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# Exfoliated clay nanocomposites of renewable long-chain aliphatic polyamide through *in-situ* polymerization

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### Abstract

The current study was performed to synthesize a series of renewable polyamide 614/organoclay nanocomposites (PAC) with the improved structural, mechanical, and thermal properties via *in-situ* polymerization. The uniform dispersion and exfoliation of clay into the PA614 matrix, particularly at a lower loading of organoclay (less than 3%), confirmed via structural analyses (XRD, SEM, and TEM). Furthermore, the mechanical tests revealed remarkable improvement; namely, the tensile strength and storage modulus increased by 27% and 30%, respectively, in the sample contained 2% organoclay. Similarly, the TGA results showed a slight improvement in the thermal stability of the nanocomposite samples. Altogether, these improvements confirmed excellent compatibility between nanofiller and matrix and the organoclay homogenous dispersion into the PA matrix achieved by employing *in-situ* polymerization. Furthermore, all the samples illustrated a shear-thinning behavior over frequency attributed to the lack of time for the polymer chain to respond to the applied oscillation. Finally, the crystallinity of the samples diminished upon increasing the filler's content, which could be due to the decrease of free volume resulting from the presence of organoclay. To sum up, the current investigation supported the benefit of employing *in*situ polymerization to synthesize renewable PA614/clay nanocomposites with enhanced physio-mechanical properties, which could be appropriate candidates for engineering applications.

Keywords: Renewable polyamide; Clay; Nanocomposite; In-situ polymerization

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### 1. Introduction

The utilization of natural renewable resources has attracted a great deal of scientific attention due to environmental concerns. Therefore, plastic materials derived from renewable resources have gained a growing interest in scientific research and industry to replace petroleum-based ones [1,2]. Due to the excellent thermal and mechanical properties, polyamides (PAs) are among the most versatile engineering polymers used in various industries, such as automobile parts, packaging, electrical, and electronic devices [3]. In particular, the renewable long-chain aliphatic PAs, which generally involve the use of fatty acid-based dicarboxylic acids, have attracted further interest. They are environmentally friendly materials and possess a range of attractive properties, including high mechanical strength, good solvent stability/resistance, and low melting temperature and moisture absorption [1-5]. However, it is reported that aliphatic PAs undergo degradation during processing and exposure to environmental, thermal, and UV-radiation, which manifested as a drastic drop in the mechanical and physical properties [1]. One of the frequently employed methods for improving the polymer matrix properties is using nanoparticles [6]. Carbon-based nanofillers such as graphene [7,8] and carbon nanotube [9,10] as well as mineral ones such as clay [11,12] and silicon dioxide [13,14] have been extensively used to improve the mechanical and thermal properties of PAs. Clay is one of the most abundant layered minerals in nature with a specific structure and chemical composition. It has attracted a great deal of interest both among scientists and engineers since its proper dispersion/distribution in a polymer matrix will be resulted in dramatic improvements, including enhanced dimensional stability, high heat resistance, and reduced gas permeability [15,16]. Accordingly, several research works have been conducted on the fabrication and characterization of PA/clay nanocomposites, which all demonstrated a significant improvement in structural, mechanical, and thermal properties of the matrix [2,11,12]. On the other side, it is well known that *in-situ* polymerization in which the fillers or

reinforcements are dispersed in an appropriate monomer, and then the mixture is polymerized, has a great potential to overcome the aggregation tendency of nanoparticles in the polymer matrix and consequently to reach improved physio-mechanical properties [17–19].

In the current study, *in-situ* polymerization was employed to synthesize PA614/clay nanocomposites, which had a renewable carbon content of approximately 70%. To the best of the authors' knowledge, it is the first research work on PA614/clay nanocomposite, which was synthesized through *in-situ* polymerization. The obtained results confirmed the remarkable effect of organoclay addition on improving thermo-mechanical properties of the PA614 and could introduce the developed renewable nanocomposites for different engineering applications.

### 2. Experimental

### 2.1. Material

Tetradecanedioic acid (TDA, Zibo Guangtong Chemical Company, China) and hexamethylenediamine (HMDA, Sigma Aldrich, USA) were utilized as monomers. Sodium hypophosphite monohydrate (99%, Sigma Aldrich, Switzerland) was used as a catalyst. Surface modified nanoclay containing 0.5-5 wt. % aminopropyltriethoxysilane and 15-35 wt. % octadecylamine (Sigma Aldrich, particle size 20 m, USA) was employed as reinforcing filler. Laboratory grade ethanol (92.4%, ETAX B, ALTIA Industrial, Finland) was used as a solvent without purification.

