

RESEARCH ARTICLE

Water absorption behavior and physico-chemical and mechanical performance of PLA-based biopolymers filled with degradable glass fibers

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Abstract

Poly(lactic acid) (PLA)-based biopolymers filled with degradable glass fibers were submitted to real life conditions, selected based on their potential applications as beverage containers, to evaluate the feasibility of their usage at the required operational conditions. To do so, several media (i.e., buffer solutions at pH = 3, 5, 7.5, 12 and alcoholic solution) and temperatures (25, 37, 55 and 70°C) were applied to mimic the storage of food, beverage, and detergents inside or in direct contact with the bio-based prototypes. Their mechanical, spectroscopic (FTIR) and morphological (SEM) features were evaluated and compared with samples after immersion. Water absorption increased with the increasing temperature, with maximum values achieved in alcoholic solutions indicating a more severe interaction of media with the functional groups of the samples. The diffusivity, D , increased with temperature, indicating faster water diffusion rate, especially in strong alkaline media. Treatments at pH 12 led to the most relevant degradation. This behavior was confirmed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis that evidenced a strong decrease of the ester band at 1755 cm^{-1} and the dissolution of the external layer of the polymeric matrix, which became more evident at higher temperatures, where several glass fibers emerged from the bulk. Tensile and flexural tests indicated a softening of the material and an increase in the plasticity of the samples with the increasing temperature. Evident embrittlement of samples was observed at higher temperatures, suggesting an increase in the crystallinity degree of the biopolymer. The obtained results showed the suitability of the PLA-based biocomposites for applications that do not require high temperatures for long periods of time. Also, the tested materials were proved to resist washing with mild detergents. These results will help in the designing of the new improved PLA-based biocomposites to meet with the target objectives on their applications.

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KEYWORDS

glass fibers, hydrolytic degradation, poly(lactic acid), temperature degradation

1 | INTRODUCTION

The worldwide production of commodity conventional plastics reached 367 Mtons in 2020, with a European contribution of 55 Mtons¹ and a decline in the production for the plastics industry due to the coronavirus pandemic in the first half of 2020.² These fossil fuel-based polymers have several advantages as their light weight and low cost. However, they present drawbacks as their dependence on oil prices and their non-renewable nature. In 2020, more than 29 million tons of plastic post-consumer waste was collected in the EU27 + 3. More than one third was sent to recycling facilities inside and outside the EU27 + 3 but over 23% was still sent to landfill and more than 40% was sent to energy recovery operations.¹ The use of bio-based plastics as alternative materials is continuously increasing in several applications as packaging, automobile manufacturing, agricultural equipment or household and toys, among other. This will lead to an unavoidable need of searching for adequate end-of-life strategies for these materials. Currently, bioplastics represent less than 1% of the global plastics production which capacity is set to increase from around 2.1 million tons in 2020 to 2.8 million tons in 2025 (<https://plasticseurope.org/>).

Poly(lactide) (PLA) is a bio-based and biodegradable polymer receiving much attention because of its versatility in many applications as packaging and disposal bottles/cutlery³ or biomedical materials and drug delivery systems.⁴ Properties as good processing capacity and the ability to biodegrade under specific conditions minimize its environmental print with respect to conventional polymers. One of its limits is its poor mechanical stability, exhibiting less than 10% elongation at break and relatively poor impact strength (1.9–2.6 KJ/m²)⁵ that it is surpassed by the addition of reinforcements as natural^{6,7} or glass fibers⁸ in the polymeric matrix. Another limit remains the relatively little knowledge about degradation behavior in different aqueous environments and the combined effect with the degradation temperature. Previous works have dealt with the aging of PLA-based biocomposites. PLA was immersed in distilled⁹ and sea water^{10,11} at room temperature, where natural aging was characterized by a slow degradation rate even after 10 weeks of immersion time. Temperature was employed to accelerate aging by Deroine et al.,¹² who immersed PLA samples in distilled water and seawater at temperatures up to 50°C to evaluate its influence on the kinetics of

degradation observing a deviation from Fickian behavior and morphological changes of the samples at higher temperatures.¹² Gil-Castell et al.¹³ tested the hydrothermal aging of PLA/sisal biocomposites below and above the glass transition (around 70°C) and observed that at tests below 70°C the polymer chains maintained their morphology and structure whereas above this temperature some changes in the internal structure of the biocomposite might occur.¹³ Few works can be found testing the stability of PLA after immersion on different media (acidic and alkaline solutions) as shown in the review by Gorrasi and Pantani,¹⁴ where tests at varying pH and their influence on the degradation mechanisms are described. Elsayy et al. showed that pH, temperature, and the autocatalytic behavior of PLA were the key parameters controlling the PLA degradation process.¹⁵ PLA was tested at different pH and temperatures mimicking biomedical applications¹⁶ obtaining high degradation rates in extreme alkaline conditions. For this work, the PLA-based biocomposite was designed and tested as food and beverage container, and thus at a specific range of pH and temperatures, to the knowledge of the author not tested before.

Several reinforcing agents have been traditionally included in the biopolymeric matrix to increase their required performance.^{17,18} In this work, ArcBiox™ degradable glass fibers were used as reinforcing agent. They are produced from a glass formulation generally called bioactive glass,¹⁹ well known for its beneficial properties for treating and healing bone defects.²⁰ Bioabsorbable glass fibers have mainly been used in the medical field to reinforce implants^{21,22} and, nowadays, they are increasing its presence in the technical sector (drinking cups or home utensils) as high-strength alternatives to fossil-based plastics like polyethylene, polypropylene and ABS. The fabrication of degradable glass fibers can be done in a similar manner than that of conventional glass fibers, although the thermal characteristics of degradable silicate glasses make their drawing into fibers very challenging.²³ In terms of processing, the glass is heated to fiber drawing temperatures and drawn into fibers. The production of continuous glass fiber made by melting and subsequent fiber drawing typically requires a sizing step on the glass fiber during the manufacturing process. This sizing step has mainly two functions: it provides protection to the filaments during the production process and enhances the fiber's adhesion properties so it firmly bonds with the polymer matrix. In this sense, the

developed degradable glass fibers were optimized on their sizing for their use in polyester matrices, as polylactic acid (PLA).

In the present work, PLA-based bioplastics were submitted to real life conditions, selected based on their potential applications as beverage containers, to evaluate their behavior at the required operational conditions. To do so, several media and temperatures were applied to mimic different beverages at different temperatures, or their cleaning in the dishwasher in an optic of material reusability. The work was carried out as part of the project BIO-PLASTICS EUROPE (<https://bioplasticseurope.eu/>) aimed at delivering sustainable strategies and solutions for bio-based plastics to support the EU-Plastic Strategy.

In this framework, the main objective of the present work is to analyze the synergetic effect of water and temperature on the main physico-chemical and mechanical properties of a PLA-based biocomposite, reinforced with degradable glass fibers. Test conditions in terms of aqueous media and exposure temperature were identified based on its expected final application. PLA-based biocomposites were tested for multiple-use cutlery by mimicking food in direct contact with the bio-based plastic, as well as alcoholic beverages and soft drinks (25°C and buffers at pHs of 3,5, 7.5 or alcoholic solution) as the tests aimed assessing its performance under real usage scenarios. Different temperatures were evaluated to simulate heated food and beverages (37°C/55°C/70°C and diverse aqueous solutions), as well as washing the cutlery material at normal (37°C/55°C and pH 12) to intensive (70°C and pH 12) dishwasher cycles.

2 | MATERIALS AND METHODS

2.1 | Materials and sample preparations

PLA-based polymer samples filled with degradable glass fibers were provided by Arctic Biomaterials OY Ltd. (ABM, Finland). According to the nomenclature adopted in the project this was BPE-C-PLA (Bio-Plastics Europe – Cutlery – PolyLactic Acid) as it was designed to produce multi-use cutlery by means of injection molding.

The initial mechanical and thermal properties of the PLA-based biocomposite (with 20% by weight of glass fibers) are reported in Table 1.

The bio-based plastic presented two different shapes (test bars C1 and C2) provided by Fraunhofer LBF to carry out different mechanical tests. The dumbbell shape test bars (C1) have dimensions of 74,5 mm with thickness

TABLE 1 Initial mechanical and thermal properties of the PLA-based biocomposites.

Property, test condition	Standard	Values, unit
Mechanical properties		
Tensile Modulus	ISO 527	6.01 GPa
Tensile Strength at Break, 23°C	ISO 527	79.73 MPa
Tensile Strain at Break, 23°C	ISO 527	2.08%
Izod Notched Impact Strength, 23°C	ISO 180/A	7 kJ/m ²
Izod Unnotched, 23°C	ISO 180/U	30 kJ/m ²
Thermal properties		
Heat Deflection Temperature A; (1.8 MPa)	ISO 75	62°C
Heat Deflection Temperature B; (0.45 MPa)	ISO 75	107°C
Other properties		
Density	ISO 1183	1.4 g/cm ³
Melt Flow Rate [200°C/5 kg]	ISO 1133	30 g/10 min

2 mm. Charpy test bars (C2) have dimensions of 70 mm with thickness 4 mm and width 10 mm.

The samples were labeled as Ci-T-pH to indicate the type of sample (C1 or C2), the temperature of immersion treatment, T (25, 37, 55 and 70°C) and the pH of the immersion media, pH (3, 5, 7.5, 12 and A). For example, a sample labeled C1-25-A indicates studies on C1 samples immersed at 25°C in an alcoholic solution.

2.2 | Methods

2.2.1 | Water uptake measurement

The samples were then immersed (in triplicate) into different aqueous solutions at the four different temperatures below and above the glass transition (~62°C). The aqueous solutions at pH 3, 5, and 7.5 have been prepared by using citrate–phosphate buffer (Buffer Reference Center (sigmaaldrich.com)); the alkaline aqueous solution (pH 12) has been prepared from potassium chloride and sodium hydroxide (<http://delloyd.50megs.com/moreinfo/buffers2.html>). A total of 60 specimens were tested.

Samples were removed from the solutions, dried, weighed, and submerged back into the corresponding solutions at specific sampling time points based on the trend of water uptake. The average content of absorbed water was calculated by weigh difference.

An initial characterization of properties was performed to establish the baseline conditions of the samples. Water uptake measurements were done until stabilization. Mechanical, thermal, SEM, and FTIR analysis were carried out at the end of the testing period (i.e., 18 days).

2.2.2 | Analytical procedure

Water uptake tests were performed according to the Standard BS EN ISO 62:2008. The initial weight (w_0) was measured and recorded. Samples were immersed in the aqueous media at the selected temperature. After certain periods of time, the specimens were weighed by means of an analytical Sartorius balance (w_t) with a precision of 0.1 mg. Then the samples were submerged back to the aqueous media. The absorbed water (M_t) was calculated according to (1):

$$M_t = \frac{w_t - w_0}{w_0} \cdot 100 \quad (1)$$

The saturation weight M_s was calculated as M_t at the equilibrium taken as the value of the weight uptake at the asymptotic line.

The diffusivity, sorption and permeation were studied using the Fickian model. When considered plane sheet geometry, given M_t at time t and M_s , Fick's law can be simplified using Stefan's approximation (2).²⁴ This approximation is used for the initial stages of water uptake (i.e., $M_t/M_s < 0.5$).

$$\frac{M_t}{M_s} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{1/2}, \quad (2)$$

where D is the diffusion coefficient, calculated according to (3) from the plot M_t/M_s as a function of the square root of time being θ the slope of the plot and l the thickness of the specimen (2 mm – C1 bars).

$$D = 0.065\pi l^2 \theta^2 \quad (3)$$

The sorption coefficient, S , was calculated as:

$$S = M_s / w_0 \quad (4)$$

Finally, the net effect of sorption and diffusion was calculated through the permeability coefficient, P :

$$P = D \cdot S \quad (5)$$

2.2.3 | Mechanical test

Static mechanical tests were obtained using an electro-mechanical universal testing machine Zwick/Roell Z50, equipped with modular sensor arm extensometer makroXtens II and load cell of 50 KN for tensile test and with sensor arms for 3-4-point flexure extensometer and load cell of 5 KN for bending tests.

Tensile tests were performed according to the Standard DIN EN ISO 527-1 on dog-bone specimens (C1 samples) at room temperature. All the tests were run with a rate of 1 mm/min, for the determination of the Tensile Elastic Modulus, and with a rate of 50 mm/min until break. The mechanical results obtained from these tests were: Tensile Young's Modulus (E_t), Ultimate Tensile Strength UTS (σ_M), namely the maximum stress recorded during the test, Strain at UTS (ϵ_M), Stress at breaking (σ_b) and Strain at breaking (ϵ_B).

Bending tests were performed according to the Standard DIN EN ISO 178 on C2 samples of rectangular shape, 4 mm in thickness and 10 mm in width. Samples were placed on two supporting pins, with span of 45 mm. All the tests were run with a rate of 1 mm/min for the determination of the flexural elastic modulus and with a rate of 5 mm/min until break. The mechanical results obtained from these tests were: Flexural Young's Modulus (E_f), Ultimate Flexural Strength UFS (σ_{Mf}), namely the maximum stress recorded during the test, Strain at UTS (ϵ_{Mf}), Stress at breaking (σ_{bf}) and Strain at breaking (ϵ_{bf}).

2.2.4 | Scanning electron Microscopy (SEM)

The morphological analysis was performed with a Scanning Electron Microscope (SEM) Hitachi S-2500, in secondary electron.

A portion of about 5 mm was obtained from the samples used for the tensile tests. The samples were observed, after gold coating, on the external surface at 50×, 100×, 500× and 1000× magnifications.

2.2.5 | Fourier transform infrared spectroscopy (FTIR-ATR)

IR-ATR spectra have been performed using a Thermo Nicolet Nexus FTIR instrument equipped with ATR accessory (diamond window), 100 scans, 4 cm⁻¹ resolution, DTGS detector, background air. Spectra were collected for all the samples in the range 4000–400 cm⁻¹ (mid-IR region). Each analysis has been repeated in different specimen and/or different points of the same sample.

3 | RESULTS AND DISCUSSION

3.1 | Water uptake tests

Figure 1 shows the percentage of water absorption, M_t , for the PLA-based biopolymers at the four different selected temperatures: 25°C (a), 37°C (b), 55°C (c), and 70°C (d) at varying pHs. Water absorption increased with the immersion time until equilibrium was achieved. Under glass transition, all curves displayed three stages, seeming to follow a Fickian behavior, with a fast absorption at the initial stages and a slower process afterwards until achieving an asymptotic saturation. However, at the temperature above the glass transition, more than three stages take place, in accordance also with bibliography.¹³ This non-Fickian behavior seems to be related to the appearance of microcracks (see Section 3.3) and the result of an accelerated water uptake. Also, the water saturation time was shortened (from over 15 days at lower temperatures to 2 days at higher ones). In addition, due to the degradation, some samples broke during the experiment; one specimen broke on day 4 and two on day 14 at tests carried out at pH 12 and 70°C.

The pH of the solution had different effects depending on the tested temperature with little effect at room temperature. At temperatures equal and higher than 37°C, samples

achieved steady state and then started losing weight in alkaline solution and evident degradation was shown in strong alkaline media, where glass fibers emerged from the bulk after dissolution of the external polymeric film (see Section 3.3). Two samples were destroyed at pH 3 and 70°C, with weight starting to decrease after 24 h of the immersion period, indicating a high aggressive media for these biopolymers, as confirmed by SEM images (Section 3.3) which show evident cracks and debris. This behavior was in accordance with what expected as glass fibers are well known to be highly susceptible of degradation under alkaline conditions, and even more at high temperatures where degradation is accelerated, where the network forming silica-oxygen (Si—O) bonds are attacked leading to dissolution of the glass surface.²⁵

3.1.1 | Water transport

The values of the saturation weight (M_s , %) and the water diffusion coefficients (D , cm²/s), sorption (S , g/g) and permeability (P , cm²/s) with the experimental deviation for PLA-based biopolymers at all tested conditions are gathered in Tables 2 and 3, respectively.

In general, M_s showed a decreasing trend with the increasing pH. Strong alkaline solutions showed

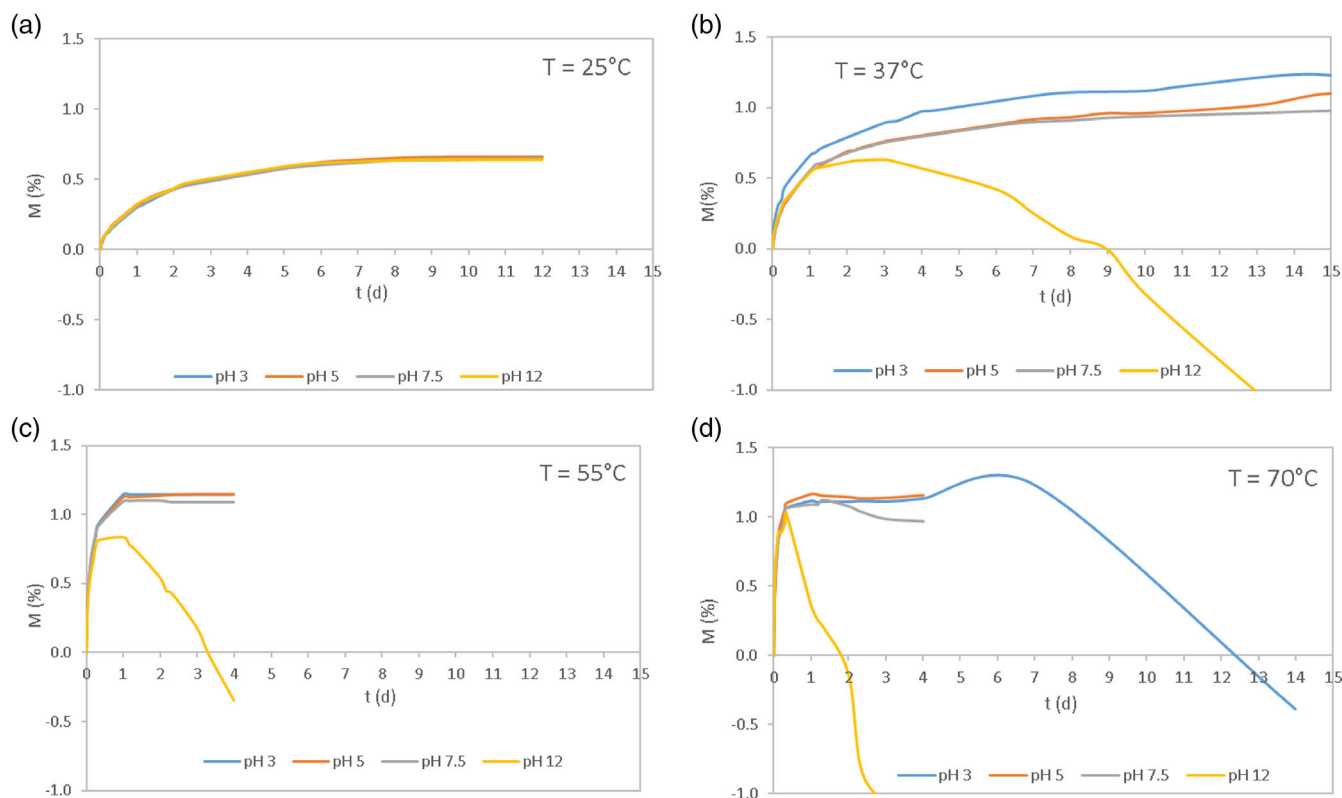


FIGURE 1 Percentage of water absorption, M_t , for the PLA-based biopolymers at the four different selected temperatures: 25°C (a), 37°C (b), 55°C (c), and 70°C (d). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

TABLE 2 Saturation weight (M_s , %) and experimental deviation for PLA-based biopolymers at all tested conditions

Aqueous solution	Test temperature (°C)			
	25	37	55	70
pH = 3	0.7069 ± 0.0364	1.2805 ± 0.1560	1.1454 ± 0.0012	1.1148 ± 0.0272
pH = 5	0.6771 ± 0.0225	0.9676 ± 0.0447	1.1489 ± 0.0035	1.1475 ± 0.0131
pH = 7.5	0.6562 ± 0.0203	0.9789 ± 0.0127	1.0909 ± 0.0057	1.0809 ± 0.0227
pH = 12	0.6057 ± 0.0209	0.6262 ± 0.0118	0.8346 ± 0.0117	0.9115 ± 0.0506
20% alcohol	1.9065 ± 0.0320	2.0723 ± 0.0318	2.0449 ± 0.0112	2.4887 ± 0.0126

TABLE 3 Water diffusion coefficients (D , cm²/s) and experimental deviation, R^2 , sorption (S , g/g) and permeability (P , cm²/s) for PLA-based biopolymers at all tested conditions

Aqueous solution	Test temperature (°C)							
	25				37			
	D ((cm ² /s)·10 ⁸)	R^2	S (g/g)	P ((cm ² /s)·10 ⁸)	D ((cm ² /s)·10 ⁸)	R^2	S (g/g)	P ((cm ² /s)·10 ⁸)
pH = 3	1.7829	0.9973	0.0065	0.0115	3.3383	0.9953	0.0130	0.0435
pH = 5	1.9897	0.9565	0.0066	0.0131	2.7074	0.9912	0.0105	0.0284
pH = 7.5	1.8910	0.9352	0.0064	0.0121	2.9559	0.9936	0.0098	0.0289
pH = 12	1.9731	0.9944	0.0062	0.0123	2.9559	0.9993	0.0063	0.0185
20% alcohol	0.0768	0.9491	0.0189	0.0014	1.0936	0.9983	0.0210	0.0230

Aqueous solution	Test temperature (°C)							
	55				70			
	D ((cm ² /s)·10 ⁸)	R^2	S (g/g)	P ((cm ² /s)·10 ⁸)	D ((cm ² /s)·10 ⁸)	R^2	S (g/g)	P ((cm ² /s)·10 ⁸)
pH = 3	27.8674	0.9995	0.0115	0.3192	47.9267	0.9995	0.0111	0.5343
pH = 5	27.8830	0.9982	0.0115	0.3201	49.6183	0.9999	0.0115	0.5706
pH = 7.5	36.0148	0.9987	0.0110	0.3944	77.4181	0.9970	0.0108	0.8368
pH = 12	37.3025	0.9998	0.0091	0.3400	124.7890	0.9962	0.0091	1.1374
20% alcohol	11.3113	0.9992	0.0204	0.2308	32.0193	0.9972	0.0249	0.7969

the highest impact on the samples degradation and the alcoholic solution enabled more water absorption presumably linked to the higher affinity between the functional groups. As expected, the saturation of the curves achieved higher values at higher temperatures. Also, the slopes of the initial grow were steeper with increasing temperatures which suggests a faster water diffusion rate. This behavior is in line with previous works in which immersion in distilled water of PLA-based biopolymers resulted in higher M_s values with the increasing testing temperature obtaining a similar range of values.^{12,13}

As expected, the diffusion coefficient increased with temperature at all pH. The pH had little impact on D at mild temperatures while it showed higher values in more alkaline solutions for higher temperatures (below the T_g) indicating a higher permeation of water in alkaline media. The effect was more notable at the highest

temperature (above the T_g) in which D achieved the highest value at pH 12. This behavior was also confirmed by visual changes as samples immersed at pH 12 and heated at 37, 55, and 70°C exhibited rough surfaces. In addition, at pH 12 and 70°C a relevant decreasing of pH was observed, reaching values around 8.7, which was readjusted during the tests, indicating bulk degradation phenomena.²⁶ The alcoholic media showed the lowest D at all tested temperatures indicating more predominant kinetic phenomena with respect to the other tested media. The obtained D values are comparable to previous studies using distilled water as immersion media.^{13,27}

The permeability coefficient, P , increases with temperature at all pH. PLA is permeable to water in amorphous phase and this variation of permeability could indicate a variation of its crystallinity as it will be seen from the variation on mechanical properties discussed in Section 3.2. Together with the permeability coefficient,

also the sorption coefficient increases with temperature from 25 to 37°C reaching a maximum at around 0.01 g/g at 37°C that remains at higher temperatures. This might

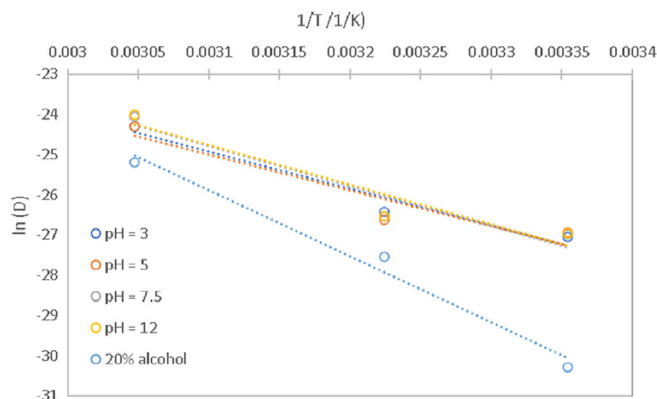


FIGURE 2 Linear fitting of $\ln D$ versus T^{-1} for the estimation of E_a . [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

TABLE 4 E_a estimated values and experimental deviation.

Aqueous solution	E_a (kJ/Mol)	R^2
pH = 3	76.02	0.954
pH = 5	73.83	0.896
pH = 7.5	82.11	0.916
pH = 12	82.02	0.908
20% alcohol	113.54	0.982

be due to the development of microcracks on the surface in a high temperature environment²⁸ also shown in the SEM images (see Section 3.3).

In addition, a linear relation is noted between the calculated D and the inverse of temperature at all aqueous solutions (Figure 2). This fact suggests that these coefficients might follow an Arrhenius law (Equation 4):

$$D = D_0 \exp(-E_a/RT) \quad (6)$$

The activation energy, E_a , is obtained from the slope of the linear fitting of $\ln D$ versus T^{-1} (Figure 2) in the range of temperatures below the glass transition.

Table 4 gathers the estimated calculated values for E_a together with the experimental deviation.

The results are in line with previous studies in which the range of estimated values was 40–80 kJ/Mol for solutions in distilled water,^{12,29} with little dependence on pH. The higher values obtained for the alcoholic solution could be explained by the difference on aqueous environment and it is in line with the previously observed kinetic phenomena, with a more limiting effect in samples immersed in the alcoholic media.

3.2 | Mechanical test

Tensile tests on the reference sample (C1) revealed a typical behavior of a rigid polymer with a negligible plastic

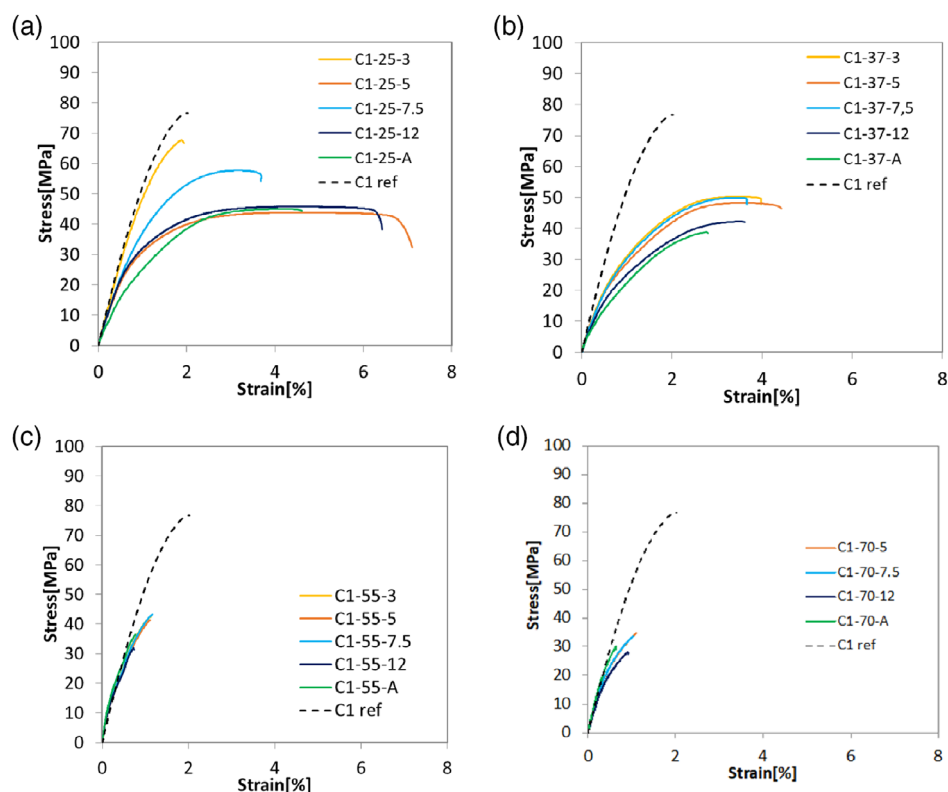


FIGURE 3 Comparison of stress versus strain plots obtained with tensile tests on C1 samples before (C1 ref) and after treatment at pH 3, 5, 7.5, and 12 and in alcoholic solution, at 25°C (a), 37°C (b), 55°C (c), and 70°C (d). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

deformation. E_t and σ_M present higher values than pristine PLA³⁰ due to the presence of reinforcing fibers. After an initial straight line corresponding to an elastic behavior, the curve shows a slight reduction on the slope until break, that occurs at 2% of strain (C1 ref in Figure 3). The pH of the immersion media had a different effect on the mechanical properties depending on the applied temperature. At room temperature, the samples immersed in acid solution (pH = 3) seemed to not be affected by immersion, maintaining E_t and ϵ_b nearly equal to the reference sample (Figure 3a). A slight reduction on E_t was observed at increasing pH with a more evident effect for the alcoholic solution. On the other hand, σ_M showed a more pronounced dependence with pH (from 80 MPa to

40–50 MPa) and ϵ_B was found to be three times higher with respect to the reference, indicating an increase on the plasticity of the sample. This plasticization can be a reversible phenomenon that disappears after drying when water molecules enter the matrix without degradation effects, while it becomes irreversible when hydrolysis processes occur, inducing molecular chain breakage and microcracks formation.³¹ Water molecules could act as lubricant making fibers in the biocomposite slide over one on another during stretching, which results in extra extensions and elongations.³²

The samples immersed in solutions at 37°C showed a behavior like that at room temperature (Figure 3b), with σ_M reduced to 50 MPa and ϵ_B around 4%.



FIGURE 4 Radar charts representing the tensile Young's modulus (E_t) and the strain at break (ϵ_B) at the different testing temperatures and immersion media. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

Interestingly, treatments at higher temperatures (Figure 3c,d) resulted in an embrittlement of the samples with ε_B below 1% and σ_M around 30 MPa, three times lower than the reference sample. This could indicate a possible increase on the crystallinity degree of the biopolymer, in agreement with the results obtained from the water uptake (Section 3.1).

The influence of the temperature on the studied mechanical properties can be summarized in Figure 4. The radar charts, one for each immersion media, show the elastic modulus (E_t) and the strain at break (ε_B) at the four studied temperatures together with the reference sample. As shown, ε_B is affected by the high temperature at all pHs, with an evident reduction of its value indicating an embrittlement of the specimen. E_t seems less influenced by temperature, with a more evident effect for the alcoholic solution, where its value is reduced even at mild temperatures. All the presented values are gathered in Table S1 at the Supplementary material.

Regarding flexural tests, reference samples (C2 ref in Figure 4) showed an elastic behavior with a brittle fracture at 3.5%–4.0% and an ultimate stress of about 90 MPa (Figure 5). After immersion at 25°C, it could be observed a remarkable growth of plasticity (Figure 4a) with an increase of ε_{bf} from 3.8% to 6.1% and a reduction of σ_{Mf} from 91 to 76 MPa. No evident changes in E_f could be appreciated. No remarkable differences were observed at 37°C with respect to the reference sample, except for the immersion in alcoholic solution which resulted in an evident reduction on σ_{Mf} (40 MPa) as well as on E_f (2.26 GPa) and on ε_{bf} (2.6%). Significant differences can be observed in the samples treated at 70°C, with an embrittlement of the specimens, in particular for those immersed in alcoholic solutions, where σ_{Mf} and ε_{bf} decreased to one third of their original value. Noteworthy, samples treated at 70°C and pH 3 showed a halving of E_f and a dramatic reduction of σ_{Mf} to 10 MPa and of ε_{bf} to 0.6%. All the presented values are gathered in Table S2 at the Supplementary material.

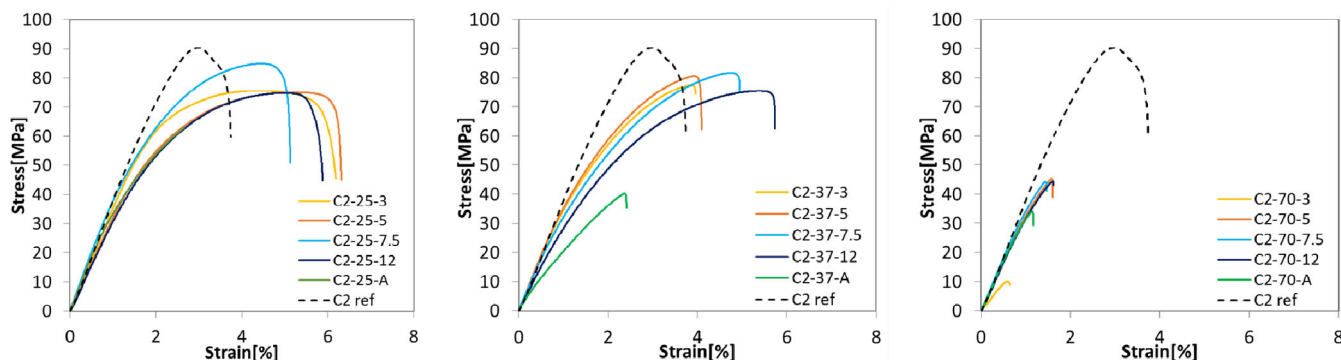


FIGURE 5 Comparison of stress versus strain plots obtained with bending tests on C2 samples before (C2 ref) and after treatment at pH 3, 5, 7.5, and 12 and in alcoholic solution at 25°C (a), 37°C (b) and 70°C (c). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

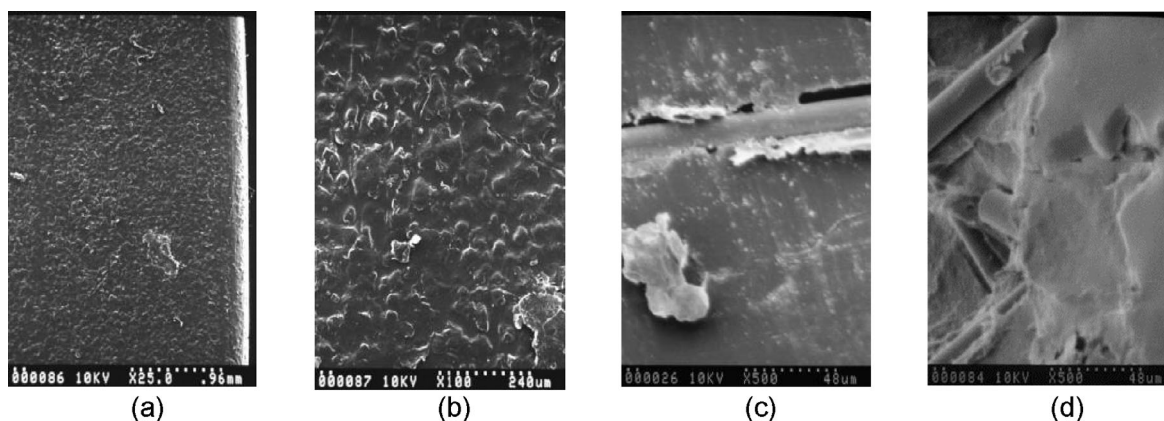


FIGURE 6 SEM images at ×25 (a) and ×500 (b) magnifications of the external surface of C1 reference samples and SEM images at ×500 magnifications of the external surface of C1 samples immersed at 25°C in alkaline solution (pH = 12) (c) and alcohol (d).

3.3 | Morphological analysis

Reference samples (C1) show a light superficial roughness where irregular particles of about 50 μm can be observed (Figure 6a). These particles are covered with a uniform layer that, at high magnification (Figure 6b), confers to the surface a uniform appearance. The specimens do not evidence morphological changes on the surface after the aqueous treatments except for samples immersed in a solution of pH = 12 (Figure 6c) and in alcoholic solution (Figure 6d). In them, a smoother surface, that can be ascribed to the dissolution of external layer of the polymeric matrix,³³ and the presence of cracks in which emerge the glass fibers can be observed. Water diffuses into the polymer in a variety of ways, including through free volumes in the polymer and through capillarity along the fibers.³⁴ The microcracks in the matrix, formed around the fiber, disrupt the fiber-matrix interfacial adhesion inducing a fiber-glass debonding³² and, consequently, a change in the mechanical properties, as observed in the previous Figure 3c,d and in Figure 6b,c.

This effect is also present in the samples treated at 37°C, except for samples immersed in the solution at pH = 5 (Figure 7a) that maintain a roughness similar to the reference. Interestingly, the surface of samples immersed in alcohol at 37°C show circular flakes partially detached (Figure 7b). A more evident degradation can be observed in the samples immersed in strong alkaline solutions (pH = 12) both at 37°C (Figure 7c,d) and at 70°C, where several glass fibers emerge from the bulk because of the dissolution of the external polymeric film. A smooth surface is also present in the other samples treated at 70°C (Figure 8a), except for samples maintained at pH = 3 where a corrugate surface with evident cracks and debris are present (Figure 8b).

3.4 | IR ATR studies.

In the IR spectrum of pristine PLA-based sample (reference material), the main band is centered at 1755 cm^{-1} ,

split, with a sharp component at 1714 cm^{-1} and is assigned to $\nu_{\text{C=O}}$ of the ester group in the polyester structure (Figure 9, REF spectrum). The complexity of this signal, showing several shoulders between the two maxima, can be due to different conformation and crystallization degree within the polymer.^{35,36} On the other side, the very evident split of the band in two maxima at 1714 and 1755 cm^{-1} , the latter consistent with the PLA carbonyl band,³⁷ suggests the presence of different ester groups likely corresponding to another ester of different chemical nature. The envelop of bands with maxima at 1180, 1157, 1130, 1085, 1045 cm^{-1} is assigned to C—O—C and CC stretching modes with some contribution of CH deformation of CH_3 group.^{36–38} Weaker bands in the region 1450–1330 cm^{-1} are specifically assigned to CH deformation modes, whose corresponding stretching modes are detected in the range 3000–2850 cm^{-1} (Figure 10, REF spectrum). Features of the glass fibers are generally expected to fall mainly in the region around 1100–900 cm^{-1} . In the biocomposite spectrum, these bands are indeed overlapped and masked by the strong bands of the polymer matrix, therefore hindering the possibility to evaluate specific interactions at molecular level between the two moieties.

Changes in the IR spectra of reference sample and of samples after pretreatments at different temperatures and

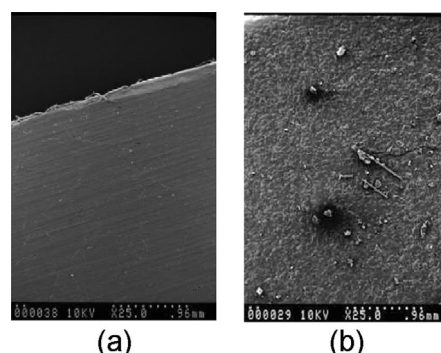


FIGURE 8 SEM images at $\times 25$ magnifications of the external surface of C1 samples immersed at 70°C in neutral solution (a) and in acidic solution (pH = 3) (b).

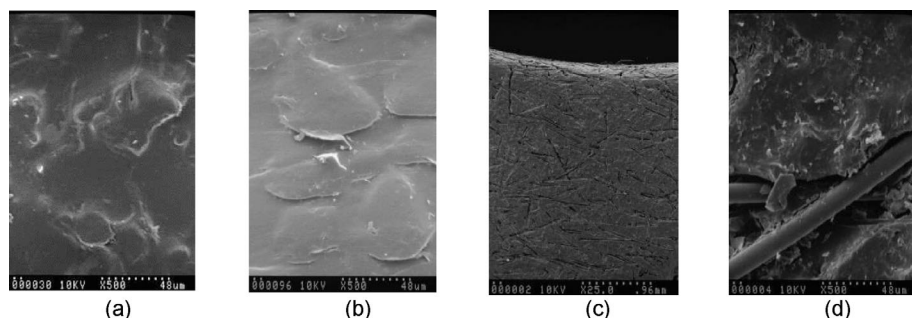


FIGURE 7 SEM images at $\times 500$ magnifications of the external surface of C1 samples immersed at 37°C in a pH = 5 solution (a) and in alcohol (b) and SEM images of the external surface of C1 samples immersed at 37°C in a pH = 12 solution, at $\times 25$ (c) and $\times 500$ (d).

pHs are highlighted in the following. The complete spectra set, recorded after each treatment, are reported in the Supporting Information section (Figures S5–S8) while spectra recorded at pH 12 are grouped in Figures 9 and 10.

The comparison of spectra recorded after treatment at 25°C with the reference spectrum shows that the main IR features of the polyester chains are not significantly affected by the pretreatment in the pH range 3–7.5. Both in the low and in the high frequency spectral region (Figures S1 and S2) only very weak differences in relative intensities of the CO and CH bands are detected. However, in the case of treatment at pH 12 (Figure 9) several significant changes appear: the component of the ester band at 1755 cm⁻¹ is strongly decreased in intensity and the relative intensities of the bands at 1157 and 1085 cm⁻¹ are inverted, that is the former band is predominant in this spectral range after the treatment. Moreover, a very weak feature appears around 3430 cm⁻¹, assignable to the stretching mode of isolated OH groups, possibly terminal OH of the polymer chain formed by some hydrolytic processes (Figure 10). Stretching bands of the CH groups are also slightly more defined after the treatment in solutions, and changes in relative intensities can be detected too.

The treatment in solutions at 37°C leads to very similar spectra in the range of pH 3–7.5, consistent with the reference spectrum (Figure S6). Once again, noticeable changes in the spectrum are reported after treatment at pH 12 (Figure 9). As discussed in the previous case, the high frequency component of the carbonyl band at 1755 cm⁻¹ becomes a shoulder of the main band at 1714 cm⁻¹ and bands in the region of the CC and CO stretching modes change in shape and relative intensity. In the high frequency region, the

spectrum after treatment at pH 12 shows a very weak feature appearing around 3430 cm⁻¹, assignable to OH groups together with a broad absorption tailing towards lower frequencies, that can be assigned to H-bond hydroxyls, both from adsorbed water and structural OHs (Figure 10).

After treatment at 55°C (Figure S3) and 70°C (Figure S4), and pH 3.5, 5, and 7.5, the analysis of the spectra shows just few changes in relative intensities of the main bands. Focusing on the C=O stretching band it is possible to notice that some shoulders of the main components are lost, suggesting changes in the crystalline structure of the polymers, and possibly corresponding to a variation in the mechanical properties with an embrittlement of the sample, as shown in Section 3.2. On the other side, both at 55 and 70°C and in strong alkaline environment, significant changes are detected in the spectrum: the high frequency component at 1755 cm⁻¹ almost disappears, and also components at 1130 and 1085 cm⁻¹ are not anymore detectable (the enlargement of these spectral regions is shown in Figure 11). This effect points out that at least one kind of the ester bonds disappears, likely the PLA component, whose diagnostic carbonyl band falls between 1750 and 1740 cm⁻¹. Moreover, some broad and weak absorptions growth in the 1600–1590 cm⁻¹ range, likely assigned to carboxylate species asymmetric stretching, whose symmetric vibrational mode can be masked by the CH deformations (Figure 9). Correspondingly, in the high frequency region of the spectra, treatment at pH 12 leads also to the detection of a weak band at 3430 cm⁻¹, as reported in the previous paragraphs, that can be assigned to “free” terminal OH groups of the polymer chain. A new broad absorption between 3600 and 3200 cm⁻¹ can be assigned to H-bonded hydroxyl groups, arising from the interaction

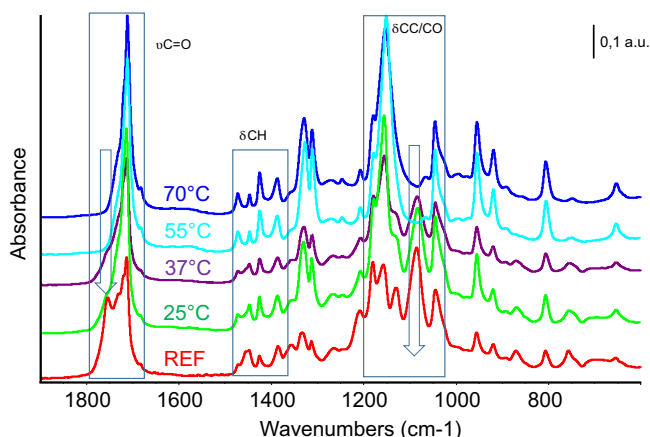


FIGURE 9 FTIR spectra of PLA-based samples pretreated in solutions at pH = 12. REF spectrum: not treated PLA based material. Spectral regions of major interest are evidenced. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

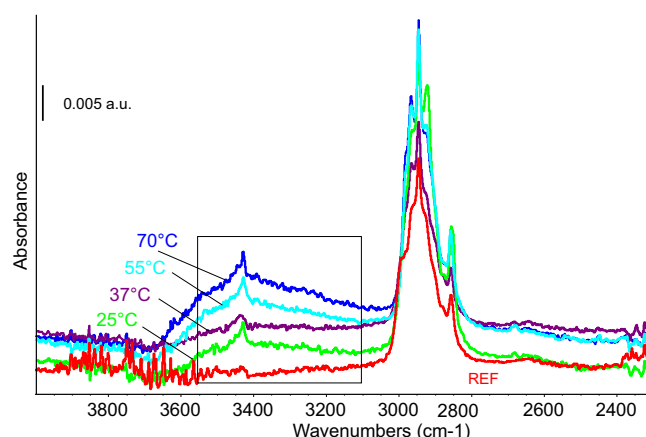


FIGURE 10 FTIR spectra of PLA-based samples pretreated in solutions at pH = 12. REF spectrum: not treated PLA based material. High frequency region. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

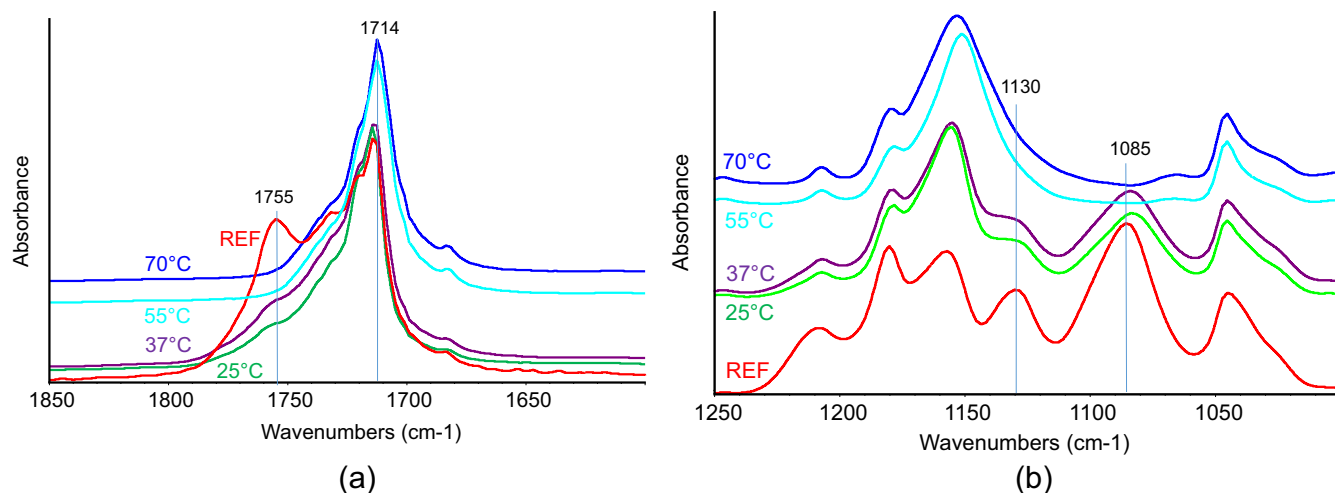


FIGURE 11 FT IR spectra of PLA-based samples pretreated in solutions at pH = 12. Enlargement of carbonyl (a) and CC/CO vibrational modes (b). REF spectrum: not treated PLA based material. Spectra not in common scale. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.54578)]

of surface terminal OHs and also from an increased amount of adsorbed water whose corresponding deformation mode can be detected as shoulder growing at $1620\text{--}1630\text{ cm}^{-1}$. This observation could confirm that water uptake is strongly dependent on the temperature increase. Moreover, the increase in the adsorbed water evidenced at 70°C (pH 7.5 and 12) may be related to the exposed glass fibers detected previously by SEM microscopy. In this hypothesis, water molecules will mainly interact through coordination or H-bonds with the hydrophilic glass fiber surfaces. On the other side, at molecular level, adsorbed water will also interact at the terminal OH and COOH groups of the polymer chains.

In sum, spectroscopic results are in agreement with data from water uptake and electron microscopy, showing some degradation in strong alkaline solutions. The loss of ester groups indicated by the disappearance of the $\text{C}=\text{O}$ band suggests some chemical degradation in the polymer chain related to the pretreatment at basic pH values, and possibly proceeding through a random ester cleavage in agreement with literature reports.^{15,39} However, the effect of the temperature appears somehow limited to the IR analysis, although it is evident that degradation of the ester groups observed at pH = 12 (decreasing of the carbonyl band at 1755 cm^{-1}) is enhanced at 55 and 70°C (disappearing of the carbonyl band at 1755 cm^{-1}).

4 | CONCLUSIONS

The synergetic effect of different aqueous media (i.e., pH = 3, 5, 7.5, 12) and temperature on the water absorption behavior of a PLA-based polymers reinforced with degradable glass fibers was studied to evaluate their

influence on morphology, physico-chemical and mechanical properties of the biopolymers.

The water saturation weight increased with temperature at all pHs, with shorter saturation times and higher diffusion coefficients. pH had little impact at moderate temperatures while alkaline media showed higher diffusion coefficients above the glass transition temperature, T_g . The water uptake for PLA biopolymers was found to be temperature dependent with increasing diffusion coefficients following an Arrhenius relationship.

The temperature of the immersion media proved to be predominant with respect to the pH on the mechanical properties of the specimens, which showed an embrittlement over 55°C at all pHs. At room temperature, the samples showed instead a strong increase of their plasticity, except for media at pH 3. Morphological changes on the surface occurred in alcohol and, in particular, in alkaline solutions, with an evident degradation of the external polymeric film and the exposition of the internal glass fibers. Instead, a smoothing due to the partial dissolution of the polymer was observed in the samples subject to acidic and neutral media at high temperature (70°C).

FTIR studies evidenced significant changes mainly in the spectra of samples treated at pH 12, such as the disappearing of ester groups, the formation of new hydroxyl groups and the increase in hydrophilicity, suggesting chemical degradation of the surface polymer layers. It is also possible to notice a small effect of the temperature that enhances the effect of pH.

The material was designed for food applications as beverage container or multiple use cutlery, resistant to dishwasher. The obtained results showed the suitability of the PLA-based biocomposites for applications that do not require high temperatures for long periods of time.

Also, the tested materials were proved to resist washing with mild detergents. These results will help in the designing of the new improved PLA-based biocomposites to meet with the target objectives on their applications.

AUTHOR CONTRIBUTIONS

Elisabetta Finocchio: Data curation (equal); formal analysis (equal); writing – review and editing (equal). **Cristina Moliner:** Conceptualization (equal); formal analysis (equal); methodology (equal); writing – original draft (lead). **Alberto Lagazzo:** Data curation (equal); formal analysis (equal); writing – original draft (equal). **Samantha Caputo:** Data curation (lead). **Elisabetta Arato:** Funding acquisition (lead); methodology (lead); project administration (lead); writing – review and editing (lead).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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