Hydrolytic aging of a biopolymer reinforced with Alfa fiber treated with dispersing agent

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Abstract

The aging of materials is a degradation or a slow evolution of the properties of the material resulting from its intrinsic instability or caused by more or less aggressive external factors. Based on the literature, the degradation of polylactic acid (PLA) biocomposites mainly consists of hydrothermal degradation and photodegradation, the PLA/natural fibers interface is one of the main factors affecting the rate of hydrolytic degradation. With the addition of vegetable fibers, greater degradation is observed. Thus, because of their hydrophobicity, the biocomposite obtained has a greater moisture uptake causing swelling at the fiber/matrix interface. This causes cracking and degradation by more significant chain cuts. This work reports on the hydrolytic aging of biocomposites which were composed of Alfa fiber and Polylactic acid (PLA) prepared by extrusion. To improve the fiber/matrix compatibility, the Alfa fiber has been treated with a dispersing agent which is BYK W-980. Spectroscopic (FTIR), thermal, and water absorption tests before and after hydrolytic aging of biocomposites have been studied and compared. The results revealed that PLA/Alfa biocomposites in the presence of BYK W-980 are more resistant to hydrolytic aging compared to untreated composites.

Keywords: *Alfa Fiber, Biopolymer, Dispersing Agent, Hydrolytic Aging.*

I. Introduction

Chemical aging by hydrolysis (or hydrolytic) is characterized by the degradation of the polymer in an aqueous medium (liquid or gaseous). This type of degradation mainly affects polycondensates such as polyesters and polyamides and in particular PLA which is aliphatic polyester. Hydrolysis is generally characterized by a process of random chain cuts and is controlled by the diffusion of water within the polymer and is catalyzed in the presence of acid or base [1].

As in the case of other types of degradation, hydrolysis tends to act in amorphous zones, which are more permeable to water molecules [2].

In the case of PLA, the hydrolysis of the macromolecular chains produces lactic acid, which makes the reaction auto-catalytic leading to rapid and catastrophic degradation for the material [3]

The hydrolysis mechanism of polyesters induces chain breaks and shows that the species formed are of alcohol and acid type. Due to the formation of shorter chains, Chemi-crystallization takes place, stiffening and weakening the PLA [4].

In addition, low molecular weight oligomers and monomers are formed and leave the parent chains, causing surface erosion with the mass loss [2].

The hydrolysis of PLA has been the subject of numerous studies and has been established as the cause of strong chain breaks, a strong crystallinity of the polymer and therefore a drop in mechanical properties. Badia et al. [5] demonstrated a lower diffusion of water in a material retransformed three times thanks to its highly crystalline character.

The vulnerability of a biocomposite to hydrolytic aging is mainly linked to the fiber/matrix interface which is a very fragile zone. Indeed, aging by water immersion of PP/flax composites was carried out by Arbelaiz et al. [6] to study the kinetics of mass gain by the latter this immersion then caused swelling of the cellulose. This generated shear stresses at the matrix/fiber interface, and therefore their decohesion affected the mechanical properties (modulus and tensile strength) of the biocomposites after immersion [7].

In addition, the temperature can facilitate the diffusion of water molecules within the material.

For example, Joseph et al. [8] observed faster water uptake of PP/sisal composites once the water was heated to 70°C to limit the absorption of water in a humid environment by composites reinforced with natural fibers, the method commonly used consists in increasing the hydrophobicity of the fibers and improving the interfacial adhesion by treating the fibers. For example, the addition of a coupling agent made it possible to limit the water uptake of the biocomposites [9-11].

This present work is focused on the study of the durability of different PLA/Alfa biocomposite materials treated with BYK W-980 and untreated, prepared via hydrolytic aging.

II. Material and methods

The polymer used in this work is Poly (lactic acid) (2003D grade) in the form of pellets. It was obtained from Nature Works LLC, USA. Alfa used as reinforcement was collected from the arid region of Algeria. The average particles size is <80 µm, obtained using a universal laboratory grinder for plastics and wood "VERDER". The chemical composition of Alfa was reported previously [12].

The dispersing agents have been kindly given by BYK-CHEMIE its properties and Alfa fiber treatment is determined according to Ibrahim et al., [13].

The hydrolytic aging was carried out according to the standard ASTM D570. The specimens (m_0) are immersed in distilled water at 23 °C, with magnetic stirring. Every 24 hours, we take a sample; we remove all the surface water with absorbent paper.

The samples are reweighed (m), the operation continues for 6 months. The variation in mass (Δm) in (%) is given by the following formula:

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

Where: Δm (%) is the change in mass (wt. %), m_o is the mass of the sample before immersion (g) and m represents the mass of the sample after immersion (g).

III. Characterization

III.1 Fourier-Transform Infrared Spectroscopy (FTIR)

The samples were dried at 80 °C for one hour and used for infrared spectroscopy analysis. Infrared measurements were made on an FTIR spectrophotometer (SHIMADZU FTIR-8400S). A resolution of 4 cm-1 was used in the 4000-400 cm^{-1} wavenumber region.

III.2 Thermo-Gravimetric Analysis (TGA)

The thermal analysis of biocomposites was realized using a TA instrument Q500. The samples were heated from 20 °C to 800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere with a flowing rate of 50 ml/min.

III.3 Water absorption test

Squares 2 cm wide were dried for 1 hour in an oven at 60 °C and weighed the initial mass (m_0) using a precision analytical balance of 0.0001g, before immersion in distilled water at room temperature. Then, they were removed from the water, gradually, wiped carefully with paper, and then the mass of the samples was weighed. The water absorption rate was calculated according to formula (2) [14]:

$$Water\ absorption\ rate(\%) = \frac{m - m_0}{m_0} \times 100 \quad (2)$$

Where: m_o is the mass of the sample before immersion (g) and m represents the mass of the sample after immersion (g).

IV. Results and discussion

IV.1 Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectral analysis was carried out on the PLA and the PLA/Alfa biocomposites having undergone hydrolytic aging. The use of the results obtained can lead to the study of the diffusion of water or interpretations concerning the different states of water and its interactions in the system after hydrolytic aging.

Figure 1 shows the IRTF spectra of (a) PLA, (b) PLA/Alfa, and (c) PLA/Alfa/2% BYK W-980 before and after 4320h (6 months) of immersion in distilled water at room temperature.

As shown in the figure, aged and not aged samples show the same absorption bands but with different intensities. This difference in intensity is a consequence of the effect of aging and the time of aging [15]. The spectrum of aged PLA (Figure 1 (a)) shows the appearance of an absorption band at 3650cm^{-1} due to the vibrations of the hydroxyl groups of the water molecules [16-18].

The same changes were detected for the biocomposites. However, we notice the appearance of a wide absorption band between 3000 and 3700 cm^{-1}, which increases in intensity after 4320 h of aging, reflecting the vibrations of elongation of the hydroxyls of the water molecules (OH) associated with the diffusion of the liquid within the matrix and the reinforcement/matrix interface [19]. The micro-voids formed in the biocomposites are the results of imperfect degassing during processing or of fiber/matrix decohesion. These micro-voids tend to accommodate water molecules [20]. Nevertheless, according to the literature, it is evident that hydrogen bonds occur [21]. It is generally accepted that the unbound water molecules are characterized by a peak around 3650cm^{-1} (case of PLA alone after aging) and that the bands between 3000cm^{-1} and 3700cm^{-1} characterize the associated water (case of biocomposites) [22]. These molecular interactions are also interpreted in the form of deformation vibration (HOH) although this mode of vibration is less sensitive to interactions of hydrogen bonds which give us less detail [16]. For untreated composites, Figure 1 (b) shows increased C-H and C = O absorption intensity for samples altered after 4320h. The increase in the carbonyl absorption band indicates certain changes in the structure of biocomposites due to chemical degradation [23]. In addition to the changes mentioned above, the spectra of the PLA/Alfa biocomposites in the absence of

BYK W-980, aged for 4320 hours, show a decrease in the intensity of the bands located in the 1300 and 900 cm^{-1} regions compared to the spectra of not aged biocomposites. This decrease is attributed to the cleavage of the C-O and C-O-C bonds of the untreated fiber and the hydrolysis of PLA under the effect of humidity [24, 25].

However, it can be observed a decrease in the absorption bands located in the regions 3500, 1600, 1001, and 600 cm^{-1}, after 4320 h of aging for the PLA/Alfa / 2% BYK W-980 biocomposites (Figure 1 (c)) but not for the PLA/Alfa formulation (Figure 1 (b)), this may be due to the decrease in micro-voids between the Alfa fiber and the PLA matrix as well as the hydroxyl groups on the surface of the fiber which are blocked by 2% BYK W-980, in other words, there are fewer hydrogen bonds.

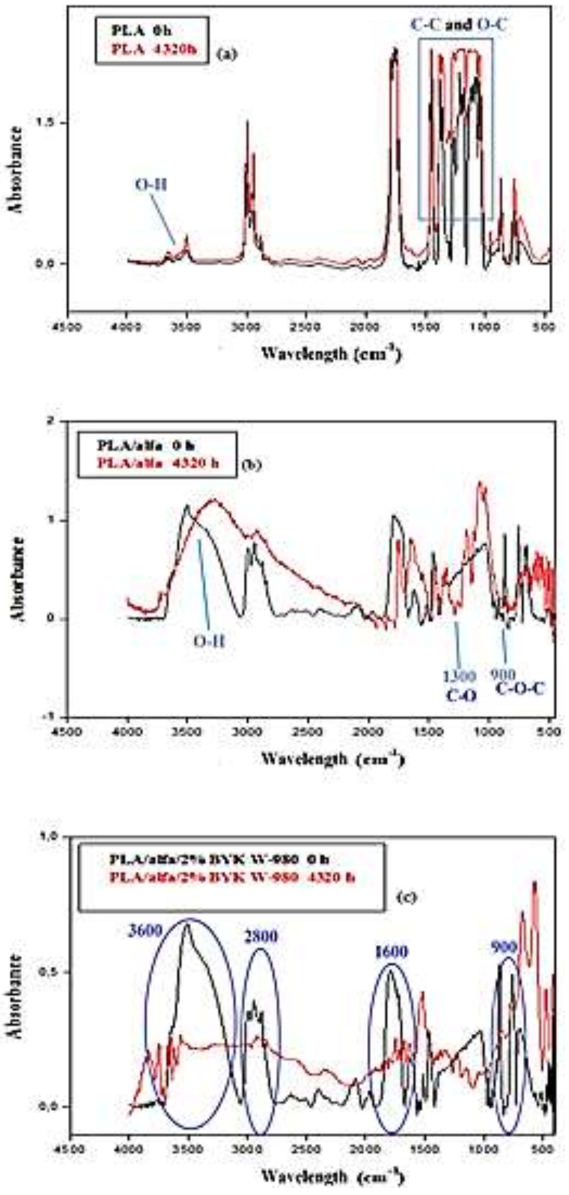

Figure 1. IRTF spectra of (a) PLA, (b) PLA / Alfa and (c) PLA/Alfa/2% BYK W-980 before and after 4320h of immersion in distilled water at room temperature.

IV.2 Thermo-Gravimetric Analysis (TGA)

The thermal decomposition of the three formulations PLA, PLA/Alfa and PLA/Alfa/2% BYK W-980 after aging was carried out by thermogravimetric analysis. Figure 2 shows the DTG thermograms of the three formulations.

The results indicate that the thermal stability of all samples decreased after hydrolytic aging. The decrease in this stability is proportional to the amount of water absorbed where it is found that the treated and untreated PLA

Alfa composites have undergone a strong decrease at temperatures $T_5\%$, $T_{50}\%$ and $T_{75}\%$ which is quite expected because Alfa is very hydrophilic due to the hydroxyl groups it contains. The fibers act as paths for the diffusion of water into the biocomposite. So, the composite containing the fiber degrades more than the pure thermoplastic matrix [26, 27].

Also, the DTG curves clearly show a large decrease in the degradation rate of biocomposites compared to unfilled PLA as there is a peak shift towards lower temperatures. From the ATG thermograms of the different materials, we could derive the values of the decomposition temperatures at 5, 50, and 75% ($T_5\%$, $T_{50}\%$ and $T_{75}\%$, respectively) of mass loss (Table 1). From the results illustrated in the table below, it is noted that the two temperatures $T_5\%$, $T_{50}\%$ and $T_{75}\%$ decrease after 4320 hours of immersion for the virgin PLA and the treated and untreated composites. This decrease may be due to the degradation of the fiber [19].

Table1. Degradation temperature of PLA, PLA/Alfa and PLA/Alfa/2% BYK W-980 biocomposites before and after immersion.

Temperature (°C)/ Formulations	PLA	PLA/Alfa	PLA/Alfa/2% BYK W-980
Before immersion			
$T_5\%$	317	240	251
$T_{50}\%$	356	306	315
$T_{75}\%$	366	322	327
After immersion			
$T_5\%$	296	238	201
$T_{50}\%$	353	302	308
$T_{75}\%$	363	315	320

Modification of PLA/Alfa biocomposites using 2% BYK W-980 influences thermal degradation behavior. The degradation temperature (T50%) and (T75%) (Table 1) of the modified biocomposite is shifted by approximately 6 °C. towards a higher temperature than that of the unmodified composites. Thus, this modification improved the thermal resistance. This effect is due to the stronger interaction between the fiber and the matrix with the formation of covalent bonds at the fiber-matrix interface and the good dispersion of the fibers [28].

The DTG thermogram showed degradation at 158 °C for PLA and at 178 °C for PLA/Alfa only present in the aged samples (Figure 2), this is due to water absorption during immersion [29]. It is essentially free water that has filled the cavities of the material during ageing [30, 31].

The shift of the peak of the derivative towards the higher temperatures for PLA/Alfa compared to PLA also suggests the formation of bound water with the creation of bonds of higher energy between the water and the fiber [32]. It is interesting to point out the absence of this peak for PLA/Alfa/2% BYK W-980 composites. Indeed, a small quantity of OH bonds on the surface of the fibers induces a low level of humidity.

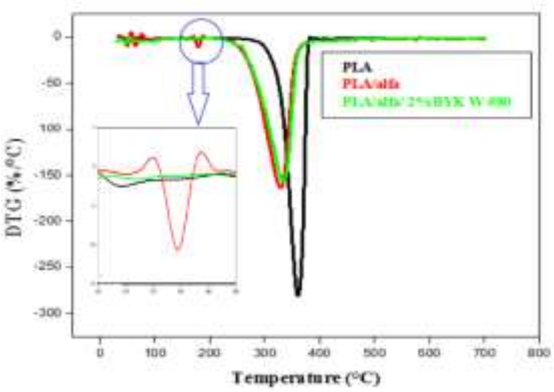

Figure 2. Thermogram DTG of PLA, PLA/Alfa and PLA/Alfa/2% BYK W-980 after 4320h of immersion in distilled water at room temperature.

IV.2 Water absorption test

Contact between a hydrophilic material and water molecules leads to the absorption of water by the surfaces and then in the volume of the material according to the laws of diffusion. According to various authors [33-36] the diffusion of water in biobased composites with an organic matrix is governed by different and successive mechanisms. First, the water molecules penetrate by capillary action between the polymer chains of the fiber and at the fiber/matrix interface, most often resulting from poor adhesion during the composite processing steps [33]. The water molecules then form hydrogen bonds with the hydroxyl groups of cellulose and hemicelluloses. Then, the water molecules diffuse at the interface and into the matrix [34,36]. At this level, some fiber components can also be hydrolysed, leading to decohesion at the fiber/matrix interface which may be responsible for the reduction of functional properties.

For each aging time, three samples: loaded and unloaded are weighed. The average mass gain values are shown in Figure 3. The mass variations of the PLA/Alfa biocomposites with and without BYK W-980 were related to the initial mass of virgin PLA to allow comparison with the unfilled matrix.

This Figure shows that the water uptake rate increases with increasing immersion time for all samples until saturation at about 180 days. As the PLA matrix does not show a significant gain in weight during this period of aging, we can therefore conclude that the penetration of water into the composites is through the reinforcement (Alfa fiber), the interface matrix/fiber, cracks and microspores that may exist on the surface of the composites that are probably formed during the manufacture of the biocomposites [19]. But still, the lower moisture absorption of PLA is expected due to its weaker hygroscopic nature compared to Alfa fiber. From the water absorption curves, it can be seen that the incorporation of the Alfa fiber into the PLA matrix caused a strong elevation in the rate of water absorption. They show a very high absorption rate (39%) compared to the virgin matrix (2.20%). Le Duigou et al. [37] evaluated the effect of immersion in distilled water at 23°C for two months of a PLA composite reinforced with 50% by mass of flax fibers on the evolution of its weight gain. While the weight gain of PLA alone does not exceed 0.5%, which of the composite increases with aging time to reach 14% after 8 weeks of aging.

This huge amount of absorbed water can be attributed to the presence of hydroxyl groups in the fiber structure. This is due to the low interfacial adhesion between the matrix and the fiber, in other words, due to the hydrophilic nature of the Alfa fiber caused by the large number of hydroxyl groups linked by hydrogen and Van der Waals bonds [38 ,39], which facilitates water insertion in PLA/Alfa biocomposites [40]. The authors explain the high water mass uptake for the composite by the high hydrophobicity and the structure of the flax fibres. The accessibility of water would also be influenced by the degree of esterification of the pectin, the size of the macromolecular chains of the hemicellulose as well as the crystallinity of the cellulose [41,42]. Other authors [43] have highlighted the influence of micro capillarity or lumen size on water diffusion. According to Okubayashi et al. [44] water can be absorbed by the hydroxyl groups of the fibers directly or indirectly. Directly, the water molecules would be easily absorbed on the hydroxyls present on the surface of the fibers or the hydroxyls of the amorphous zones. This “free” water would easily evaporate. Water molecules would also be absorbed on the inner surface of the voids and could thereby be trapped and bound to the fiber skeleton. These water molecules would be inserted between the cellulose chains, thus promoting their sliding relative to each other, causing the fibers to swell.

The introduction of BYK W-980 in the PLA/Alfa biocomposites decreased the water absorption rate from 39 to 15.91%. This improvement in the resistance to water absorption can be explained by the formation of bonds between the hydroxyl groups of the Alfa fiber and those of BYK W-980, which leads to the reduction of the hydrophilic character of the fiber. Indeed, the use of BYK W-980 reduces the diffusion of water in the PLA matrix reinforced by the Alfa fiber which is due to a better matrix/fiber adhesion, therefore, reduction of micro-voids in the interfacial region as well as the hydroxyl groups which are blocked by the groups of carboxylic acids (BYK W-980) to form an ester.

According to Joseph et al. [45] the decrease in the water absorption rate can also be explained by the reorganization of the polymer chains and the migration of compatibilizers to the surface during the aging process. We have also noticed that from 150 °C, there is a slight declination of the curve which can be explained by the hydrolysis of PLA and consequently loss of mass.

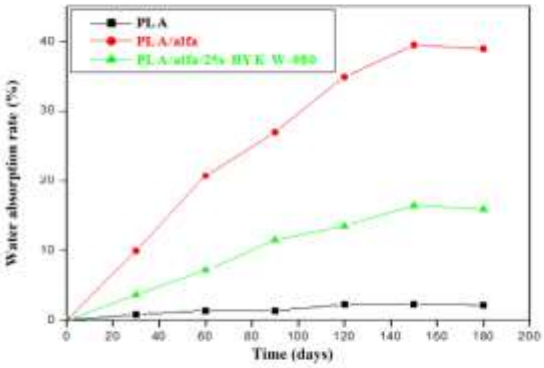

Figure 3. Evolution of the water absorption rate for pure PLA, PLA/Alfa and PLA/Alfa/BYK W-980 biocomposites

V. Conclusions

In this work, polylactic acid reinforced with Alfa fibers with and without the dispersing agent which is BYK W-980 underwent hydrolytic aging 4320 hours (180 days). Considering all the results, we were able to draw the following conclusions:

With the addition of vegetable fibers, greater degradation is observed. Thus, because of their hydrophobicity, the biocomposite obtained has a greater moisture uptake causing swelling at the fiber/matrix interface. This causes cracking and degradation by more significant chain cuts.

The presence of BYK W-980 influences the properties of biocomposites before and after immersion. These results are confirmed by measuring the weight gain which decreased in the presence of the dispersing agent. The latter reduces the number of hydroxyl groups in the fiber which are responsible for its hydrophilic nature and protects the fiber from degradation as seen in the Thermogravimetric Analysis results.

Conflict of interest. The authors report no conflict of interest.

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