### 2.2. Synthesis of nylon salt

Polyamide was synthesized via a two-step method; salt preparation of TDA and HMDA, followed by salt melt polycondensation [5]. A predetermined amount of TDA was dissolved in ethanol at 60 °C under gentle mixing at a three-neck glass reactor equipped with a heating jacket, condenser, and mechanical stirrer to obtain a 10 wt.% solution. 5% mole excess of

HMDA was dissolved in ethanol separately at room temperature and then added drop by drop to the TDA solution while the temperature of the system was kept at 60 °C. After 3 h of mixing, the system was cooled down and stirred for another 1 h in an ice bath. Subsequently, the precipitation was vacuum filtered using filter paper (Whatman No. 3), washed several times with ethanol to remove any unreacted monomers, and then vacuum dried at 40 °C for 24 h. The FT-IR and <sup>1</sup>H-NMR spectra of the synthesized nylon is presented in Fig. S1. For the preparation of nylon salt/clay, a calculated amount of organoclay was dispersed into the TDA solution using sonication. The rest of the method was similar to that described for the pure nylon salt.

### 2.3. Polyamide and polyamide/clay nanocomposites polymerization

The prepared nylon salt was poured into a stainless-steel reactor equipped with a mechanical stirrer, heating jacket, pressure gauge, and purging inlet and outlet for nitrogen gas. Initially, the reactor was kept at nitrogen purge, and the temperature was then gradually increased to  $230 \degree$ C. Afterward, the reaction was kept at this temperature under stirring (15 rpm) for 8 h. The resulting polymer was removed by cooling the reactor vessel using an ice bath while kept at nitrogen purge to avoid any oxidation. The FT-IR and <sup>1</sup>H-NMR spectra of the synthesized PA614 is depicted in Fig. S2.

PA614/clay nanocomposites were synthesized via *in-situ* polymerization employing nylon salt/clay mixture as a feed, similar to the conditions described for the pure PA614 synthesis. The amount of clay in the matrix was selected as 0.5, 1, 2, 3, and 5%, and the prepared nanocomposites were coded as PAC0.5, PAC1, PAC2, PAC3, and PAC5, respectively. The synthesized PA614 and PAC nanocomposites were milled using Retsch SM 300 Cutting Mill at 1000 RPM with a blade size of 1 mm, then hot-pressed (220 °C, 150 kPa) to prepare the film for further characterizations.

### 2.4. Characterization

*Fourier transform infrared spectroscopy.* The chemical structure of the nylon salt, PA614, clay, and PAC nanocomposites and the hydrogen bonding status were investigated at room temperature with FT-IR spectra using PerkinElmer FT-IR with an ATR at a wavenumber of 4000 to  $500 \text{ cm}^{-1}$ , resolution of  $4 \text{ cm}^{-1}$ , and rate of 32 scans.

**Proton nuclear magnetic resonance spectroscopy.** <sup>1</sup>H-NMR measurements were performed with a Bruker NMR Spectrometer AV III 400 operating at 400 MHz (9.4 T).  $D_2O$  and chloroform-d1 (deuteration at no less than 99.8%) with 10% v/v trifluoroacetic anhydride were utilized as the solvent for nylon salt and PA614, respectively. The test was done at room temperature.

*X-ray diffraction spectroscopy.* The XRD test was performed on the organoclay, PA614, and PAC nanocomposites using a PANalytical X Pert Powder XRD (alpha-1) with Cu-K radiation (= 1.54 Å) at 45 kV and 40 mA. The data was collected in the 2 range from 2 to 30° with a scanning speed of 3°·min<sup>-1</sup>. The d-spacing or gallery spacing between montmorillonite sheets was calculated using Bragg's equation (Eq. 1).

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where n is the order of reflection (it was considered 1), is the wavelength of the X-rays (1.54 Å), d represents the interplanar spacing of the crystal, and is the angle of incidence. *Scanning electron microscopy and transmission electron microscopy*. The morphology of the samples was evaluated from a cryofracture surface using a scanning electron microscope (SEM, Zeiss Sigma VP) at a voltage of 10 kV. Moreover, a transmission electron microscope (TEM, FEI Tecnai F20) with a 200 kV acceleration voltage was used to study the organoclay shape and dispersion inside the PA614 matrix.

*Tensile test.* The static mechanical properties of the dog bone-shaped samples, including Young's modulus (tensile modulus), tensile strength, elongation at break, and toughness, were measured using a tensile machine (Universal Tester Instron 4204) at 25 °C and 50% RH. The

crosshead rate and load were 5 mm.min<sup>-1</sup> and 2 kN, respectively. At least three specimens of each sample were tested, and the results were presented as means of these replicates  $\pm$  standard error of the mean.

