

Natural hydrolytic ageing of PA6 and bio-reinforced composites

Oumayma Oulidi*, Asmae Nakkabi, Mohammed Fahim, and Noureddine Elmoualij

Laboratory of Bioinorganic Chemistry, Molecular Materials, and Environment, Faculty of Sciences, Moulay Ismail University, Morocco

Abstract. Hydrolytic ageing or hydrolysis is the destruction of chemical bonds by the action of water. Among the polymers most affected by hydrolysis are the polyamides, since PA6 is hygroscopic, due to the amide groups. PA6 with its interesting technical applications could be found in humid environments, which probably impedes its durability. The estimation of the modifications that PA6 could undergo has attracted the attention of several research subjects, which have recorded a deterioration of the mechanical and thermal properties. The objective of this study is to compare the hydrolytic ageing of PA6 with its composites reinforced with peanut shell powder (PSP), olive pomace powder (OPP), and plaster (PL). The aim is to evaluate the impact of the reinforcements on the ageing of the composite. The weight changes, the structural properties, and the morphology were monitored and related to the modification of the polymer encountered during the ageing process thanks to the weight gain, DRX and SEM methods.

1 Introduction

Natural ageing is related to variations that may affect material properties. It provides direct way for assessing the durability of materials. But, it often requires long-term exposure to identify actual material degradation [1]. The main agents of degradation are light, temperature, oxygen, and water. Also, the water absorption capacity depends on the affinity of the polymer to water [1]. Due to its excellent mechanical properties, chemical resistance, and high thermal stability, polyamide 6 (PA6) has a wide range of applications in the industry [2,3]. Like any other polymer, PA6 absorbs heat and light, especially in the presence of moisture or oxygen. The amide group of the PA6 main chain is sensitive to humid environments and can undergo a hydrolysis reaction, resulting in a significant deterioration of the chemical structure and physical properties. This limits the use of polyamide based materials [4-5].

Researchers have studied the degradation of polyamides when exposed to water. Murthy et al. [6] concluded that the water molecules diffused almost exclusively in the amorphous regions of PA6 where the mobility of water molecules is more possible. Guerira et al. [7], mentioned that the mechanical characteristics of the samples were weakened with the ageing time ranging from 4 to 28 days at room temperature. This weakening of mechanical properties is explained by the penetration of water molecules within the macromolecule, breaking the secondary bonds of van der Waals type or hydrogen bonds between the polar groups of the neighboring macromolecular chains that have just preferentially bonded to a water molecule. This rupture causes an increase in mobility of the chains and thus a disturbance

of properties.

Ageing by immersion in water has also been performed for composites. The immersion of polylactic acid PLA /10% ramie fibers in water heated to 60°C induced a considerable decrease in tensile and flexural strengths of 87% and 77%, respectively, in less than 3 weeks [8]. On the other hand, polypropylene PP/40% Kraft fibers (fibers more sensitive to water absorption than ramie fibers since they are mainly carbohydrates) showed a rate of decrease in tensile strength of only 30% after immersion at higher temperature (70°C) [9].

The objective of this work is to study the hydrolytic ageing of PA6 by immersion in tap water and salt water. The influence of the incorporated reinforcements: peanut shell powder (PSP), olive pomace flour (PSP), and plaster (PL) on this ageing process is also evaluated. The effects of water and salt water on PA6 and its composites are evaluated by weight gain and X-ray diffraction (XRD) techniques. The morphology of the discs is evaluated by scanning electron microscopy (SEM).

2 Materials and methods

2.1 Synthesis of PA6 and the manufacture of composites

The reagents ϵ -caprolactame, N-acetylcaprolactam, and NaH are from Sigma-Aldrich. The synthesis method of PA6, PA6/PSP, PA6/PL composites are described in detail in our previous studies [10]. In this study, the composites with 10% and 20% by weight for each reinforcement were used.

* Corresponding author: oumaymaoulidi@gmail.com

2.2 Water absorption test

The tap water used in this study is provided by the company RADEM of the city of Meknes, Morocco. Its physical characteristics are described by Lamrani et al. [11]. The salt water is obtained by dissolving table salt (37g/l of NaCl) [12]. The PA6 and its composites were conditioned in the form of discs (12mm diameter / 2mm thickness) then immersed in small glass bottles, some containing salted water (SW) the others filled with tap water (TW), the total duration of immersion is six months (April-October) at room temperature, according to the standard NF 51-002. The sampling of the discs is done after 1 week, 2 weeks, 1 month, 2 months, 4 months, and 6 months. At each sampling, all surface water is removed with absorbent paper. The discs are weighed (m), and then returned to the flasks. The mass variation in (%) is given by the following formula:

$$\Delta m(\%) = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

with m_0 and m are, respectively, the masses of the disks before and after immersion. The weighing was done in a Lab balance NAHITA-BLUE 5133 with a precision of 0.001g .

