical properties of the polymer. Tensile strength and elongation were tested at a temperature of 20 °C. The sample was stretched at 50 mm/min from a gauge of 35 mm.

Crystallinity and crystalline structures were examined by wide angle X-ray diffraction (WAXD). X-ray diffraction was carried out by an EMPYREAN diffractometer system (PANalytical, The Netherlands) equipped with a filtered Cu-K $\alpha$  radiation source ( $\lambda = 1.540598$  Å), and a PIXcel-3D area detector. The scanning range for PEA samples was from 3.3° to 80° (2 $\theta$ ) with a step size of 0.026°, 2920 points were collected in this process. The application software was Data Collector 3.0, and the data were analyzed using X'Pert HighScore 3.0 software.

## 3. Results and discussion

## 3.1. Characterization

The chemical structure of the synthesized polymers was confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR and FTIR spectroscopy. All three PEAs demonstrated similar number average molecular weight  $(M_n)$ . The molecular weights and distribution values of PEAs as determined by GPC are listed in Table 1.

The <sup>1</sup>H NMR characteristic peaks of the amide and ester linkages of the PEAs were observed at 6.37-6.12 and 4.15-4.01 ppm, respectively (Fig. 1). These two peaks are characteristic of the hydrogen atom attached to the nitrogen in the amide linkage and the methylene groups adjacent to the oxygen in the ester linkage, respectively. The ratio of the 6.37–6.12 to 4.15–4.01 ppm peak integrals was 1:2 for PEA (I), 1:4 for PEA (II) and 1:6 for PEA (III). This is consistent with the actual ratio of ester to amide groups in the PEA structures since the integration of the 6.37–6.12 ppm peak provides the amount of the amide linkages and the integration of the 4.15–4.01 ppm provides twice the amount of ester linkages.

The <sup>13</sup>C NMR results were also fully consistent with the actual ester to amide ratios in the PEA structures as revealed by the type of ester and amide observed. The analysis of the <sup>13</sup>C NMR peaks which represent the carbon atom in ester carbonyl (in the range of 174.1–173.5 ppm), and the peak which represent the carbon atom in the amide carbonyl (at 172.9 ppm or 173.0 ppm) indicated that only one type of ester and one type of amide are shown in the spectrum of PEA (II), two types of ester and one type of amide in the spectrum of PEA (II) and three types of ester and one type of amide in PEA (III).

The IR spectra fully confirmed the anticipated chemical structures. As can be seen in Fig. 2 representing the IR of the three PEAs in the 4000–700 cm<sup>-1</sup> range, the absorption bands characteristic of the ester carbonyl stretching vibration are observed at 1736 cm<sup>-1</sup>, and the infrared bands characteristic of amide groups, i.e., N–H stretching vibrations, amide carbonyl stretching vibrations (Amide I), and C–N–H deformation vibrations (Amide II) are found at 3300 cm<sup>-1</sup>, 1645 cm<sup>-1</sup> and 1537 cm<sup>-1</sup>, respectively [26,27]. The ratio of C=O (ester) peak area to the N–H (amide) peak area was 0.62 for PEA (I), 1.27 for PEA (II), and 1.90 for PEA (III), i.e., a 1:2:3 series, consistent with the actual ratio of ester to amide groups in the PEA (I):PEA (II):PEA (III) structures.

#### 3.2. Hydrogen bonding structures of the PEAs

The chemical structure of PEAs repeat units and hypothetical arrangements of the hydrogen bonding structures in the synthesized PEAs with ester to amide ratio of 1:1, 2:1 and 3:1 are shown in Fig. 3a–c, respectively. PEA (I) has a repeating unit with the shortest chain length (molar mass of 484 g/mol), followed by PEA (II) (molar mass of 712 g/mol and a chain length ~30% longer), then PEA (III) (molar mass of 1025 g/mol and a chain length ~30% longer than PEA (II)). Due to the existence of one amide group in each structure, the polymer chains are anchored by two hydrogen bonding sites, regardless of the chain length, imparting a decreasing hydrogenbond density from PEA (I) to PEA (II) to PEA (III). The data related to the repeating units and the hydrogen bonding of the PEAs are listed in Table 2.