*Dynamic mechanical analysis.* The viscoelastic properties of the strip-shaped samples including storage modulus (E'), loss modulus (E''), and tan , which is the ratio of the loss modulus and the storage modulus, were measured with a dynamic mechanical analysis (DMA) using a TA Instruments Model Q800. The samples were cut into rectangular strips and were tested employing the tension geometry with a temperature sweep method. The temperature range was set to be from 0  $^{\circ}$ C to 200  $^{\circ}$ C with a heating rate of 5  $^{\circ}$ C.min<sup>-1</sup>. The frequency, strain, and pre-load were fixed at 1 Hz, 0.5%, and 1 N, respectively [20]. The glass transition temperature was determined from the peak of the tan curve.

*Differential scanning calorimetry*. The crystalline structure of the synthesized samples was investigated using differential scanning calorimetry (TA Instruments MT-DSC Q2000) under nitrogen flow (80 mL.min<sup>-1</sup>). Initially, approximately 5 mg of the sample sealed in an aluminum pan was heated from 25 to 250 °C at a heating rate of 10 °C.min<sup>-1</sup> (first heating scan), subsequently equilibrated at 250 °C for 5 min. Afterward, the system was cooled down to 25 °C using a cooling rate of 10 °C.min<sup>-1</sup> and then kept isothermal for 5 minutes. This heating-cooling scan was performed to eliminate the thermal history of the sample. The second heating-cooling scan was applied with the identical conditions previously described for the first one. It was employed to determine the crystallization temperature (T<sub>e</sub>), melting temperature (T<sub>m</sub>), melting enthalpy ( $H_m$ ), and crystallization enthalpy ( $H_c$ ). The degree of crystallinity ( $_e$ ) was calculated using Eq. 2 in which,  $\mathbb{ZZ}_{\square\square\square}$  is the heat of cold crystallization, and  $x_f$  is the filler fraction [21]. To the best of the authors' knowledge, there is no reported

value for 100% crystalline PA614; therefore, the value of purely crystalline PA612 (258  $J \cdot g^{-1}$ ) [5,22] was used, which has the closest structural counterpart to the synthesized PA614.

$$\mathbb{D}_{\mathbb{Z}} \mathbb{Z} \xrightarrow{\mathbb{Z}} \mathbb{D}_{\mathbb{Z}} \mathbb{D} \mathbb{D}_{\mathbb{Z}} \mathbb{D}} \mathbb{D}_{\mathbb{Z}} \mathbb{D}$$

*Thermogravimetric analysis.* The thermal degradation of the samples was investigated by thermogravimetric analysis (TGA) using TA instruments Q500, under a nitrogen atmosphere with a heating rate of 10  $^{\circ}$ C.min<sup>-1</sup> from room temperature to 700  $^{\circ}$ C.

*Rheology test.* Melt rheological properties of the samples were investigated using an Anton Paar Physica MCR 301 rotational rheometer at 220  $^{\circ}$ C in a nitrogen atmosphere with a plate-plate geometry. The samples were hot-pressed to a disk shape with a diameter and a thickness of 25 mm and 1 mm, respectively, then dried at 50  $^{\circ}$ C for 24 h in a vacuum oven ahead of the test. The oscillatory dynamic measurements were performed at a constant strain of 1%. The behavior of storage modulus (G'), loss modulus (G''), and the complex viscosity (1212) of the samples were studied as a function of frequency between 0.01 and 100 Hz.

### 3. Results and discussion

### 3.1. Chemical study, crystallization, and morphology

The FT-IR spectra of organoclay, neat PA614, and the PAC nanocomposites are illustrated in Fig. S3. In this work, commercial bi-functionalized montmorillonite (organoclay) was used to prepare the nanocomposites. According to the technical datasheet, the inner galleries of montmorillonite are expanded with octadecylamine (ODA), while 3-aminopropyltriethoxy silane (APTES) is used to treat the surface and edges of the clay layers to enhance dispersion in polymer resin. The amine groups of APTES furthermore can involve in PA614 polymerization through reaction with carboxylic groups of TDA. The organoclay showed characteristic peaks similar to unmodified clay (sodium montmorillonite) as follows: two peaks at 3624 and 3315 cm<sup>-1</sup> attributed to O-H stretching for the silicate and water, respectively, a peak at 1629 cm<sup>-1</sup> related to O-H bending, and a peak at 1040 cm<sup>-1</sup> owing of