2.3 X-ray Diffraction (XRD)

Structural analysis by X-ray diffraction (XRD) is performed on an X-RD-6100-Shimadzu type diffractometer ($\lambda_{Cu} = 1.54 \text{ \AA}$). The diffraction spectrum is performed for values of 2θ between 2° and 80° , at a scanning speed of $1^\circ/\text{min}$.

2.4 Scanning Electron Microscopy (SEM)

The disks are fixed on the sample holder with a double-sided carbon adhesive, the morphology was examined by a JEOL JSM-IT 500 HR scanning electron microscope operating at an accelerating voltage of 5 kV and in secondary electron image mode. The analysis is done in the Innovation Center of Technology Transfer of Moulay Ismail University, CITT-UMI, Meknes, Morocco.

3 Results and discussion

3.1 Water absorption test

Fig. 1 shows the masses absorbed by PA6 and its composites PA6/PSP, PA6/OPP, and PA6/PL throughout six months of immersion. It can be seen that the water uptake for all composites essentially showed two-stage behaviors: an initial linear portion followed by an equilibrium plateau. PA6 was found to have different behavior with each of the solutions, the mass absorbed in ES is 9% while it did not exceed 4% in ER.

This difference is due to the polarity of the NaCl and H_2O molecules that have just settled in the amorphous areas within the macromolecule, causing a strong absorption by the PA6 chains and thus an increase in mass. The incorporation of the reinforcement had a significant effect on the absorption rate of the PA6 macromolecule. The masses absorbed in SW by the PA6/10PSP and PA6/20PSP composites are approximately the same as raw PA6 while they are increased in TW, especially for 20PSP. The same observation can be done for PA6/10OPP and PA6/20OPP composites, except that these composites absorbed more than PA6/PSP.

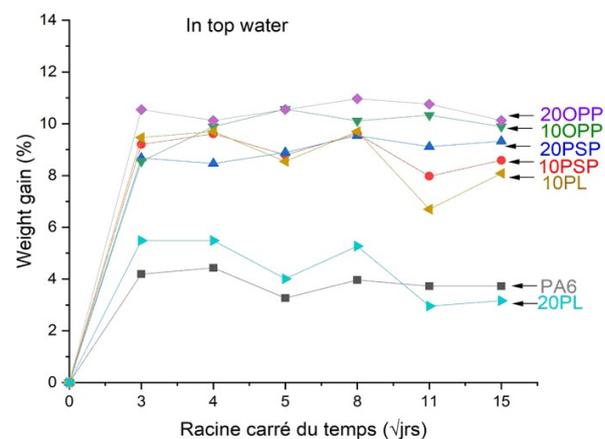
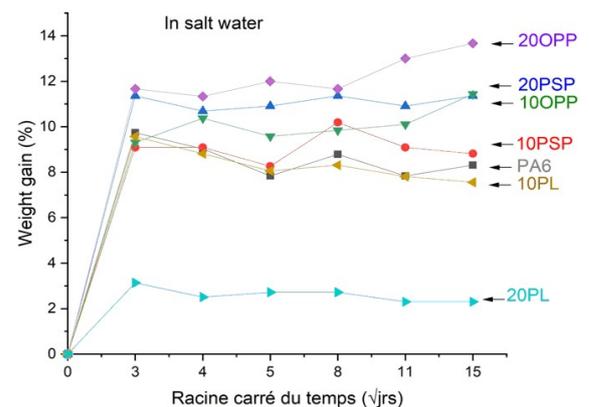


Fig. 1. Evolution of water uptake of PA6 and its composites PA6/PSP, PA6/OPP, and PA6/PL being aged at 23 °C.

This increase is due to the vegetable nature as well as the composition of PSP and OPP which contain lignocellulosic materials, having both hydroxyl groups and other oxygen containing groups that attract moisture by hydrogen bonding [13]. Therefore, as the rate of reinforcement increases, the rate of absorption also increases. The phenomenon observed for the composite PA6/PL was different, PA6 reinforced by 20% by weight had an absorbed mass of 3% in SW and 5% in TW, on the other hand, its analog of 10% by weight reached 8% and 9% for SW and TW, respectively. In this case, it was found that the PA6/PL composites studied improved the water resistance compared to PA6, this can be explained by the interactions between calcite and water that act to

tighten the cavities within the composite, which prevents the insertion of more water and therefore a low absorption rate compared to PA6.