#### 3.3. Thermal and phase behavior of PEAs

Fig. 4a displays the TGA thermogram profiles of the PEAs obtained under a constant nitrogen flow. Overall, the three PEAs were found to be thermally stable to around 300 °C and to have similar complex decomposition behavior as clearly displayed by the TGA derivative curves (Fig. 4b). However, PEA (III) displayed slightly higher thermal stability compared to PEA (I) and PEA (II), explainable by its relatively higher molecular weight, a parameter known to affect proportionally the decomposition temperature [28,29].

Table 1

GPC results of the PEAs ( $M_n$  is the number average molecular weight;  $M_w$  is the weight average molecular weight; PDI =  $M_w/M_n$ ).

	M <sub>n</sub>	M <sub>w</sub>	PDI
PEA (I)	$2.08 \times 10^4$	$2.98 \times 10^4$	1.43
PEA (II)	$2.09 \times 10^4$	$3.44 \times 10^4$	1.64
PEA (III)	$2.26\times10^4$	$3.63\times10^4$	1.61



Fig. 1. <sup>1</sup>H NMR spectra of the polyester amides with varying ratios of ester to amide linkages. (a) PEA(I): ester: amide = 1:1, (b) PEA(II): ester: amide = 1:2, (c) PEA(III): ester: amide = 1:3.



**Fig. 2.** FTIR spectra of the polyester amides with varying ratios of ester to amide linkages. PEA (II): ester:amide = 1:1, PEA (II): ester:amide = 1:2, PEA (III): ester:amide = 1:3.

The different decomposition stages and the degradation temperatures of each stage were associated with specific common decomposition processes of the PEAs. The two initial stages of decomposition were attributed to the breakage of the ester and amide linkages, respectively, based on similar degradation studies on PEA using combined differential thermal gravimetry (DTG) and FTIR techniques conducted by Sudha and Pillai [30]. A thermal degradation study comparing the weight loss for polyester amide copolymers with varying ratios of ester and amide blocks also suggested that the first decomposition event is attributable to the ester blocks, and the second to the amide blocks [31].

The DSC thermogram obtained by heating (10 °C/min) the preformed polymer films to 140 °C and referred to as the first heating cycle is shown in Fig. 5a. The second DSC heating (3 °C/min) thermogram obtained after the sample was crystallized from the melt (140 °C) at a rate of 5.0 °C/min down to -60 °C then heated (3 °C/min) is shown in Fig. 5b. The apparent glass transition, melting and melt-crystallization temperature, and enthalpy of melting ( $T_{g}$ ,  $T_{m}$ ,  $T_{mc}$ , and  $\Delta H_{m}$ , respectively) of the PEAs obtained from the two cycles are listed in Table 3.



**Fig. 3.** Chemical structure of repeat units and hypothetical arrangements of the hydrogen bonding structures in the synthesized PEAs with ester to amide ratio of (a) 1:1; (b) 2:1; (c) 3:1.

#### Table 2

Structural and hydrogen-bond information of the PEAs.

	PEA (I)	PEA (II)	PEA (II)
Molar mass of the repeating unit (g/mol)	484	712	1025
Number of HB sites per repeating unit	2	2	2
Total HB sites in each polymer	86	58	44
Length of the repeating unit (Å)	31	48	73
Hydrogen-bond density (1/Å)	0.065	0.042	0.028

HB: Hydrogen bonding.

The thermograms obtained by heating the preformed samples displayed a glass transition and three endotherms (Fig. 5a). Note that beside the prominent endotherm, PEA (I) showed also two very small and well-resolved endotherms (not evident but indicated by arrows in Fig. 5a and listed in Table 3). The first endothermic event observed in PEA (II) and PEA (III) showed as a leading shoulder to the more important and well-resolved peak, indicating the overlap of two melting events. Obviously, two solid phases having different crystal stabilities were involved. Note that the peak maxima were well located using the first and second derivative of the heat flow signal, but only their combined area has been measured (values listed in Table 4). PEA (I) did not show any exotherm, whereas, PEA (II) and PEA (III) displayed a broad and intense exotherm following the two first unresolved endotherms.

The recording of an exotherm in both PEA (II) and PEA (III) is characteristic of melt crystallization. As the temperature was increased, their polymer chains acquired more mobility, recrystallized from the melt into their most stable form possible then subsequently melted.

Note that the enthalpy of melting recorded for the combined first two peaks of PEA (I) and PEA (II) was 30 J/g, practically the same value of the total enthalpy recorded in the melting of PEA (I). This low value can be linked to the relatively low crystallinity achieved in these samples as will be discussed in the crystalline structure section. This constant value of the enthalpy of melting irrespective of the repeating unit length indicates the crucial importance of the total hydrogen bonding in the polymorphism of the PEAs, for the preformed polymers. However, the recording of an overlap between these endotherms and the following exotherm indicated that the enthalpy of melting of the second phase was not totally recorded, alluding to other important contributions to the polymorphism of the PEA, such as the van der Waals forces.

The differences observed in the transformation paths are explainable by the relative size of the repeating units and hydrogen bonding density. The cooling at room temperature of the preformed polymers was probably slow enough to allow for the shorter chains with the densest hydrogen bonding structure of PEA (I) to pack preponderantly in a relatively well-developed, thermodynamically most stable phase (melts at the highest temperature of 87.8 °C). For the same processing conditions, the polymer chains of PEA (II) and PEA (III), which are longer and have significantly lower hydrogen bonding density than PEA (I), thermodynamically less stable solid phases were formed.

The lower temperature of melting of the crystals detected in the preformed PEA (III) compared to those in PEA (II) (49 vs. 55 °C) is not insignificant – PEA (II) has 30% shorter repeating units. meaning that PEA (II) chains are relatively easier oriented, allowing for more stable crystal packing, and of course, PEA (II) has significantly denser hydrogen bonding, resulting in more attractive forces acting in the crystal lattice. Indeed, this trend of course is strongly supported with the significantly higher melt temperature of the crystals formed by PEA (I). It should also be noted that the DSC scans do not indicate that the entire polymer in any case was crystalline - indeed, since we did not have either a totally amorphous polymer or totally crystalline polymer for comparison purposes, DSC is not useful in ascertaining the degree of crystallinity. However, as will be discussed later, WAXD scans of the polymers studied indicate a significant amount of the polymer chains existed in amorphous form. Additionally, as is also discussed later, WAXD measurements support the presence of different type of crystals in the polymers.

The second DSC heating cycle shown in Fig. 5b further supports the arguments proffered above to explain the first melting cycle. The melted polymer films in this case were cooled at a rate of 5 °C/ min, a relatively much faster cooling rate than the ambient cooling for the formation of the polymer films the first time. Interestingly, at this faster rate, even the relatively short repeating units in PEA (I) are unable to orient before the glass transition temperature is reached, but as the polymer is melted, above the  $T_{g}$ , chains acquire enough molecular mobility to orient and a burst of crystallization is experienced, these crystals then immediately remelting at the melt point of 87.2 °C as before. This behavior is seen also with PEA (II), with a burst of crystallization occurring above the  $T_{g}$ , although again because of the relatively longer chain segments and because of the smaller density of hydrogen bonding sites, the types of crystals formed through the relatively limited mobility of the chains above T<sub>g</sub> are weaker, less organized crystals compared to the most thermodynamically stable crystal type possible to be formed by this polymer. These less stable crystals melt, and mediate a second crystallization event, the most thermodynamically stable crystals then finally melt at 76.2 °C. The effect of lower density of hydrogen bonding and longer repeating segments is exacerbated in PEA (III) as evidenced by the very small crystallization event which occurs above the  $T_{\rm g}$  (indeed the extent of the crystallization event above the  $T_g$  steadily decreases from PEA (I) to PEA (II) to PEA (III)). As with PEA (II), the relatively weak crystals formed are melted



Fig. 4. TGA (a) and TGA derivative (b) curves of PEAs at a heating rate of 10 °C/min.



Fig. 5. DSC heating thermograms of the PEAs (a) First heating cycle obtained by heating (10 °C/min) the preformed polymers. (b) Second heating cycle obtained by heating (3 °C/min) a sample crystallized (5 °C/min) from the melt.

immediately after the initial crystallization event, which mediates a sharp crystallization event of the most stable crystals, which melt, together with the finite amount of thermodynamically most stable forms which may have formed during cooling, at the temperature of 74.3 °C as before. The shifts in the melting peak maximum of the most stable thermodynamic forms of crystals for the three PEAs between the first and the second heating cycles is not unexpected the melting events are broad and there is an annealing effect caused by successive melting and crystallization, resulting in slight changes to packing. However, the relative differences between these events are similar, so that the analysis can be with confidence conducted in the manner it was above.

The  $T_g$  obtained by DSC versus hydrogen bonding density is displayed in Fig. 6. The PEA type is reported in the top axis of the figure. As can be seen,  $T_g$  was highest for PEA (I) followed by PEA (II) then PEA (III). The relatively large drops in  $T_g$  as the ester to amide ratio was increased can be well explained by the hydrogen bonding structure of the polymers. The intermolecular hydrogen bonds present in PEA, due to the amide groups, contribute significantly to preventing the mobility of the polymer chains. As the chain length between amide groups increases, hydrogen-bond density decreases from its highest value in PEA (I) to its lowest in PEA (III)

## Table 3

Melting values obtained from the heating cycles of the PEAs. The peak temperature of the endotherm and exotherm ( $T_{\rm m}$  and  $T_{\rm mc}$ , respectively) are numbered from the highest to the lowest temperature. Enthalpy (in J/g) is the area under the peak. The  $T_{\rm g}$  values obtained from DMA measurements (Peak of tan  $\delta$ ) are listed for comparison purposes.

	1st heating cycle			2nd heating cycle				
T (°C) PEA (I) ΔH (J/g) PEA (II) ΔH (J/g) PEA (III)	T <sub>m1</sub> 87.8 25 77.4 44 76.0	T <sub>mc</sub> NA NA 56.0 30 58.8	T <sub>m2</sub> 64.9 1 49.3 29 54.9	T <sub>m3</sub> 45.3 4 40.0 41.0	T <sub>m1</sub> 87.2 33 76.2 48 74.2	T <sub>mc1</sub> 66.1 33 52.5 31 55.8	T <sub>m2</sub> NA 48.0 9 50.4	T <sub>mc2</sub> NA 14.2 24 31.9
$\Delta H$ (J/g)	50	32	30		56	32	22	1.5
$T_{\rm g}(^{\circ}{ m C})$								
	DSC DMA							
PEA (I) PEA (II) PEA (III)	$\begin{array}{ccc} 3.4\pm0.8 & 17.9\pm0.3 \\ -20.0\pm0.3 & -1.6\pm0.1 \\ -34.1\pm0.1 & -15.0\pm0.1 \end{array}$							

NA: not applicable.

(see Fig. 3) requiring lower temperatures to initiate the movement of the chain segments, thus yielding lower  $T_{g}$ . It is also worth noting that the hydrogen bonding is not only limited to the amide-ester groups shown in Fig. 3, but may also extend to ester groups adjacent to the primary ester groups indicated in the figure. This would result of course in some heterogeneity in the degree of hydrogen bonding, as the polymer chains themselves are also mobile, bringing adjacent ester groups closer or further away from the amide linkages. This heterogeneity will further contribute to a deviation from linearity of the dependence of  $T_g$  on the primary hydrogen-bond density as presented in Fig. 6. However, the effect of the primary (as drawn in Fig. 3) hydrogen-bond density was predominant in this study as indicated by the approximately linear change of  $T_g$  vs. hydrogen-bond density displayed in Fig. 6. The above structural considerations also of course extend to the mechanical properties of the polymers, and therefore although in succeeding sections only the predominant effects of the primary hydrogen-bond density is discussed in detail, it is meant to be understood that there is a certain level of heterogeneity in the hydrogen bonding of the polymer chains. The information of  $T_{\sigma}$ change in relation to the ester to amide ratio can help in the design of similar structures derived from oleic acid, with targeted  $T_{g}$  values according to the required application conditions.

Multiple melting behavior of polymers, related to the formation of different polymorphs due to limited mobility of the long polymeric chains have been noted by numerous studies, and in particular for polyesters and polyester amides [31–34]. Although the thermal stability was not affected by the ester to amide ratio from the thermal decomposition perspective, it was affected at the melting level – with the crystals formed by PEA (I) being more thermally stable than those formed by PEA (II), which in turn are more stable than those formed by PEA (III). This motivates the postulate that the thermal behavior of the PEAs is indeed significantly affected, but only at the  $T_g$  and the crystalline melting levels, i.e., phase development, not at the degradation of the polymer

able 4	
lechanical properties of the PEAs obtained from tensile analysis.	
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	Ultimate strength (MPa)	Maximum strain (%)	Young's modulus (MPa)
PEA (I)	$19.6\pm0.3$	$12.4\pm0.8$	$586\pm7$
PEA (II)	$10.2\pm0.1$	$14.3\pm0.3$	$310\pm3$
PEA (III)	$8.5\pm0.1$	$11.8\pm0.8$	$234\pm4$



**Fig. 6.**  $T_g$  value obtained by DSC as a function of hydrogen-bond density. The ester to amide ratio is reported on the top axis. The dashed line is a fit to a line ( $R^2 = 1.000$ ).

linkages. That is, it seems that the degradation of the ester and amide linkages are unaffected by the fact that they are both present in a single polymeric chain, at least in these polymers.