stretching vibration of Si-O-Si from silicate [23]. Moreover, some other peaks in the organoclay FT-IR spectrum were characteristic peaks of modified clay. Two peaks at 2920 and 2850 cm<sup>-1</sup> attributed to the C-H bond, two peaks at 1468 cm<sup>-1</sup> and 720 cm<sup>-1</sup>, respectively attributed to -CH<sub>2</sub>- scissoring vibration absorption and to -CH<sub>2</sub>- vibration absorption of the longer hydrocarbon chain (ODA), a peak at 798 cm<sup>-1</sup> assigned to Si-O bond, and two peaks around 1610 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> corresponded the amine N-H bend and C-H stretching in APTES [11,23]. The appearance of new peaks in modified clay confirmed the presence of the organic guest molecule in the clay. Additionally, the FT-IR results also revealed the maintained chemical structure of clay after being intercalated by organic surfactant. On the other side, the PAC nanocomposites displayed the characteristic peaks similar to the neat PA614 (Fig. S2a), revealing that the addition of organoclay did not change the chemical structure of the PA614. Furthermore, some new peaks appeared in their spectra, which could prove the presence of the organoclay in the samples; A peak at 1040 cm<sup>-1</sup> corresponded to the Si-O bond and a peak at 1440 cm<sup>-1</sup> due to a longer hydrocarbon chain of ODA. Moreover, the organoclay characteristic peak at 1610 cm<sup>-1</sup> vanished in all PAC nanocomposites (there was no shoulder in PA characteristic peak at 1631 cm<sup>-1</sup>), suggesting the reaction between amine groups of organoclay and carboxylic groups of TDA during the polymerization.

The FT-IR spectra were further used to study the hydrogen bonding status at room temperature. Fig. 1a illustrates the FT-IR spectra of PA614 and PAC nanocomposites in the range of  $3500-2700 \text{ cm}^{-1}$ . The major IR bands of interest for hydrogen bonding in polyamide/clay nanocomposites are as follows [24,25]: free N-H stretch at ~3444 cm<sup>-1</sup>, hydrogen-bonded N-H stretch in the crystalline phase at ~3300 cm<sup>-1</sup>, hydrogen-bonded N-H stretch in the amorphous phase (it was not observed in the current study), and Fermiresonance of N-H stretching with the overtone of amide II at ~3070 cm<sup>-1</sup>. No free N-H stretching absorption at ~3440 cm<sup>-1</sup> was detected, suggesting there was nearly 100%

hydrogen bonding in all the samples at room temperature [25]. Furthermore, the intensity of the Fermi resonance of N-H stretching showed no significant differences between the pure PA614 and all the nanocomposites; nevertheless, the intensity of the N-H stretch in the crystalline phase at ~3300 cm<sup>-1</sup> revealed significant differences. This peak weakened upon increasing the organoclay content suggesting that the addition of silicate layers reduced the extent of hydrogen bonding in PA614, which was in good agreement with the literature [24]. The XRD patterns of the organoclay, PA614, and the PAC nanocomposites are presented in Fig. 1b. The organoclay revealed a diffraction peak at  $2 = 3.99^{\circ}$ , corresponding to the basal spacing of 2.2 nm (Bragg's equation, Eq. 1), which was in good agreement with similarly modified clays reported in the literature [11,26]. This value was higher than that reported for unmodified sodium montmorillonite [12], indicating an intercalated structure formed in the organoclay due to the grafting ODA molecules. However, a week diffraction peak was detected at 2 =  $7.91^{\circ}$  (Fig. S4), corresponding to the d-spacing of 1.1 nm for the layered silicates in sodium montmorillonite [12,27]. In other words, although most of the clay layers were intercalated through surface modification by long-chain alkyl amines, certain layers were remained unmodified. These two peaks disappeared in all the PAC nanocomposites. It has been reported that *in-situ* polymerization can directly produce bulky and long-chain polymers in the interlayer space of clay [19]. Additionally, the organo-modification can convert the hydrophilic interior clay surface to a hydrophobic or organophilic; therefore, the polymer chains can easily diffuse into the clay galleries, thereby separating the layers and/or increasing the distance between them [26]. Accordingly, the aforementioned peaks' disappearance might suggest that the clay layers were exfoliated via the employed in-situ polymerization. On the other side, the synthesized PA614 exhibited two peaks at  $2 = 20^{\circ}$ , and 2 =  $24^{\circ}$  attributed to the inter-chain distance (200) and inter-sheet distance (002)/(202) of the -crystalline phase, respectively. In other words, the -crystalline phase with different

degrees of perfection has been formed in PA614 [28–31]. These characteristic peaks repeated in all the nanocomposites; however, their intensity changed, indicating that the interfacial interaction between PA614 and clay promoted the 2-crystalline phase [29]. Additionally, a small peak appeared at  $2 = 22^{\circ}$ , particularly at a higher filler loading, which could be attributed to the presence of organoclay.