3.2 XRD characterization

The diffusion of water within PA6 and PA6/PSP, PA6/OPP, and PA6/PL composites depends mainly on the spatial organization of the macromolecular chains of PA6. The latter is a semi-crystalline polymer, the diffused H₂O molecules will settle in the amorphous areas.

From Fig. 2, we can see that the intensity of the peaks has slightly decreased especially for bio-reinforced composites (PA6/PSP and PA6/OPP). This is because the water molecules will also diffuse inside the reinforcement passing through the matrix/reinforcement interface, where the hydrophilic components will absorb the water. This last will be transported inside the reinforcement causing its swelling and the matrix will be cracked around this swollen reinforcement [7]. It appears that water causes a slight plasticization, hence a deterioration of some crystalline properties, see Table 1.

Table 1. The crystallinity of PA6 and its composites before and after ageing on melt and tap water

| | Xc Before | Xc After 6 months | |
|--------------|-----------|-------------------|--------------|
| | | On Salt water | On tap water |
| PA6 | 38.5% | 35.8% | 37.5% |
| PSP10 | 37.5% | 35.5% | 36.1% |
| PSP20 | 35.4% | 29.0% | 36.9% |
| OPP10 | 36.5% | 29.7% | 33.0% |
| OPP20 | 37.5% | 27.8% | 30.9% |
| PL10 | 42.4% | 35.5% | 34.7% |
| PL20 | 43.5% | 40.4% | 35.1% |

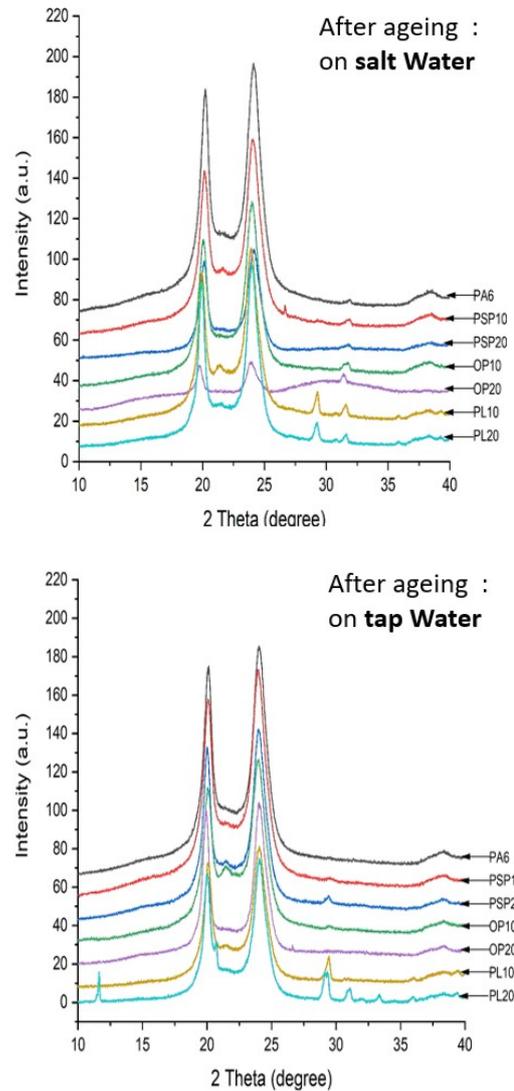
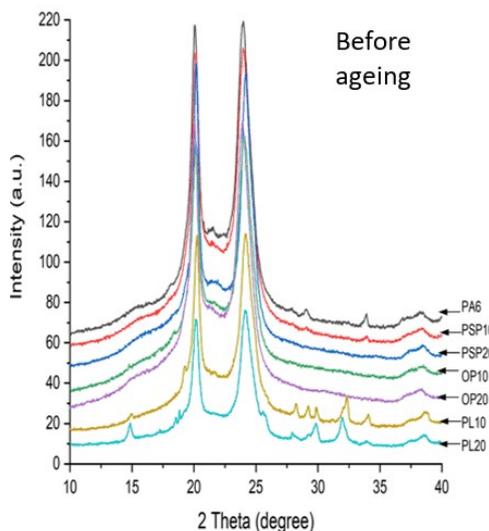


Fig. 2. X-ray diffraction of PA6 and its composites before and after ageing on salt water and on tap water.



The ageing mechanisms can be summarized in three different stages: the first one includes plasticization and swelling of the materials. The second is the propagation of microstructural damage to the fibers and matrix. The third step is the hydrolysis of the matrix and fiber components. These last steps irreversibly change the properties of the materials. In addition, depending on the mass absorbed the crystallinity changes. The composites reinforced with PSP and OPP has a large absorption rate. Therefore, their crystallinity decreased, especially for PA6/20PSP and PA6/20OPP, while PA6/PL absorbed only a modest amount of water and therefore it could maintain its crystallinity. These data show that the water absorption resistance of composite reinforced with 20% by weight is better than those reinforced with 20% by weight of plant reinforcements (PSP and OPP). In addition, the composite PA6/10PSP shows an interesting crystallinity after 6 months of immersion.

3.3 SEM characterization

Fig. 3 presents the modification due to ageing which affects the morphology of the discs of PA6 and its composites. It can be seen that this has changed completely. Cracks and propagated pores appear on the surface in addition to swelling on the main surface. These observations, which are valid for PA6 and its composites, prove the diffusion of water inside the macromolecular chains.

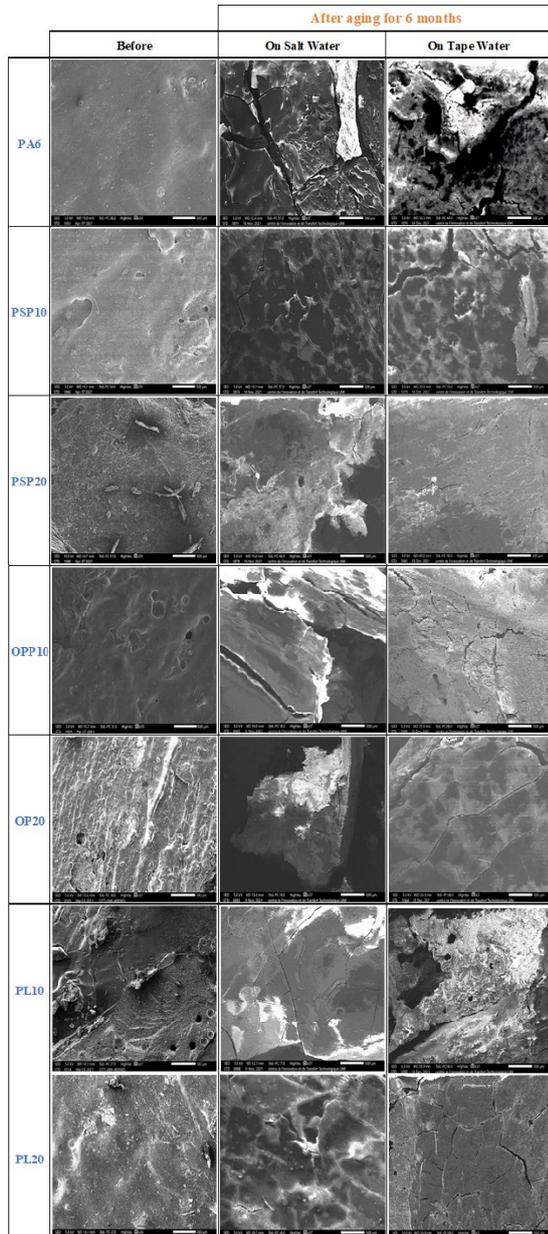


Fig. 3. SEM images before (left) and after 6 months of immersion: in saltwater (middle) and tap water (right) of PA6, PSP10, PSP20, OPP10, OPP20, PL10, PL20, scale 500µm.

4 Conclusions

This study was conducted on natural hydrolytic ageing

during 6 months for PA6 and PA6/PSP, PA6/OPP, and PA6/PL composites. The results showed that the nature of the reinforcement, as well as the immersion environment, has a considerable impact on the absorption rate of the PA6 matrix. The plant reinforcements (PSP and OPP) incorporated increased this absorption thanks to their richness in hydrophilic cellulosic materials, whether in the salty or tap environment, due to the H₂O and NaCl molecules being highly attracted by the amide functions of the PA6 matrix. The PA6/PL composite was able to resist absorption better than the other composites, and therefore, the plaster plays a role in printability with a very eligible crystallinity rate. These results can be interesting in terms of resistance in salt water for long period, especially for PA6/PL and PA6/10 PSP which show a good resistance in salt water.

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