## 3.4. Mechanical properties of the PEAs

Fig. 7 displays the storage moduli of PEAs as a function of temperature. It was shown that the storage modulus decreased as the ester to amide ratio changed from 1:1 to 2:1 and to 3:1. It was also worth noting that the stored energy at room temperature (around 20 °C) was largely reduced from PEA (I) to PEA (II), but the reduction was much smaller from PEA (II) to PEA (III). As explained above, PEA (I) had approximately 86 hydrogen-bond sites in a linear chain, whilst PEA (II) had 58 and PEA (III) had 44. Clearly, there was a large decrease in the density of hydrogen bonding between PEA (I) and PEA (II), but not as drastic a decrease between PEA (II) and PEA (III). This trend of mechanical properties was further confirmed by the results of tensile analysis.

The value of tan  $\delta$  (Fig. 8) may also be analyzed for each PEA film to investigate elasticity of the polymer. Because tan  $\delta$  is the ratio of loss modulus to storage modulus, it is the ratio of viscous to elastic components of the modulus (tan  $\delta = E''/E'$ ). The smaller tan  $\delta$  is, the larger the E' is relative to E'', which means more of the energy



Fig. 7. Storage modulus as a function of temperature measured by DMA for PEAs.

required to deform the sample is elastically recovered instead of being dissipated as heat [35]. It is clearly shown in Fig. 8 that at room temperature (around 20 °C), tan  $\delta$  decreases from PEA (I) to PEA (III), indicating that the film of PEA (III) had the highest rubbery elasticity, and the film of PEA (I) recorded the lowest.

The  $T_g$  was also investigated by DMA under a frequency of 1 Hz.  $T_g$  values reported as the peak value of tan  $\delta$  are listed along the  $T_g$  values obtained by DSC in Table 3. Because DSC measures the changes of heat capacity during the glass transition, whereas, DMA measures the mechanical response of the polymer chains during the transition; the respective recorded values for  $T_g$  value are different. The trend is however the same.

Mechanical properties were also examined using tensile analysis. The tensile stress versus strain curves of the PEAs are displayed in Fig. 9. The slope of the linear segment in each curve (shown as extended straight lines in Fig. 9) is used to determine Young's modulus. The ultimate tensile strength, maximum strain and Young's modulus for PEAs are listed in Table 4. PEA (I) has the highest ultimate tensile strength (19.6 MPa) followed by PEA (II) (10.2 MPa) then PEA (III) with the lowest ultimate tensile strength (8.5 MPa).

The difference in ultimate tensile strength (Fig. 10) between PEA (I) and PEA (II) is much larger (9.4 MPa) than the difference between PEA (II) and PEA (III) (1.7 MPa), outlining the dramatic effect of hydrogen bonding density on tensile properties of the PEAs, in accordance to what has been discussed earlier to explain the dynamic mechanical properties of the PEAs.

Young's modulus (Table 4) was determined by the slope of the linear segment in the stress versus strain curve. The Young's modulus decreased dramatically with hydrogen-bond density, (Fig. 11) indicating a monotonous dependence on hydrogen bonding. The addition of a first amide block decreased the value of Young's modulus by 47%, whereas the second decreased it by a further 25%, which if the uncertainty attached to the measurements is taken into account, is consistent with the amide ratio 1:2:3 of the PEAs. This trend can help to design oleic acid-derived PEA structures with targeted mechanical properties.

Fig. 9 also shows that the elongation at break is statistically similar for PEA (I) and PEA (III), but it is higher for PEA (II). At this time, we can find no structural reason for this noted difference.

## 3.5. Crystalline structure

The crystalline structure of the PEA samples was investigated by wide angle X-ray diffraction (WAXD). The WAXD patterns of PEA (I),



**Fig. 8.** Tan  $\delta$  as a function of temperature measured by DMA for PEAs.



Fig. 9. Tensile stress versus strain curves of PEAs. The straight lines are extensions of the linear segment in each curve.

(II) and (III) shown in Fig. 12, suggest similar but complex polymorphic structures. The WAXD patterns present a large amorphous halo and resolved diffraction peaks indicative of the semicrystalline nature of the samples. It is well known that the X-ray scattering pattern of an amorphous polymer contains one or more halos corresponding to van der Waals spacings or larger [36]. As customarily done in the case of semicrystalline polymers, the amorphous contribution was fitted with a linear combination of two amorphous profiles and were located at the diffraction angles  $(2\theta)$  of approximately 10.5° and 19.3°, similarly to what has been reported in several papers (see for example [37–39]).

The presence of halos indicates the existence of a degree of packing regularity in amorphous polymers that should be considered in understanding of polymer chain conformation [40]. As usually done for similar polymers which do not have any side chains, the amorphous profiles were attributed to interchain distances in the amorphous phase ( $d_{amorph}$ ) which were calculated using the relation [41]:

 $d_{\rm amorph} = 1.11 \times d_{\rm Bragg}$ 

where  $d_{\text{Bragg}}$  is the largest Bragg *d*-spacing of the two amorphous profiles.



**Fig. 10.** Ultimate strength of PEAs in this study as a function of hydrogen-bond density. Sample type is reported on the top axis.



Fig. 11. Young's modulus of PEAs as a function of hydrogen-bond density. Sample type is reported on the top axis.

The observed intensities of the crystalline phases were evaluated by integrating the crystalline peaks observed in the X-ray diffraction profiles, after the subtraction of the background and amorphous contributions. The relative crystallinity was obtained from the integrated intensity over the observed Bragg reflections normalized by that over the whole WAXS profile. Results of WAXD data analysis are summarized in Table 5.

Under the right conditions, almost all of the semicrystalline polymers can form different polymorphs. Because the thermal and mechanical studies indicated a very strong effect of the hydrogen bondings, we will discuss the crystal structure of the PEAs in light of the polymorphism reported for the polyamides. Note that



**Fig. 12.** Wide angle X-ray diffraction patterns of preformed PEA films measured at room temperature. (a) PEA (I) with ester:amide = 1:1; (b) PEA (II) with ester:amide = 2:1; (c) PEA (III) with ester:amide = 3:1.

similarities can be drawn from the structures reported for other crystalline polymers such as particularly polyesters [42–45] or poly (vinylidene fluoride) [46–49]. However, because there is no common labeling scheme for the different forms observed in the (semi)crystalline polymers, a comparative analysis, which is not the topic of our report, would be onerous. The WAXD spectra were therefore primarily analyzed in light of the very extensively studied structures observed in nylon, a prominent member of the polyamide class of semicrystalline polymers [50].

Two sets of WAXD lines corresponding to two conformations similar to those observed in the case of Nylon have been isolated. The first set is constituted of the 20.1, 23.2 and 24.7° lines (4.41, 3.84 and 3.64 Å, respectively) and the second set 16.9 and 19.1 (5.24 and 4.64 Å, respectively). In addition to the peaks characteristic of the  $\alpha$  and  $\gamma$  crystals, there remains a diffraction peak at  $2\theta = 21.18^{\circ}$ , with a spacing of 4.2 Å related to another polymorph formed in the PEA samples.

The first set (4.41, 3.84 and 3.64 Å) corresponds to room temperature spacings from the (100), (010)/(110) and (1 $\overline{10}$ ) reflections of the  $\alpha$ -form and the second (5.24 and 4.64 Å) corresponds to the spacings from the (121), and (010) reflections of the so-called  $\gamma$ -form, both of which are well known to form in nylon [40,51,52]. Note that the  $\alpha$  structure is also well known for the *n*-alkanes [53]. The  $\alpha$ -phase has monoclinic structure, contains zig–zag chains with the hydrogen bonds situated between antiparallel chains, whereas, the  $\gamma$ -phase although also having a monoclinic structure, contains helical chains allowing hydrogen bonds to be formed between parallel chains [54]. The main structural difference between the  $\alpha$ - and  $\gamma$ -crystals come from the molecular packing within the unit cell. The  $\alpha$ -form in fact represents a variation from the helical to the planar (or nearly planar) zig–zag type of chains [55].

The diffraction peak at a spacing of 4.2 Å represents probably a hexagonal structure, which has also been reported for this type of material [50,56]. Note that these phases are known to possibly coexist with relative content of the phases depending on the processing conditions [57].

Quantitative evaluations of the relative content of the crystalline forms possibly present in the samples were estimated from the  $2\theta = 15^{\circ}-30^{\circ}$  region of the WAXD patterns. The percent content of the different forms in the crystalline fraction was estimated using the relation:

% Phase 
$$(i) = 100 \times \frac{A(i)}{\sum_{i} A(i)}$$

#### Table 5

Structural data obtained from the WAXD spectra of the PEAs:  $d_{hkl}$  is Bragg distance with the indices obtained by comparing the experimental reflection to similar forms observed in polyamides and polyesters.  $P_x$ ,  $P_y$ , and  $P_{H}$  are the relative phase contents of the  $\alpha$ -,  $\gamma$ -, and hexagonal phases, respectively.  $d_{amorph}$  is the interchain distance in the amorphous phase. Calculated uncertainties are ~5% as determined by the standard error obtained for three replicates.

α-form		γ-form		Hexagonal form		
d (Å)	(hkl)	d (Å)	(hkl)	d (Å	<b>(</b> )	(hkl)
4.4 3.8 3.6	(100) (010)/(110) (110)	5.2 4.6	(121) (010)	4.2		(100)
	$X_{ m cryst} \pm 5$ (%)	$d_{\mathrm{amorph}}\pm$ 0.5 (Å)		Relative phase content (%)		e
				$P_{\alpha}$	Pγ	P <sub>H</sub>
PEA (I)	45	10.7		33	27	40
PEA (II)	50	10.8		54	20	26
PEA (III)	52	10.3		52	24	24

where A(i) is the area of the characteristic peaks of  $i = \alpha$ ,  $\gamma$  and hexagonal phase. The results are listed in Table 5.

Taking into account the uncertainties attached to the calculations, one can notice that the estimated amount of  $\alpha$ -phase was the same in the three PEAs. The  $\gamma$ -phase increased from 33% in PEA (I) to  $\sim$  53% in both PEA (II) and PEA (III), whereas, the hexagonal phase decreased from 40 to  $\sim 25\%$ . Clearly, the lower hydrogen-bond density due to the addition of one amide block promoted the "twisted" phase at the detriment of the less stable hexagonal phase, whereas, a further addition of an amide block did not. The polymers' processing conditions have obviously limited the effect of hydrogen bonding distribution on further phase development. This limitation can be linked to size and mass effects. However, with increasing ester to amide ratio, a decrease in the width of the characteristic lines of the three phases was observed, indicating an increase in crystalline homogeneity and perfection. This ordering effect is therefore attributable to the ester blocks.

Also, the ester groups of the anti-parallel chains within the unit cell play an important role the formation of the  $\gamma$ -form as suggested by conformational analysis based on intramolecular potential energy calculations of poly- $\beta$ -hydroxybutyrate [58]. Similarly to this polymer, the ester groups in the PEAs may be nearly at the same level allowing for the dipole-dipole interaction to play a balancing role in the development of the molecular packing of the PEAs. It is therefore understandable that the  $\gamma$ phase content increase was not only due to the decrease in hydrogen bonding density but also that the electrostatic dipole-dipole interactions between the dipoles associated to the ester groups contribute considerably to the stabilization of the helical conformation of  $\gamma$ -form crystals as argued by De Santis and Kovacs [59] in the case of poly(S-lactic acid). The relatively higher width displayed by the characteristic lines of the  $\alpha$ -form indicates significant disorder both along and perpendicular to the chain axis similarly to what has been observed in several aliphatic polyesters such as PCL [60].

The structural features of the  $\alpha$ -,  $\gamma$ - and hexagonal forms and their relative amounts in the samples can explain the phase developement displayed by the DSC heating profiles of the different PEAs. The recorded thermal events (endotherms and recrystallization) are obviously related to the melting and further phase change of the preformed solid phases (solid  $\alpha$  and  $\gamma$ , and hexagonal form). Phase change in polymeric materials such as our PEAs is very complex. The  $\gamma$ -phase is stable and may be converted into the  $\alpha$ phase by melting and recrystallization [61] and the hexagonal phase can be converted into the  $\alpha$ -phase by annealing [51]. The similar and relatively low crystallinity (~50%) estimated from the WAXD patterns of the PEA can be related to the similar and low enthalpy of melting recorded for the melting of the solid phase already formed. The increase of  $(\gamma + \alpha)$  at the detriment of the hexagonal phase content as the ester to amide ratio increases can explain the differences in thermal behavior displayed by the samples as discussed in the melting behavior section.

## 3.6. Comparison of PEAs

#### 3.6.1. Comparison with lipid-based PEAs

Compared to other lipid-based PEAs [20,21,62,63], the polymers prepared in this study displayed superior decomposition stability and lower  $T_g$ , indicating that they can be used over a wider range of temperature. The above-cited studies did not report any mechanical property value or even mention if films were made or tested. As expected, the melting temperatures reported for PEAs presenting aromatic groups [21,63] were higher than those measured in PEA (I) to (III).

#### 3.6.2. Comparison with petroleum-based PEAs

The  $T_g$  and  $T_m$  of PEA (I)–(III) are well in the range of the values reported for petroleum-based PEAs and tensile strength is comparable [1,7,27,64–69]. The elongation measured in PEA (I)–(III) is rather smaller than most of reported values, but the elongation does not pose a problem if these PEAs were to be used as coating materials. The decomposition temperatures measured for our PEAs (~300 °C) are relatively lower compared to the ~340 °C reported by Lips et al. [27] or 380 °C by Amelin et al. [69], but are better compared to the 230–280 °C values reported in Refs. [64,65,68].

## 4. Conclusions

It was shown by TGA analysis that the thermal stability of the PEAs is not significantly influenced by the ratio of the ester to amide linkages. However, the melting point of PEAs decreased from PEA (I) to PEA (III), indicating a correlation to the decrease of ester to amide ratio.

The  $T_g$  values measured by DSC and DMA revealed that the  $T_g$  is largely affected by the hydrogen-bond density of the polymer. As the ester to amide ratio increased from 1/1 to 3/1, the hydrogen bonding sites in the polymer chains decrease and so does the  $T_g$ .

Mechanical properties were also significantly influenced by the hydrogen-bond density of the PEAs. tan  $\delta$  decreases from PEA (I) to PEA (III) at room temperature, indicating that elasticity of the polymer film increases from PEA (I) to PEA (III).

The storage modulus measured using DMA showed that the stored energy in PEAs decreased from PEA (I) to PEA (III). The tensile analysis also indicated that the ultimate tensile strength and the Young's modulus of the PEA were reduced when the hydrogen bonding decreases. However, the effects of ester to amide ratio on mechanical properties did not change linearly, due to the non-linear decrease of the hydrogen-bond density of PEAs. The hydrogen-bond density had a significant change between PEA (I) and PEA (II), and the change decreases between PEA (II) and PEA (II).

The crystallinity of the various PEAs was a function of their structure, particularly repeating unit length and density of hydrogen bonding sites. Wide angle X-ray diffraction confirmed the nature of the crystalline structures of the PEAs, The characteristic peaks presented in the X-ray patterns revealed that two forms of crystalline structures were formed in each polymer –  $\alpha$  form and  $\beta$  form. The  $\alpha$  form which represents a helical conformation was increased from PEA (I) to PEA (III). This is due to the fact the PEA (I) has the highest hydrogen-bond density, and it is relatively harder for the polymeric chains to rotate to the helix structures.

The polymers all demonstrated a degree of crystallinity which is strongly influenced by the kinetics of cooling, particularly as evidenced by melt-mediated transformations and by the shifting of melting peaks on cycling. This suggests that more work should be done on elucidating the various local thermodynamic minima that are presented in these structures, constrained by the kinetics of the system, and investigation of the relative time-stability of these states and their concomitant physical functionalities. It is quite likely that significant physical functionality changes may be effected through a modification of the degree and type of crystallinity developed in the films, as a result of varying cooling kinetics.

Comparison of the PEAs reported in the literature suggests that the properties of PEAs in this study are superior to all other lipidbased PEAs and comparable with the petroleum-based PEAs. In addition, the relationships established between mechanical and thermal properties and structure can significantly help to predict thermo-mechanical properties of PEAs designed from similar structures.

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