The final properties of nanocomposites mostly depend on the dispersion of the nanofillers and compatibility between nanofillers and matrix. Accordingly, SEM micrographs of the fractured samples (PA614, PAC2, PAC5) were taken to investigate the dispersion of nanofillers into the matrix and their a nity with the PA614 matrix (Fig. 1c, 1d, and 1e). In the PAC2 sample, organoclay dispersed uniformly in the PA614 matrix, and no large aggregates were found, suggesting a good exfoliation of clay via the employed *in-situ* polymerization [32]. Furthermore, the appropriate a nity/interfacial adhesion between PA614 polymer matrix and nanofillers could be confirmed by the absence of the pullout phenomena and the lack of voids at the interface of organoclay and PA614 [11]. However, at a higher loading of nanofiller (PAC5, Fig. 1e), the morphology of the cryofracture surface changed, probably owing to the beginning of the aggregation of organoclay layers. In other words, at a higher amount of nanofillers, the formation of hydrogen bonds between nanolayers and PA matrix was not suffice to counterbalance the strong van der Waals interactions between the layers [21]. The decrease in the extent of hydrogen bonding at higher loading of organoclay was previously observed from FR-IR spectra.

TEM images were taken to investigate the morphological structure of PAC2 nanocomposite further. In Fig. 1f, the dark lines that were dispersed uniformly in the matrix were the silicate layers' intersection. Moreover, the small clusters of organoclay platelets in the 10-30 nm range could be observed in the matrix. Accordingly, it could be concluded that most of the primary particles were exfoliated, and certain parts of the clay platelets were intercalated and

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dispersed as tactoids of limited size. In general, the TEM micrographs, which were in line with the SEM and XRD results, firmly clarified exfoliation and uniform dispersion of clay layers in the PA614 matrix.



Fig. 1. a) FT-IR spectra of the PA614 and PAC nanocomposites; b) XRD patterns of the organoclay, PA614, and PAC nanocomposites; c, d, e) SEM images of the PA614, PAC2, and PAC5 nanocomposites with 5.00 KX magnification; f and g) TEM images of PAC2 nanocomposite with different magnifications

### 3.2. Static mechanical property

The stress-strain curves obtained by uniaxial tensile testing of the PA614 and PAC nanocomposites are illustrated in Fig. 2. Additionally, the tensile properties, including Young's modulus, tensile strength, elongation at break, and toughness extracted from the raw data, are summarized in Table 1. On one side, elongation at the break of the samples decreased dramatically with the increase in clay content, from 211% for the PA614 down to 10% for PAC5 nanocomposite. On the other side, the tensile strength of the PA614 increased from 31.86 MPa to 40.40 MPa in PAC2, corresponding to a 27% improvement. Furthermore, a slight reduction was observed at higher loadings of nanofiller (3 and 5%) in perfect agreement with the literature [11,26,27]. The enhancement in tensile strength could be owing to the high shear resistance between clay and matrix and uniform dispersion of nanoparticles into the matrix. It could also be due to the covalence bonding between polymer chains and nanofillers, as previously observed in FT-IR results. The reduction in tensile strength at a higher loading of organoclay could be associated with the beginning of the fillers' aggregation, as observed in the SEM images. As Table 1 depicts, the area under forcedisplacement curves (kJ.m<sup>-2</sup>), which represented the toughness of the samples [27], decreased dramatically with the increase in the clay content. However, organoclay addition led to substantial improvement in the sti ness of nanocomposites (Fig. S5). Namely, Young's modulus increased with the clay content increase, from 1013 MPa in pure PA614 to 1342 MPa in PAC5 nanocomposite. This improvement could be due to the outstanding platelets Young's modulus of 178-265 GPa and the high interfacial area existing between PA614 and organoclay [33].

It is worth noticing that the reported values for the mechanical property of neat PA614 and the nanocomposites and the observed trend had a perfect agreement with other research works. Namely, Yu et al. [26] confirmed that the tensile strength and modulus of the PA6 matrix increased by 18.37% and 57.44% in the sample with the organoclay loading of 7.5%.

However, they reported a 23% reduction in elongation at break. Moreover, Mekhzoum et al. [11] showed that Young's modulus increased from 1207 MPa to 1512 MPa, and the tensile strength enhanced about 11% in the PA6 nanocomposite containing 5% organoclay. Similarly, significant improvement in Young's modulus of the PA6 nanocomposite with 8.6% nanofiller was reported by Touchaleaume et al. [27]. They furthermore observed a dramatic reduction in elongation at break, from 276% down to 6%.



