Innovative PA6/PL Composites Unveil Intriguing Transformations in the Pursuit of Materials Similar to PA6

Oumayma Oulidi^{1*}; Ibtissam Elaaraj¹; Asmae Nakkabi¹; Mohammed Fahim¹; Noureddine El Moualij

1. Laboratory of bio-inorganic chemistry, molecular materials, and the environment Faculty of Sciences Moulay Ismail University, Meknes, Morocco

Abstract:

For decades, plaster (PL) has been a renowned decorative material for walls and ceilings worldwide, cherished for its exceptional insulation, fire resistance, and aesthetic appeal. While the reinforcement of PL with Polyamide 6 (PA6) is a well-explored avenue in scientific research, the reciprocal—PA6 reinforced by PL remains untapped as of now. In the face of industrial competition, we embarked on the creation of a PA6/PL composite matrix, seeking materials that align with societal and economic expectations. With reinforcement rates ranging from 2% to 20% wt., our investigation employed FTIR, X-ray, DSC, TGA-TD, and SEM for comprehensive characterization. The outcomes revealed intriguing alterations; a slight increase in density and crystallinity, emergence of new peaks in FTIR spectra and X-rays, particularly prominent at 20% PL. Remarkably, the melting and crystallization temperatures of the composites remained consistently stable, while the decomposition temperature experienced a marginal elevation. **Keywords**: polyamide 6, plaster, composite, crystallinity.

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I. Introduction:

Due to its availability, relatively low cost, high ease of use, and mechanical characteristics suitable for many uses, plaster is a widely used building material; it is used in the manufacture of false ceilings and other decorative items (such as plasterboard) for buildings. It contributes to thermal and sound insulation and good fire resistance. It is derived from plaster, which is calcium sulfate dehydrated with the formula $CaSO_4$, $2H_2O$ and occurs naturally as alabaster or selenite crystals [1].

Plaster comes from gypsum, a mineral essentially composed of hydrated calcium sulfate. It can be mined in the open or an underground quarry. After an initial grinding, the fine calibrated powder is baked at a rate of 5 t per hour, in "Beau four" type ovens which indirectly bake the gypsum placed in a rotating shell above oil burners. After cooking, the stones are crushed according to 2 principles: either by standard crushing where the plaster is reduced to particles of 200 μ m thanks to a system of hammers rotating inside a sieve (guarantee of maximum grain size). Either by crushing/selection, the plaster is crushed by rotating hammers and then sucked through a rotating "squirrel cage". Depending on its weight (therefore its size), the grain of plaster, subjected to 2 opposing forces (centrifugal and suction), passes through the squirrel cage or not as illustrated in Figure 1.



Figure 1: Plaster manufacturing process

The work of S. Eve et al. was focused on the reinforcement of commercial plaster with combined polyamide (PA) and polypropylene fibers [2]. The reinforcement by PA alone was studied in detail by considering the evolution of the mechanical [3], and microstructural behavior [4]. They deduced that the presence of these water-absorbing fibers prevents the hydration of plaster grains located near the fibers, this disturbs the hydration of the plaster and leads to a weakening of the fiber/matrix interface. This reduces Young's modulus and flexural and compressive strengths as the fiber concentration increases. J. Sustersic et al [5] studied the reinforcement of a lightweight plaster with different types of polymer fibers (FRLP): high modulus aramid fibers (AR), medium and high modulus polypropylene fibers (PVA). The results obtained show that all the polymer fibers were used to improve the toughness of FRLP under bending and compressive loading at 28 days of age and after accelerated aging.

In our paper, we will examine the opposite effect of what was done in the previous study, and we will reinforce polyamide 6 (PA6) with plaster. Considering PA6 is one of the most widely used polymers in several industrial fields due to its excellent physical, chemical, thermal, and mechanical properties. In particular, it can be found in the textile field thanks to its high mechanical resistance and in the automotive industry because of its high thermal stability. PA6 is known for its good compatibility with inorganic fillers and mineral clays. These fillers increase the modulus, the toughness as well as the barrier properties [6]. This polyamide has been largely reinforced with mineral reinforcements such as montmorillonite clay sheets (MMT)[7] and like a nanocomposite PA6/clay [8].

The effect of chemical modification was studied using Fourier transform infrared (FTIR) spectroscopy. Structural enhancement is achieved using X-ray diffraction (XRD) techniques, and thermal properties were evaluated using differential scanning calorimetry (DSC) thermal gravimetric (TGA), and differential thermal analysis (DTA). The morphology of samples was analyzed by using Scanning electron microscopy (SEM).

2.1 Synthesis of PA6:

II. Materials and methods:

The ε -caprolactam, N-acetylcaprolactam, and NaH reagents come from the company Sigma-Aldrich. The synthesis is described in details in our previous study [9][10].

2.2 Composite manufacturing:

2.2.1 Technical data of plaster:

The plaster used comes from the company Gazelle Taloche 60 and has Technical data :

- Density: 1 g/cm 3
- Compressive strength: ±2.50 N/mm².
- Modulus of elasticity: $\pm 2.327 \text{ N/mm}^2$.
- Vapor diffusion resistance modulus μ (mu) DIN 4108: 8
- Conductivity: 0.25 w/m/k

2.2.2 The particle size distribution :

The particle size distribution was determined by sieving. The technique consists in studying the distribution of the grains, using a column of stainless steel sieves (diameter of 20 cm) installed in descending order on a mechanical vibration sieve from the company FRITSCH, using mesh sieves aperture squares (in μ m): 1000; 800; 630; 500; 400; 315; 250; 160; 125; 63; 0. The device is programmed with an amplitude of 2.5 mm and an inter-time of 15 seconds with a rest time of 1.5 min. The samples dried well in the oven for 72 hours at 60°C are sifted dry for 30 min. The plaster used is mainly of homogeneous powder consisting essentially of fine grains that have a diameter of less than 160 μ m.

2.2.3 Preparation of PA6/PL composites :

We followed the same protocol adopted for the manufacture of PA6, except that we will substitute a quantity of ε -caprolactam to replace it with Plaster (PL) according to the following rate: 2% (P2), 10% (P10), 15% (P15), and 20% (P20) by weight, we ensure the homogenization with agitation at 100 tr/min, for better dispersion of the reinforcement within the matrix.

2.3 Characterization techniques

2.3.1 Density measurement:

The density was measured by the flask method using the glass pycnometer, consisting of a small balloon (approximately 25 cm^3) fitted with a hollow ground cap surmounted by a capillary tube and a guard bulb. The density was expressed by the equation (1) [11]:

$$d = \frac{mL}{mw} = \frac{ML - Me}{Mw - Me}$$

(1)

- mL: The mass of liquid contained in the pycnometer

- $m_{\rm w}\!\!:$ The mass of the water contained in the pycnometer

- M_L : pycnometer filled with liquid up to the gauge line

- M_w: pycnometer filled with water up to the gauge line

- M_e: empty and dry pycnometer

The Weight measurements are done with a lab balance NAHITA-BLUE 5133 series with a precision of 220g/0.001g and repeatability of $\pm 0.0002 g$.

2.3.2 Fourier Transform Infrared Spectrophotometry (FTIR):

The dry sample was blended in a mortar with dry KBr crystal. Then the mixture was pelletized under a land press to form a thin film wide was sicked to the FTIR analyzer. The equipment used in our study is a Fourier Transform spectrophotometer of the brand Jasco 4100. The analysis of the spectrum is carried out in the 4000-400 cm⁻¹ wavenumber region.

2.3.3 X-ray diffraction (XRD):

X-ray diffraction (XRD) structural analysis is performed on an X-RD-6100-Shimadzu type diffractometer (λ Cu = 1.54 Å). The diffraction spectrum is carried out for values of 2 Θ between 2 ° and 80 °, at a scanning speed of 1 ° / min.

2.3.4 Differential Scanning Calorimetry (DSC):

The tests were carried out on a DSC 131 EVO from Setaram, the heating rate is set at 10 ° C/min. The device operates between -170 ° C and 700 ° C.

2.3.5 Thermogravimetric (TGA) and Differential Thermal Analysis (DTA),:

The machine is the TG-60 Shimadzu used for thermogravimetric measurements relating to degradation in isothermal mode. It operates between room temperature and 900 $^{\circ}$ C, with freely adjustable heating rates between 0.001 and 100 $^{\circ}$ C / min.

2.3.6 Scanning electron microscopy (SEM):

The morphology, as well as the elemental mapping of the samples, are evaluated by a JEOL JSM- IT 500 HR scanning electron microscopy coupled to the elemental detector scanning (EDS) operating at an accelerating voltage of 3 kV and in secondary electronic image mode. The pellets are glued separately to the sample holder with a double-sided carbon adhesive. The analysis is done at the Innovation and Technology Transfer Center of Moulay Ismail University (CITT-UMI) in Meknes, Kingdom of Morocco.

3.1 Effect on density :

III.Results and discussions :

The density of the manufactured composites was determined to evaluate the effect of the incorporation of PL within the PA6 matrix. As can be seen from **Figure 2**, the density of the composites remains unchanged up to 20% by weight (P20) where it has experienced a slight increase compared to that of the PA6, it is a jump of 4%, which is otherwise a very low value and therefore permissible.



Figure 2: Density of PA6/PL composite

3.2 Characterization by FTIR:

The FTIR spectra of PA6 (**Figure 3**) show key functional groups. Strong absorption bands appear at 3299 cm⁻¹ (N-H stretching) and 1542 cm⁻¹ (N-H bending). Antisymmetric CH bands are seen at 2932 cm⁻¹, while symmetric CH bands occur at 2864 cm⁻¹. A strong band at 1639 cm⁻¹ corresponds to C=O stretching, and medium bands at 1262 cm⁻¹ and 1200 cm⁻¹ indicate C-N stretching. The bands at 688 cm⁻¹ and 578 cm⁻¹ are due to C-C stretching, while weak bands at 3064 cm⁻¹ and 959 cm⁻¹ are attributed to N-H and CH₂ deformation, respectively [12][9].



Figure 5 shows the IR spectrum of the plaster (PL) used in our study. It can be seen as a very strong doublet at 3610 - 3558 cm⁻¹ assigned to the stretching and bending vibrations of the hydroxyl group of the water of crystallization [13]. The elongation vibrations of the C-O bond of calcite are characterized by the absorption bands at 1431 cm⁻¹ and 876 cm⁻¹ [14]. These three bands are accompanied by harmonics at 2220 cm⁻¹, and 2139 cm⁻¹. The peak at 1623 cm⁻¹ is assigned to the deformation of the H-OH group of water absorbed by the plaster due to its hydrophilic character. The very strong band having the profile of a plateau towards 1172 cm⁻¹ is also observed by M. Anastasiou, it is attributed to the S-O stretching vibrations due to the SO₄²⁻ group [15], another very strong band at 1004 cm⁻¹ is assigned to the Si-O stretching vibrations of the group (SiO₂). The two strong bands at 665 cm⁻¹ and 605 cm⁻¹ are attributed to the S-O deformation of the CaSO₄ group. However, at 467 – 417 cm⁻¹, the Si-O vibrations of the (SiO₂) group are present [15]. These results are in harmony with the conclusions of G. Anbalagan [16], F. Farcas, P. Touzé [17], M. Anastasiou [15], and A. Khalil [13]. The plaster is submitted under the thermal process adopted during the manufacture of the composites to investigate the effects of the thermal operating conditions on the structure of the plaster. This consisted of exposure to 130°C / 20 min and then to 140°C /10 min. A comparison between the two IR spectra, Figure 5 shows that the treated plaster (PLt) records mostly its structure with a decrease in intensity. Especially for the bands at 3558 cm⁻¹ and 1623 cm⁻¹, attributed to the water of crystallization, accompanied by a slight decrease at 1172 cm⁻¹ attributed to S-O of the CaSO4 grouping. This can be explained by the partial dehydration of calcium

 $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O$

dehydrate to calcium hemihydrate [18], itself dehydrated to calcium according to the following reaction:

 $CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4 + 1/2H_2O$

It can be deduced that the temperature adopted during the polymerization process only affects the hydration profile of the plaster.



Figure 5: FTIR spectra of Plaster at room temperature (PL) and treated at 130-140 ° C (PLt)

[19][20].

Wavenumber (cm ⁻¹)	Attributions
417 (m) - 467 (m)	Vibration Si-O of the (SiO ₂) group
605 (S) - 665(S)	Deformation S-O of the (CaSO ₄) group
876 (w)	Elongation C-O of the (CO ²⁻ ₃) group
1004 (S)	Vibration Si-O of the (SiO_2) group
1172 (S)	stretching vibration S-O of the group (CaSO ₄)
1431 (w)	Elongation C-O of the group (CO^{2-3})
1623 (S)	Deformation O-H of water crystallization
2139 (m) - 2220 (w)	Harmonic bands accompanied by the grouping (CaCO ₃)
3215 (w)	Elongation O-H of water crystallization
3558 (S)	stretching vibrations O-H of water crystallization
3610 (S)	bending vibrations O-H of water crystallization

Table 1: Attribution of the characteristic bands of the Plaster (PL) (S: Strong, m: medium, w: weak)

To identify structural changes within the composite, FTIR spectroscopy was performed for all composites. In Figure 6, the FTIR spectra of all composites save the same characteristic bands of the matrix PA6. The only observation is the extension of the intensity of many bands towards 1080-1200 cm⁻¹, as well as at 3300 cm⁻¹ for the composite P20, these bands come mainly from the (SO4²⁻⁾ group and the water of crystallization, respectively, coming from the plaster incorporated.



Figure 6: FTIR spectra of PA6/PL composites

3.3 **Characterization by DRX :**

The crystal structure was analyzed by wide-angle diffraction (XRD). Figure 7 shows that PA6 predominantly exhibits two reflections characteristic of the thermodynamically stable α monoclinic crystalline phase, observed at $2\theta = 19.94^{\circ}$ and $2\theta = 23.88^{\circ}$, corresponding to the (100) [21] and (002/202) [22] crystal planes, respectively. Additionally, a metastable γ phase of PA6 is detected at $2\theta = 19.81^{\circ}$ [6][9].





The XRD diffractogram of Plaster (PL) is shown in **Figure 8**. It can be noted that the mineral morphology of the plaster used is particularly rich in CaSO4 hemihydrate characterized by peaks positioned at $2\theta=15^{\circ},26^{\circ},30^{\circ},32^{\circ},42^{\circ},49^{\circ}$, and 50°, while at $2\theta=26^{\circ}$ corresponds to anhydrite. Calcite is marked by the peaks at $2\theta=29^{\circ}, 38^{\circ}$, and 53°. In accordance with [23] and [18].



The diffractograms of the composites show several characteristic peaks. Figure 9 shows that the incorporation of the PL into the PA6 matrix is accompanied by the appearance of new peaks that characterize particularly the (CaSO₄, $\frac{1}{2}$ H₂O), the main component of the plaster, especially for the composite 20P. It appears from Table 2 that this incorporation had a good effect on the crystallinity of the composite material as the (PL) content increased. That means that the plaster had not reacted with the matrix, but its small granulometry (160 µm) facilitated its coating by the PA6 matrix during polymerization without affecting the latter in its crystalline properties. Considering the crystalline nature of the plaster, as explained in Table 2, the 20P composite material had a very high crystallinity content. This result may also be an advantage for the modulus and moisture absorption as explained by [24].



Figure 9: Wide-angle X-ray diffraction patterns of PA6/PL composites

Composites	Xc (%)	
PA6	38.53	
P2	38.63	
P10	39.19	
P15	42.73	
P20	43.47	
PL	97.22	

Table 2: crystallinity rate of composites PA6/PL determined by XRD

3.4 Characterization by DSC:

The thermal properties of PA6 and its composites were analyzed using differential scanning calorimetry (DSC). Figure 10 displays a double endothermic peak at Tm1 = 203 °C and Tm2 = 199 °C, corresponding to the α and γ crystalline phases of PA6, respectively. During the cooling phase, a single exothermic peak is observed, indicating crystallization at Tc = 165 °C. [10].



Figure 10: DSC curves of PA6

Figure 11 shows a thermogram of the plaster. According to Ciemnicka et al [25], the endothermic transformation associated with the dehydration process started at 117.1 °C and continued at 153.9 °C according to the following equations:

 $CaSO_4 \cdot 2H_2O \rightarrow \beta \cdot CaSO_4 \cdot 1/2 H_2O + 3/2H_2O \uparrow$

 $\beta\text{-CaSO}_4\text{-}1/2 \text{ H}_2\text{O} \rightarrow \beta\text{-CaSO}_4\text{-}\text{III} + 1/2\text{H}_2\text{O} \uparrow$

Figure 12 shows the evolution of the thermal properties of the manufactured composites.





Figure 12 : DSC thermogram of PA6/PL composites.

Table 3: glass transition temperatures, crystallization temperatures, and melting temperatures of composites PA6/PI

Rate of PL	Tc (°C)	Tm (°C)	$\Delta Hf(g/j)$	
P2	175.15	205.95	41.40	
P10	173.64	197.91	38.93	
P15	172.52	197.67	37.08	
P20	177.55	201.05	36.82	

Figure 12 and Table 3 show the melting temperature (Tm), crystallization temperature (Tc), and enthalpy of melting (Δ Hm). The results show that the melting temperatures of the composites appear very close. The Tm remains around 200°C even after the addition of 20% by weight (20P) of the plaster. We can also see a small plateau for the 20% composite around 142°C which reflects the dehydration of CaSO₄ as already mentioned in Figure 11. The composite material crystallizes at a slightly higher temperature while increasing the plaster content regarding the crystallization temperature. Therefore, the addition of plaster will not damage the thermal properties of PA6, up to 20% by weight incorporated in plaster. These results are corroborated with those obtained by Rusu [26].

3.5 Characterization by TGA-TD:

To identify the effect of PL on the thermal aspect of our composite, we performed typical thermal curves of PA6 (Figure 13), PL (Figure 14), and finally composites (Figure 16) with different rates of PL.



Figure 13 indicates that the initial degradation temperature of PA6 is around 180°C, with a minimal mass loss of 13%, likely due to traces of reactive assembly residues (activator, residual monomer, catalyst) and minor water evaporation absorbed during storage, given PA6's hydrophilic nature [27][24]. As the temperature rises to 380°C, there is a substantial mass loss exceeding 75%, attributed to C-C bond scission leading to depolymerization. This involves the formation of hydroperoxide fractions at the methylene group adjacent to the amide nitrogen, a process highlighted in studies on polyamide combustion retardation [28].





Figure 14 shows the curves representing the heat flux and mass loss measured between 25 and 900°C at a heating rate of 20°C/min highlighting the different decomposition steps occurring during the dehydration of the plaster. It can be seen that the temperature range can be divided into four regions corresponding to the mass loss in the thermal curve [29]: the first region (<120°C) is attributed to absorbed water (hygroscopic water). The second region between 130 and 200°C is attributed to the dehydration of plaster (CaSO₄ - $_2$ H₂O), as suggested by [19], [30], which takes place in two steps according to equations (1) and (2): [15]

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O \quad (1)$$

$$CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4 + 1/2H_2O$$
(2)

The third region (200-600°C), refers to water chemically bound to hydrates of calcium silico-aluminates [31]. Finally, the fourth (600- 800°C) corresponds to the carbon dioxide developed during the decomposition of carbonates, and the decomposition of calcite according to equation (3)

$$CaCO_3 \rightarrow CaO + CO_2$$
 (3)

The DT curve has enriched the information exported from the TGA thermogram. The loss that takes place around 130 °C is attributed to a loss of 1.5 moles of water to pass to the hemihydrate form (CaSO₄, $0.5H_2O$), which then, will end up losing the remaining half a mole of water around 180 °C to pass to anhydrite III (CaSO₄) and then to anhydrite II at around 410 °C. This is in agreement with the results of the thermal study carried out on a sample of plaster [32][17]. Figure 15 summarizes the reactions that the main component of the plaster can undergo as a function of temperature.



CaSO₄ I

Figure 15 : Structural changes during dehydration of CaSO4, xH2O (x=0,0-2,0)[33]



Figure 16: Thermal curves of PA6/PL composites

Figure 16 illustrates the changes after the addition of (PL). It can be seen from the TGA thermograms of the composites, that the thermal degradation patterns have undergone some changes, starting with the first decomposition which shows a small mass loss recorded at 10% around 200°C which comes back to the loss of small molecules comes from PA6, as well as bound water comes from the plaster, induce the decomposition of the polymer at a lower temperature [26]. The second thermal decomposition starts around 390°C with a very high mass loss record of 70% attributed to the destruction of the hydrogen bonds within the macromolecule. The addition of 20% by weight of plaster could delay the thermal degradation of the PA6 matrix. It was shown from Figure 16 that the second decomposition was moved towards 400°C (i.e. an increase of 20°C compared with PA6) causing a mass loss of 60%, this may be due to the mineral composition of the plaster which is resistant to high temperature.



3.6 Scanning electron microscopy (SEM):

Figure 17 : SEM images of a) PA6, b) PL, c) P10 and d) P20, scale: 10µm

From Figure 17 the SEM images of PA6, PL, and composite 10P and 20P were presented. We can see the semicrystalline appearance of PA6 with the appearance of square and rectangular-shaped crystallites in Figure 17a; the plaster adopts a rough morphology as shown in Figure 17b. By incorporating P10 by weight of PL, the structure of PA6 was most affected, but small bodies with rectangular shapes from PA6 are still seen in Figure 17c. By increasing the reinforcement rate to 20% weight (P20), a new inhomogeneous and rather rocky shape is seen with the appearance of pores as shown in Figure 17d.

IV.Conclusion:

In the present study, plaster-reinforced (PA6/PL) matrix composites were fabricated at different rates (2% to 20% by weight). The PA6/PL composites were characterized by the following methods: FTIR, X-ray, DSC, TGA-TD, and SEM. The results showed that this incorporation was accompanied by some interesting changes in both physicochemical and thermal properties. The density is slightly increased, and the FTIR spectrum and X-ray show new peaks, thus increasing the crystallinity, especially for 20 wt% PL. In terms of thermal properties, the melting temperature Tm and the crystallization temperature Tc values of the composites are nearly constant, in addition to a slight increase in the decomposition temperature Td, which means that this incorporation has been evaluated for thermal stability, therefore, these new materials can have more applications that are specific to thermal insulation. The morphology of the composite material has completely changed. Consequently, the current work may open up a new way of developing material by polymerization in situ with interesting properties, this material can be used in applications such as tanks, sheaths, and dedicated boxes for the automotive industry. Other studies are in progress to study the other performances of these composites.

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