Fig. 2. The stress-strain curves of the PA614 and PAC nanocomposites

Tuble 1. The mechanical test results (tenshe test and Divirity								
Sampla	Young's modulus	Tensile strength	Elongation at break	Toughness	T <sub>g, DMA</sub>			
Sample	(MPa)	(MPa)	(%)	$(kJ.m^{-2})$	(C)			
PA614	1013±45	31.86±1.15	211.67±8.25	26.61±1.19	51.90			
PAC0.5	1055±49	35.31±1.23	110.39±4.25	13.58±0.49	52.93			
PAC1	1110±47	36.12±1.32	85.47±3.34	$11.03 \pm 0.48$	54.89			
PAC2	1154±55	$40.40 \pm 1.49$	51.66±2.43	$7.48 \pm 0.24$	55.79			
PAC3	1305±57	39.83±1.77	$22.45 \pm 0.67$	$1.92 \pm 0.09$	56.56			
PAC5	1342±63	38.60±1.70	$10.5 \pm 0.46$	$0.68 {\pm} 0.02$	58.77			
TACJ	1342±03	J8.00±1.70	10.5±0.40	$0.06 \pm 0.02$	56.77			

Table 1. The mechanical test results (tensile test and DMA)

### 3.3. Dynamic mechanical property

The glass transition temperature  $(T_g)$  and viscoelastic characteristics of the synthesized samples, including tan , storage modulus (E'), and the loss modulus (E''), were investigated by DMA. The trend of E' and tan over-temperature and organoclay loading are depicted in Fig. 3. On one side, for all the samples, E' dropped upon the increasing of temperature, significantly around 50  $^\circ C,$  corresponding to the increased segmental mobility and  $T_g$ transition [34]. On the other side, at all temperature values, E' and E'' (Fig. S6) increased with the increase in the mineral content; for instance, the storage modulus of PA614 was 1436 MPa at 25 °C while it was 1867 MPa for PAC5, indicating the reinforcing effect of the organoclay achieved by homogeneous dispersion of fillers into the matrix. The improvement was more noticeable at the higher temperature, which was justified by the Tg of the samples. It is well known that when the amorphous phase is in a glassy state, the improvement is limited, while it will be more notable when the temperature is higher than Tg [27]. The  $T_g$  of the PA614 measured from the tan peak (Fig. 3b) was approximately 52 °C and shifted to the higher values as organoclay content increased (Table 1) attributed to the limitation of the polymer chain mobility following the addition of rigid particles concerning molecular dynamics [11]. The same trend was reported by Shabanian et al. [12] for the Tg values of the PA6/organoclay nanocomposites.



Fig. 3. a) Storage modulus and b) Tan curves of the PA614 and PAC nanocomposites

versus temperature

#### 3.4. Differential scanning calorimetry

The second heating and cooling DSC curves of the synthesized PA614 and PAC nanocomposites are represented in Fig. 4. Furthermore, melting temperature (T<sub>m</sub>), crystallization temperature (T<sub>c</sub>), melting enthalpy (H<sub>m</sub>), crystallization enthalpy, and crystallinity ( <sub>c</sub>%) are provided in Table 2. All the samples revealed two endothermic and one exothermic peak with a broad shoulder, confirming that the addition of organoclay did not result in the formation of a new crystalline form in PA614 [26]. Similarly, Siddique et al. [21] and Anoukou et al. [35] reported two prominent endothermic peaks for PA6 corresponding to the melting point of - and -form crystalline phases. However, Nguyen et al. [5] suggested that the multiple melting peaks of polyamides might be attributed to the fusion of imperfect crystals or the presence of the same crystal phase, yet with varying thickness. Of note, the XRD patterns (Fig. 1b) confirmed the absence of the formation of the -form crystalline phase since no characteristic peak appeared at  $2 = 22^{\circ}$  [29]. Accordingly, the observed peaks at 196 °C and 208 °C could be attributed to the melting of -crystalline phases with different degrees of perfection (2 and 1) [28,29]. Although the presence of the organoclay did not reveal any significant effect on  $T_{m,\ 2},\ T_{m,\ 1}$  reduced from 209.28  $\degree C$  to 206.57  $^{\circ}$ C upon increasing the filler loading. Additionally, H<sub>m, 1</sub>, and <sub>c, 1</sub> decreased with the increase in the organoclay loading, whereas  $H_{m, 2}$ , and c, 2 revealed an increasing trend. In other words, the 2-crystalline phase grew upon in nanocomposites, in good agreement with XRD results. Altogether, the overall crystallinity decreased with the increment of organoclay content, which could be due to the reduction of the free volume of polymer caused by the organoclay. It is also reported that filler sheets act as rigid obstacles and does not allow polymer chains to rearrange and form crystals comfortably [36]. On the other side,

the crystallization enthalpy and temperature decreased upon increasing the organoclay content, indicating a reduction in the crystallization rate of PA614. It seems that the clay platelets hindered the crystal growth by limiting the mobility of the amorphous phase, and as a result, retarded the crystallization [26,27]. A similar trend has been reported for PA6/clay nanocomposites. For instance, Yu et al. [26] confirmed that crystallization temperatures, melting temperatures, and degree of crystallinity of PA6 shifted slightly to a lower temperature upon increasing the organoclay content.

It is noteworthy that the reported melting point for PA614 in the present study was relatively lower than that reported for commercial PA6 (about 220 °C) [26,27], which makes PA614 a more exciting candidate in different engineering fields. It is known that the amide linkages in the PA backbone could potentially partake in hydrogen bonding; these hydrogen bond sites restrict chain motion, and consequently, the required energy for glass-rubber transition (T<sub>g</sub>) and melting point (T<sub>m</sub>) increase. Accordingly, a lower number of amide linkages per repeat unit in the developed long-chain aliphatic PA614 and PAC nanocomposites could be the main factor in having such a low melting point [5,22].



Fig. 4. The DSC curves of the PA614 and PAC nanocomposites; a) heating and b) cooling

cycles

Table 2. The DSC data of the PA614 and PAC nanocomposites

Sample	T <sub>m, 2</sub> (°C)	T <sub>m, 1</sub> (°C)	T <sub>c</sub> (°C)	H <sub>m, 2</sub> (J/g)	H <sub>m, 1</sub> (J/g)	H <sub>c</sub> (J/g)	c, 2 (%)	c, 1 (%)	c,total (%)

PA614	195.43	209.28	184.22	36.43	44.40	45.41	14.12	17.21	31.33
PAC0.5	196.18	208.07	181.54	42.90	21.07	45.32	16.71	8.21	24.92
PAC1	196.96	207.26	180.31	41.09	11.03	41.34	16.09	4.32	20.41
PAC2	196.82	206.55	180.36	42.72	7.67	42.65	16.90	3.03	19.93
PAC3	196.52	205.71	179.13	45.28	3.71	40.98	18.09	1.48	19.58
PAC5	197.21	206.57	178.12	48.81	1.94	41.92	19.91	0.79	20.71

### 3.5. Thermogravimetric analysis

Since the thermal stability of synthetic polymers is of great importance for processing operations, the thermal behavior of PA614 and PAC nanocomposites was investigated with thermogravimetric analysis (TGA). The TGA and DTG curves of the PA614 and PAC nanocomposites under the nitrogen atmosphere are provided in Fig. 5. The 5% weight loss temperature  $(T_5)$ , the 10% weight loss temperature  $(T_{10})$ , the maximum degradation temperature (T<sub>max</sub>), and the charred residue at 700 °C extracted from TGA curves are summarized in Table 3. None of the samples showed thermal decomposition before 350 °C, signifying excellent thermal stability. They exhibited a single degradation state between 390 and 470 °C, attributed to the structural decomposition of the PA614 matrix [12,37] and suggesting a one-step mechanism of thermal decomposition [30]. Further heating did not significantly affect the samples, and all of them showed a stable charred residue at 700 °C. Although the TGA curves profiles were similar, the decomposition course seemed to have been a ected by the organoclay structure. Once 2% organoclay was added (PAC2),  $T_5$ ,  $T_{10}$ , and T<sub>max</sub> increased by 2.94, 3.18, and 6.1°C, respectively, while all the decomposition temperatures decreased for PAC3 and PAC5. Namely,  $T_5$ ,  $T_{10}$ , and  $T_{max}$  were reduced by 11.66, 6.63, and 2.65 °C, respectively, in PAC5 nanocomposite. In other words, in thoroughly exfoliated samples, the thermal stability of the polymer was improved.

It is worth noting that certain research groups reported a significant decrease in onset temperature of decomposition of PA/clay nanocomposites attributed to the thermal degradation of the modifying cations, which occurred around 200 °C by a Hoffman degradation mechanism [11,38]. Nevertheless, some others observed a slight increase in

thermal stability of the PA matrix [37,39,40]. The improvement could be due to the uniform dispersion of montmorillonite nanolayers with high thermal stability in the matrix and a robust interface between the organoclay/matrix. The former could trigger the excellent barrier properties and, consequently, minimize the permeability of volatile degradation products and heat insulation. The reduction of motion of polyamide chains at the organoclay interface in the intercalated/exfoliated systems could be another reason for thermal improvement [37]. On the other side, the observed reduction at higher loading of clay could be due to the catalytic properties of organoclay. Furthermore, a lower interfacial area and higher volatile content induced by the flocculation of organoclay could lead to a decrease in thermal stability [11,37].

Table 3 represents the residual of the PA614 and PAC nanocomposites at 700 °C. The actual residual of nanocomposites was also calculated considering the residual of added clay (Fig. S7) and the PA614 at 700 °C, whose results are listed in Table 3. There was a good agreement between the calculated and observed residue of organoclay. It could be another proof for the uniform distribution of organoclay into the PA matrix achieved by the *in-situ* polymerization. As reported by Yu et al. [26], a difference was observed between the added and actual nanofiller content, particularly at higher organoclay concentrations in melt-extruded samples, since some of the organoclay was left behind due to the difference in the density of organoclay and polymer.



Fig. 5. a) TGA and b) DTG curves of the PA614 and PAC nanocomposites

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Sample	T <sub>5</sub> (C)	T <sub>10</sub> (C)	$T_{max}(C)$	The observed charred	The calculated charred
				residue (%)	residue (%)
PA614	398.07	408.08	436.32	0.29	
PAC0.5	400.01	409.15	440.98	0.66	0.67
PAC1	400.69	409.78	440.98	1.1	1.04
PAC2	401.01	411.26	442.42	1.71	1.79
PAC3	394.06	406.35	438.92	2.49	2.54
PAC5	386.41	401.45	433.67	3.98	4.04

Table 3. TGA data of the PA614 and PAC nanocomposites

#### 3.6. Melt rheology

Measurement of the rheological properties of polymeric materials in a molten state is crucial to gain a fundamental understanding of the processability and structure-property relationship. It can also provide useful information about the state of dispersion of nanofillers within the polymer matrix [36,41]. The rheological properties of PA614 and PAC nanocomposites, including storage modulus (G') and complex viscosity (ITPI versus frequency are depicted in Fig. 6. At the temperature and frequency employed for the rheological measurements, the PA614 chains were fully relaxed and exhibited a liquid-like or typical terminal behavior in which the storage modulus was dependent on frequencies [11,20,41]. Accordingly, the storage and loss moduli (Fig. S8) of all the samples increased significantly upon increasing the frequency. However, the G' of the specific samples (PAC2, PAC3, and PAC5) presented a plateau at lower frequencies, indicating percolated clay particle networks at higher loadings. Furthermore, the storage modulus and loss modulus increased with the increase in the clay content due to the reduction in the mobility of the macromolecules resulted from the uniform dispersion of nanoparticles and the strong interaction between clay layers and polymer matrix chains [27,41].

On the other side, the complex viscosity ( 2 increased upon increasing the nanofiller content, meaning that the organoclay enhanced the shear stress; however, the samples illustrated shear-thinning behavior versus frequency. The increment of the viscosity could be

due to the uniform dispersion of nanofillers into the matrix via the employed *in-situ* polymerization and the strong hydrogen bond interactions between particles and matrix, while its reduction could be attributed to the lack of time for the polymer chain to respond to the applied oscillation [11,20].



Fig. 6. a) storage modulus and b) complex viscosity of PA614 and PAC nanocomposites versus frequency

### 4. Conclusion

Renewable long-chain polyamide/organoclay nanocomposites were successfully synthesized via *in-situ* polymerization. Uniform dispersion of nanofillers into the PA614 matrix and the appropriate filler-matrix interaction was confirmed with FT-IR, XRD, SEM, and TEM results. The tensile modulus, tensile strength, and storage modulus of the PA614 matrix improved significantly, with the increase in the filler content contributing to the uniform dispersion of nanofillers into the matrix and excellent compatibility between organic/inorganic phases. Moreover, the crystallinity and crystallization rate of the samples revealed a reduction upon increasing the organoclay content due to limiting the mobility of the amorphous phase. The TGA results confirmed a slight improvement in the thermal stability of the nanocomposites attributing to the strong interface formation between organoclay and polymer matrix and the barrier properties of the files. Ultimately, the samples' behavior under oscillating frequency, which was studied via rheometric test, showed

improved storage modulus over frequency and clay loading contributed to reducing macromolecules' mobility caused by the strong interaction between clay layers and polymer matrix chains. To sum up, the findings of the current work could support the benefit of employing *in-situ* polymerization to produce renewable PA614/clay nanocomposites with elevated physical, mechanical, and thermal properties for their application in various engineering fields.

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- Development a series of renewable PA614/organoclay nanocomposites ٠
- In-situ polymerization of exfoliated PA614/organoclay nanocomposites ٠
- Good dispersion of nanofiller and appropriate interaction between fillers and matrix ٠
- Improved mechanical and thermal properties via employed in-situ polymerization ٠
- The acceptable potential of the developed nanocomposites for different engineering • applications

### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: