

Article

Effectiveness of Sodium Acetate Treatment on the Mechanical Properties and Morphology of Natural Fiber-Reinforced Composites

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Abstract: This paper aims to investigate the ability of an eco-friendly and cheap treatment based on sodium acetate solutions to improve the mechanical properties of flax fiber-reinforced composites. Flax fibers were treated for 5 days (i.e., 120 h) at 25 °C with mildly alkaline solutions at 5%, 10% and 20% weight content of the sodium salt. Quasi-static tensile and flexural tests, Charpy impact tests and dynamical mechanical thermal (DMTA) tests were carried out to evaluate the mechanical properties of the resulting composites. Fourier transform infrared analysis (FTIR) was used to evaluate the chemical modification on the fibers surface due to the proposed treatment, whereas scanning electron microscope (SEM) and helium pycnometry were used to get useful information about the morphology of composites. It was found that the treatment with 5% solution of sodium acetate leads to the best mechanical performance and morphology of flax fiber-reinforced composites. SEM analysis confirmed these findings highlighting that composites reinforced with flax fibers treated in 5% sodium acetate solution show an improved morphology compared to the untreated ones. On the contrary, detrimental effects on the morphology as well as on the mechanical performance of composites were achieved by increasing the salt concentration of the treating solution.

Keywords: flax fibers; alkaline treatments; sodium acetate; fiber–matrix adhesion; mechanical performance



Citation: Badagliacco, D.; Fiore, V.; Sanfilippo, C.; Valenza, A.

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J. Compos. Sci. **2022**, *6*, 5. <https://doi.org/10.3390/jcs6010005>

Academic Editor: Francesco Tornabene

Received: 9 December 2021

Accepted: 23 December 2021

Published: 25 December 2021

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1. Introduction

In the last decades, due to improved sustainability, competitive properties and lower cost, natural fiber-reinforced polymer composites (NFRPCs) have attracted the attention of researchers as a potential substitute of synthetic fiber-reinforced polymer composites. For these reasons, they have also found an application in several engineering fields such as the automotive, marine and sports equipment fields. Nevertheless, a crucial issue related to these materials is their lower mechanical performance in comparison to synthetic counterparts such as glass or carbon fiber-reinforced composites, mainly due to the weak fiber–matrix adhesion. This drawback can be mainly ascribed to the hydrophilicity of natural fibers and hydrophobicity of several thermoset polymers (i.e., epoxy), respectively [1]. Indeed, it is widely known that hydrophilic natural fibers are covered with pectin and waxy substances, which prevent the hydroxyl groups from reacting with polar and hydrophobic organic matrices. This fact leads to early aging and low mechanical strength of the composites. A weak interface limits the capacity of stress transfer between the composites' constituents (i.e., matrix and fibers), thus worsening the mechanical response of the resulting composites. By contrast, suitable interfacial bonding allows proper load transfer from the matrix to the reinforcement, which helps to reduce stress concentrations as well as improving the overall mechanical properties [2,3]. To overcome this issue, several physical [4–6] and chemical treatments [7–10] of natural fibers have been widely carried out with the main aim of enhancing the adhesion with hydrophobic polymeric matrices. The

mercerization or “alkalization” is one of the most widely used chemical treatments, which consists in the soaking of natural fibers in an alkaline solution to reduce the contents of lignin, pectin, waxy substances and natural and artificial impurities covering the external surface of the cell wall of the fiber. The most commonly used chemical is sodium hydroxide (NaOH), and the reaction can be represented by the following equation:



Apart from the removal of cementing constituents such as hemicellulose and lignin, alkalization leads to fiber fibrillation. In particular, fiber bundles (i.e., technical fibers) are reduced to thinner fibers (i.e., elementary fibers), increasing the effective surface area available for contact with the matrix. This kind of treatment can also increase the superficial roughness of the natural fibers, thus improving the mechanical interlocking between fiber and matrix as well as facilitating the bonding reactions, due to the exposure of the hydroxyl groups to the matrix.

Hence, a stronger fiber–matrix interface can be obtained, leading to noticeable increments of the composite performance, as shown by a wide literature on the subject [11–13].

However, it should be noticed that this method also presents some shortcomings. In particular, it was demonstrated to be expensive and unsustainable due to the use of hazardous chemical such as sodium hydroxide [14–17]. Furthermore, the highly alkaline treatment can significantly affect the mechanical properties of the fibers, hence dramatically limiting their suitability as reinforcement of composite materials [18–20]. In such a context, new eco-friendly and inexpensive treatments based on sodium bicarbonate and sodium carbonate salts have been considered recently [21–27]. Through these approaches, natural fibers are soaked in a mildly alkaline solution that has sodium cations, thus leading to a reaction analogous to the one described by Equation (1). In another work, seawater was also used to treat sugar palm fibers and their epoxy composites. The test results indicated that the seawater treatment increased the mechanical properties of the composites due to the improved surface characteristics of fibers by removal of the external layers rich in pectin and hemicellulose, thus improving the fiber–matrix interface [28].

It is worth noting that when a mildly alkaline baths is used to treat natural fibers, higher concentrations of the treating solution and/or longer treatment durations are needed in comparison to the NaOH based treatment [14,21,26] to achieve a similar effect.

The main aim of this paper is the evaluation of the feasibility of using a new mildly alkaline compound having sodium cations to improve the adhesion between natural fibers (i.e., flax) and a thermoset matrix (i.e., epoxy).

Sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) is a cheap, broadly available and non-toxic salt of acetic acid, which can be used in biology as the carbon source for culturing bacteria and for increasing yields of DNA isolation by ethanol precipitation. Sodium acetate can be added to food as a seasoning in the form of sodium diacetate, a one-to-one complex of sodium acetate and acetic acid [29]. It is also used to confer a salt and vinegar flavor to potato chips or even as a vinegar substitute since it doesn't increase the moisture content of the product [30]. Sodium acetate is widely used as a shelf-life extending agent [31–33] and pH control agent [34]; it is safe to eat at low concentrations [35]. Given that it is able to act as a concrete sealant, this salt can also be employed in the mitigation of the water damage to concrete. Moreover, it is more eco-friendly as well as cheaper than the commonly used epoxies for sealing concrete against water permeation [36,37].

To the best of our knowledge, sodium acetate has not yet been used to strengthen the adhesion between polymeric matrices and natural fibers.

In such a context, the main purpose of the present paper is the evaluation of the effectiveness of an inexpensive and green treatment based on the use of sodium acetate solution without the addition of other chemical compounds on the performance of flax fiber-reinforced composites.

2. Experimental Section

2.1. Materials and Composites Manufacturing

Different weight contents (i.e., 5%, 10% and 20%) of sodium acetate were added in demineralized water in order to evaluate the influence of the concentration of the treating solution on the properties of composites. In particular, flax fibers were treated for 120 h at 25 °C, then stored at 25 °C for 24 h and finally dried in an oven (Enrico Bruno s.n.c., Torino, Italy) at 103 °C for a further 24 h. Raw fibers (i.e., untreated) were also oven dried at the same conditions to remove the moisture.

Four epoxy-based panels (30 × 30 cm²) reinforced with raw and treated fibers (i.e., named R, A5, A10 and A20) were manufactured by means of a vacuum infusion process through a two-stage vacuum pump model VE 235 D by Eurovacuum (Reeuwijk, The Netherlands). The vacuum infusion is a close mold technique where the dry fabric layers are laid into the mold inside a vacuum bag. The dry layup is then impregnated by resin, which flows through, mainly driven by vacuum. Two flow mesh layers were also placed externally the lay-up assembly to facilitate and regulate the resin flow during the infusion. SX8 EVO epoxy (Bisphenol A diglycidyl ether resin supplied by Mates Italiana s.r.l., Segrate, Italy) mixed with an amine-based hardener (100:30 by weight) was used as a matrix. Six twill weave woven fabrics of flax fibers (Lineo, Valliquerville, France) with areal weight equal to 320 g/m² were used as reinforcement. Each panel was cured at 25 °C for 24 h and post-cured at 50 °C for further 15 h. Specimens for each mechanical test were cut from panels by using a diamond blade saw.

2.2. Mechanical Characterization

Quasi-static tensile tests were carried out by using a U.T.M (electromechanical Universal Testing Machine) model ETM-C by WANCE (Shenzhen, China), equipped with a load cell of 50 kN. A total of five specimens for each condition (25 mm × 250 mm) were tested in displacement control mode by setting the crosshead speed equal to 2 mm/min, in accordance with ASTM D3039 standard. The displacement was measured through an extensometer model YYU-10/50 by WANCE (Shenzhen, China), having a gauge length of 50 mm.

Quasi-static three-point bending tests were carried out by means of a U.T.M. model Z005 by Zwick-Roell (Ulm, Germany) equipped with a 5 kN load cell. In total, five specimens (15 mm × 90 mm) for each composite were tested in displacement control mode at crosshead speed equal to 2 mm/min, following the ASTM D790 standard. Since the composites' thickness varies in the range between 4.1 mm and 5.1 mm as function of the treatment condition, flexural tests were performed by keeping the span to thickness ratio equal to 16.

Dynamic mechanical thermal tests (DMTA) were carried out in tensile configuration, following the ASTM D4065 standard. A dynamic mechanical analyzer model DMA +150 (Metravib, Limonest, France) was employed to test three prismatic samples (3 mm × 46 mm) of each composite from room temperature to 150 °C, at a heating rate equal to 3 °C/min. The frequency and dynamic displacement were set equal to 1 Hz and 1×10^{-5} m, respectively.

Charpy impact tests were carried out in accordance with EN ISO 179 standard, by using an impact tester model 9050 by CEAST (Pianezza, Italy) equipped with a pendulum of potential energy equal to 5 J. In particular, five prismatic specimens (80 mm × 10 mm) were impacted at a speed of 3.8 m/s.

2.3. Morphological Characterization

The experimental density (ρ_e) of composites was measured by using a helium pycnometer model Pycnomatic ATC by Thermo Electron Corporation (Waltham, MA, USA) and an analytical balance model AX 224 by Sartorius (Gottinga, Germany). Ten measurements were performed for each sample and density average values were recorded. All the measured standard deviations measured were lower than 0.01 g/cm³.

The theoretical density ρ_t was calculated as given by the following equation:

$$\rho_t = \frac{1}{\left(\frac{W_f}{\rho_f}\right) + \left(\frac{W_m}{\rho_m}\right)} \quad (2)$$

where ρ_m is the experimental density of the epoxy matrix, equal to 1.1661 g/cm³. The experimental densities of flax fibers (ρ_f) were measured for each treatment condition. W_m and W_f are the weight contents of matrix and fiber, respectively.

The comparison between the experimental and theoretical densities allows the evaluation of the void volume fraction (ν_V) of each composite, through the following equation:

$$\nu_V = \frac{\rho_t - \rho_e}{\rho_e} \quad (3)$$

The morphology of the fractured surfaces of tensile samples was analyzed with the aid of a scanning electron microscope (SEM) model Quanta 200F ESEM by FEI (Hillsboro, OR, USA). Each sample was covered with a thin layer of gold to avoid electrostatic charging during the analysis and rubbed over an aluminum disc.

In order to evaluate the chemical changes in flax fibers due to the proposed treatment, an FTIR/ATR analysis was performed on both untreated and treated fibers by using a spectrometer model Spectrum II by Perkin Elmer (Waltham, MA, USA). IR spectra were recorded with a resolution of 1 cm⁻¹ in the frequency range 4000–500 cm⁻¹.

3. Results and Discussion

3.1. Mechanical Characterization

Figure 1 shows the average values of tensile strength and modulus of composites. This figure shows the beneficial effect of the proposed treatment on tensile properties, for a treating solution with concentrations up to 5%. In fact, composites reinforced with flax fibers soaked in 5% sodium acetate solution show tensile strength and modulus equal to 73.7 MPa (i.e., +7.5%) and 6.94 GPa (+26%) in comparison to untreated composites with values of 68.5 MPa and 5.50 GPa, respectively. By contrast, a reduction of tensile properties was found for composites reinforced with 10% and 20% treated flax fibers. In particular, A10 composites have a tensile strength and modulus equal to 51.7 MPa and 4.64 GPa, respectively: i.e., –24.5% and –15.8% lower than R composites (i.e., untreated). Furthermore, the tensile strength and modulus of A20 composites are –31.3% and –12.3% lower than untreated ones: i.e., 47.1 MPa and 4.83 GPa, respectively.

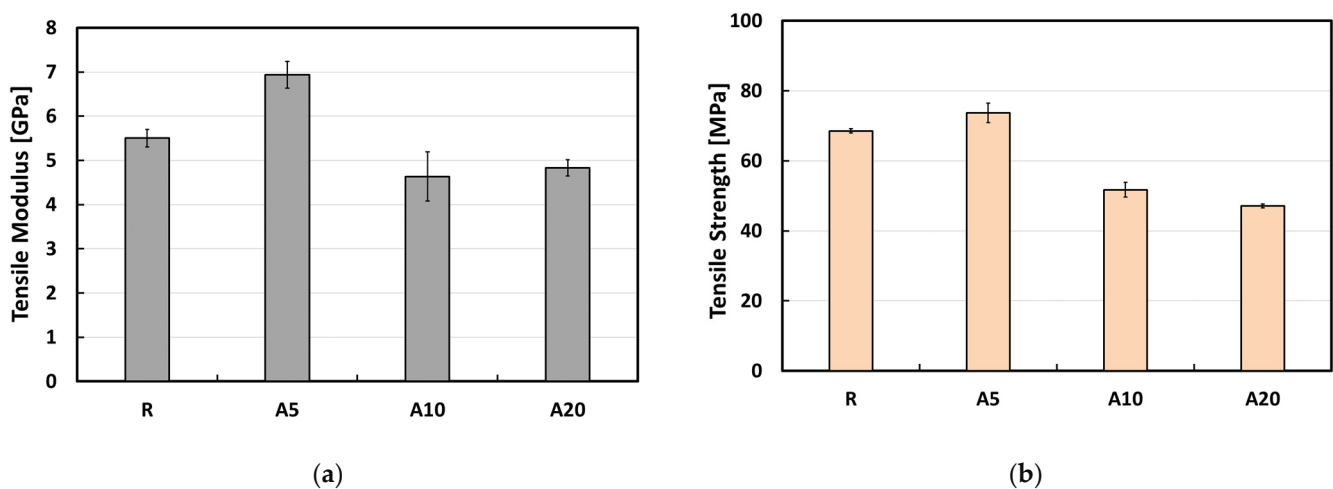


Figure 1. (a) Tensile Modulus and (b) strength average values of composites.

The three-point bending characterization evidences analogous findings (see Figure 2). Indeed, the best flexural properties are shown by A5 composites: i.e., flexural strength and modulus +3.7% and +14.1% higher than R composites (i.e., untreated), respectively. By contrast, the flexural properties of composites tend to decrease by treating flax fibers with 10% and 20% sodium acetate solutions. In particular, A20 composites show the worst properties in terms of flexural strength, 61.8 MPa: −25.1% in comparison to the untreated composites. On the other hand, A10 composites evidence the lowest flexural modulus, 3.4 GPa (−15.0%).

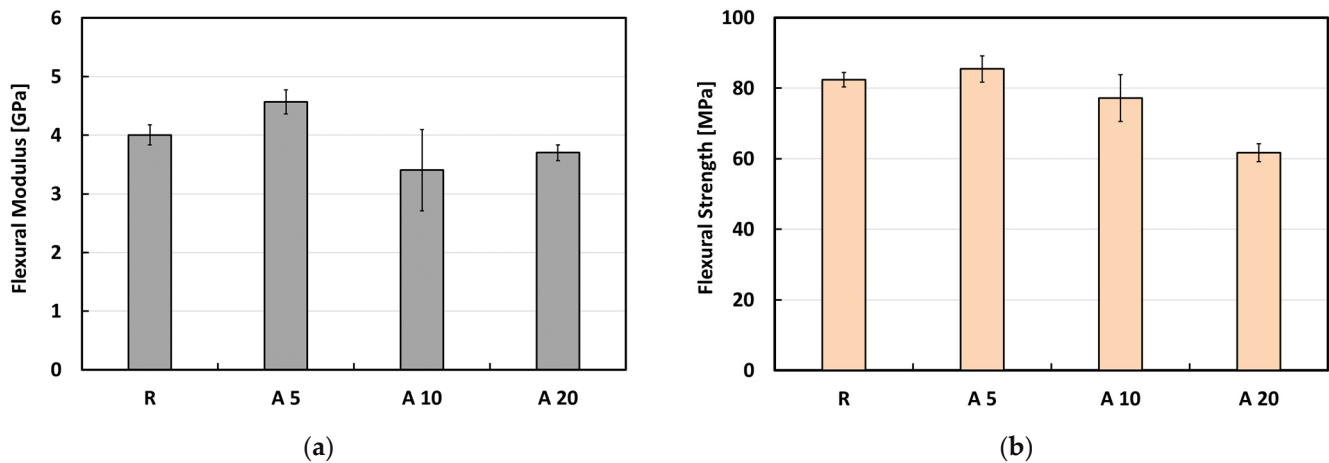


Figure 2. (a) Flexural modulus and (b) strength average values of composites.

Figure 3 shows that, regardless of the treatment condition, all the stress–strain flexural curves shown are characterized by three different phases: (i) an initial linear phase for strain values up to about 1% that allows the measurement of the modulus value; (ii) a subsequent stage of non-linear trend due to the softening of the composite; (iii) a final phase with a slight decreasing slope until the catastrophic brittle failure of the sample. No further plastic deformation can be noticed after this load drop, meaning that the crack propagates rapidly without increase in the applied stress.

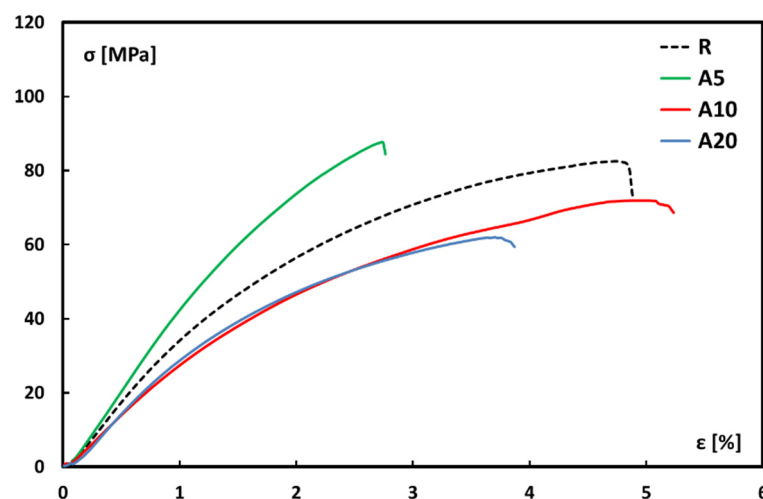


Figure 3. Typical stress–strain flexural curves of untreated and sodium salt treated flax fiber-reinforced composites.

The highest slope values in the initial branch of the stress–strain curve were observed for A5, followed by untreated composites, evidencing the positive effect on the composites' stiffness of the treatment with mildly alkaline solution. By contrast, treated composites at

10% and 20% concentrations showed the lowest flexural strength in comparison to A5 and R composites. In particular, A5 composites shows higher flexural strength than untreated composites, while A10 and A20 composites show higher and lower strain at break in comparison to untreated composites, respectively.

All these results evidence that the flax fiber–epoxy matrix adhesion is remarkably enhanced due to the proposed treatment, for solution concentrations up to 5%. In particular, the increase in both tensile and flexural stiffness shown by A5 composites in comparison to the R composites is due to the stronger fiber–matrix adhesion that, in turn, leads to more restrictive constraints on the relative displacements between fiber and matrix, particularly in the linear elastic phase [26]. This positive effect also results in a clear strengthening of the A5 composites, that show tensile and flexural strength higher than R composites (i.e., untreated). Several papers about the increase in tensile and flexural strength of natural fiber-reinforced composites due to effect of chemical treatment on fiber–matrix adhesion can be found in the literature [38–40].

Furthermore, the experimental results evidence that the proposed treatment has a greater effect on the tensile properties in comparison to flexural properties of the resulting composites (see Figures 1 and 2). Other authors [39] explained this finding by taking into account that the failure mode in flexural configuration evidences less fiber pull-out events.

The better mechanical properties can also be ascribed to other effects of the fiber treatment: i.e., the presence of less voids inside the composites, thanks to the proposed treatment [41,42]. Similar to other alkaline treatments [43–45], the sodium acetate approach is able to remove chemical components such as hemicellulose and lignin in addition to wax and oils from the surface of the natural fiber. Moreover, the fiber surface roughness could increase, along with the number of cellulose chains exposed on the fiber surface. In such a way, a positive influence on the number of bonds between the polymeric matrix and the fiber surface is obtained [27,46].

Figures 1 and 2 clearly evidence that a decline in the quasi-static mechanical properties of treated composites is achieved when the concentration of the sodium acetate solution exceeds 5% in weight. This finding means that, similar to the NaOH based treatment [47,48], too high concentrations of the treating solution can have detrimental effects on the fiber–matrix adhesion.

The influence of the concentration of the sodium acetate solution on the impact behavior of composites is shown in Figure 4. From this graph it is possible to ascertain that the impact strength average values of R composites (i.e., untreated) are higher than those of treated composites, regardless of the treatment condition. In particular, the impact strength is reduced by increasing the sodium acetate concentration: i.e., A5, A10 and A20 composites evidence impact strength values of 43.8%, 43.9% and 53.9% lower than that of the reference, respectively.

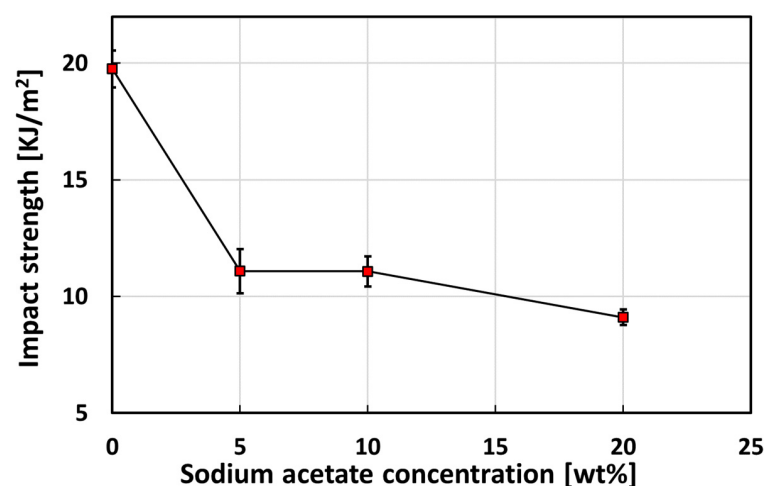


Figure 4. Impact strength of composites at varying sodium acetate concentrations.

In order to get further insights on these results, it is of utmost importance to take into account the influence of the treatment on the maximum displacement and peak load average values of the impacted composites. In this regard, Figure 5 shows the trends of these impact properties.

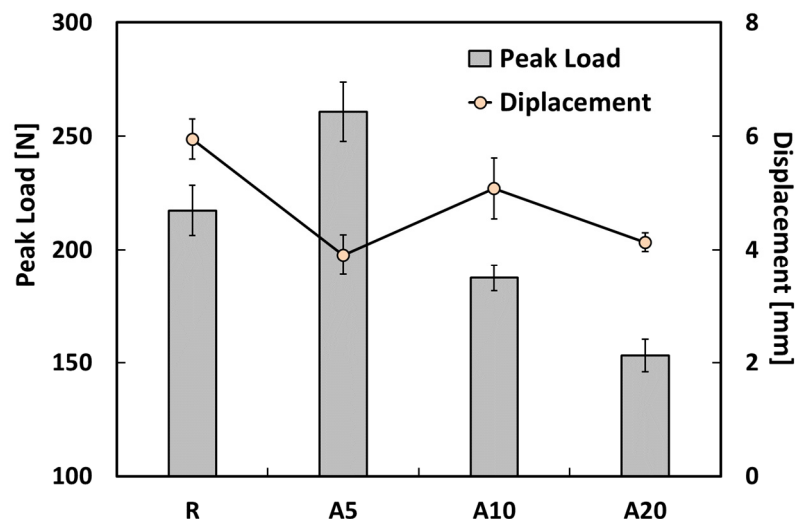


Figure 5. Peak load and maximum displacement average values of composites.

This figure clearly evidences that the impact strength decrease experienced by A5 composites in comparison to the reference is coupled by an improvement in their peak load as well as by a decrease in their maximum displacement (i.e., displacement at peak load). These results are in accordance with the finding of quasi-static tensile and flexural characterizations. In more detail, the beneficial effect of the sodium acetate treatment on the adhesion between flax fibers and epoxy matrix, for concentrations of the treating solution up to 5%, is clearly confirmed. In fact, several papers reported that the improvement of the fiber–matrix compatibility due to fiber treatments also results in a decrease of the impact strength of natural fiber-reinforced composites [8,25] by reducing the energy correlated to fiber pull-out phenomena. Furthermore, the stronger interface between matrix and reinforcement allows the composites to improve their carrying load capacity as well as reducing their displacement at peak load.

Figure 4 also shows that, similarly to A5 composites, A10 and A20 composites exhibit impact strength values (i.e., 11.08 KJ/m² and 9.11 KJ/m², respectively) markedly lower than R composites (i.e., 19.75 KJ/m²). Unlike A5 composites, the impact property decrements experienced by A10 and A20 composites can be ascribed to the worsening of the fiber–matrix adhesion occurring when flax fibers are soaked in 10% and 20% solutions of the proposed sodium salt. These samples evidence peak load average values lower than R composites (see Figure 5). Moreover, the maximum displacement of A10 and A20 composites are somewhat lower than R composites though higher than A5 composites. These results confirm that the adhesion between the epoxy matrix and flax fibers can be negatively influenced if the solution concentration is too high (i.e., higher than 5%).

The storage modulus of composites (E') versus temperature trends obtained through the DMTA characterization are shown in Figure 6. Each curve can be divided in two phases [49]. In particular, all the composites evidence a stiff behavior for temperatures lower than the glass transition temperature T_g of the epoxy matrix (i.e., glassy region). In this region, fiber-reinforced composites show high storage modulus values because both phases (i.e., matrix and reinforcement) are almost immobilized. By contrast, both components improve their mobility at temperatures higher than T_g (i.e., rubbery region) and, as a consequence, an evident reduction of the storage modulus is found by increasing the temperature.

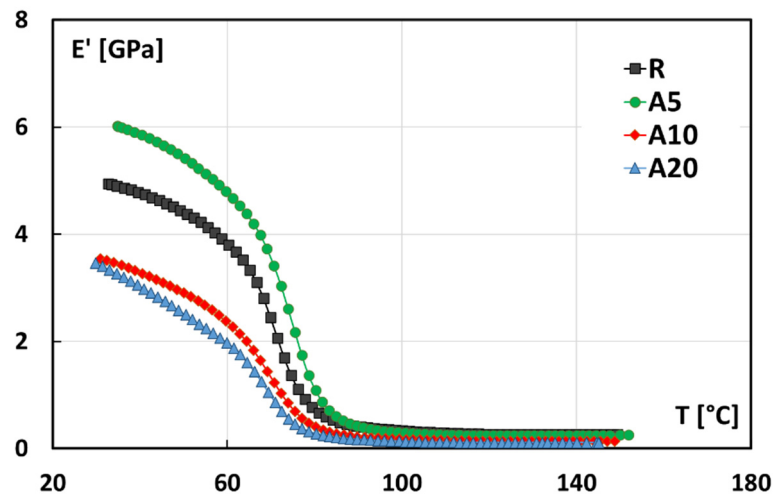


Figure 6. Typical storage modulus E' trends of composites.

The storage modulus E' in the glassy region can be linked with the composite stiffness: i.e., the capability of composites to store the applied energy can be measured through it [50,51]. The storage modulus values at 30 °C increases with increasing of the solution concentration up to 5% (Figure 6). Conversely, A10 and A20 composites evidence E' values at 30 °C (i.e., 3.63 GPa and 3.47 GPa respectively) lower than untreated composites (i.e., 4.95 GPa). This finding is in agreement with the quasi-static and impact characterizations experimental results, thus confirming the effectiveness of the sodium acetate treatment on the fiber–matrix adhesion if the solution weight concentration does not exceed 5%.

In order to get further insights on the interfacial bonding between flax fibers, the damping factor (i.e., $\tan \delta$) of composites versus temperature trends can be observed in Figure 7. Damping factor is measured as the loss modulus E'' (i.e., material tendency to dissipate the applied energy) to storage modulus E' ratio. The shape of $\tan \delta$ curves is strictly influenced by the fiber–matrix interfacial adhesion [49]. In more detail, a scarce fiber–matrix interface results in higher values of the damping factor. Stronger adhesion, limiting the mobility of the polymer chain, reduces the in addition to increase the glass transition temperature [27,52,53].

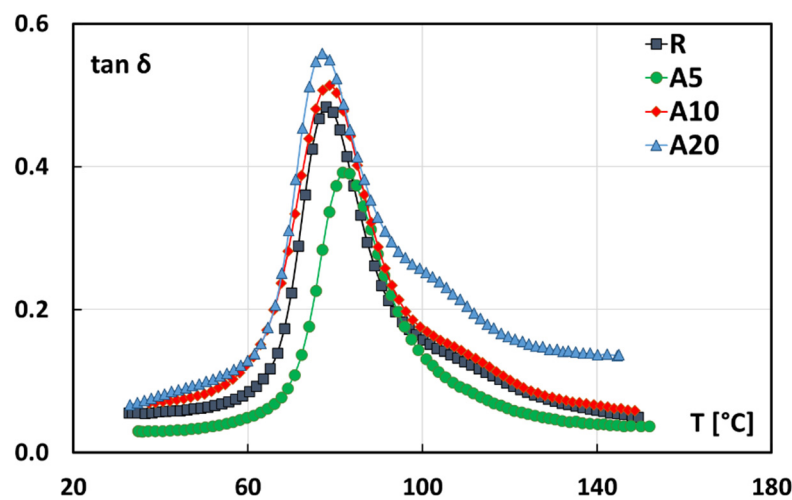


Figure 7. Typical $\tan \delta$ trends of composites.

From Figure 7 it can be evidenced that the average value of the $\tan \delta$ peak for A5 composites, 0.405, is lower than that of R composites, 0.479, due to the enhanced fiber–matrix adhesion. By contrast, a noticeable increase of the average values of the $\tan \delta$ peak is

recorded for the 10% and 20% treated composites, 0.525 and 0.553, respectively, indicating that A10 and A20 composites are progressively characterized by an inferior capacity of carrying the applied load in comparison to R composites.

Moreover, the average glass transition temperature values of the investigated composites, calculated as the temperature at which the $\tan \delta$ curves reach their maximum values [54–56], are between 77.5 °C and 81.9 °C. In more detail, A5 composites show an average value of T_g equal to 81.9 °C, which is more than 4 °C higher than that recorded for untreated composites (i.e., 77.5 °C), thus confirming the beneficial effect of the sodium acetate treatment on the mechanical response of flax fiber-reinforced composites. On the contrary, A10 and A20 composites evidence lower glass transition temperatures (i.e., 78.9 °C and 77.5 °C, respectively) than A5 composites. This result confirms that weaker fiber–matrix interfaces are obtained if the solution weight concentration is more than 5 wt.%.

3.2. Morphological Characterization

In order to obtain further insights on the mechanical behavior of the investigated composites, the fractured surfaces of tensile samples were observed through a scanning electron microscope (SEM). The morphologies of composites at magnification 1500× are observable in Figure 8. In particular, several extended cracks (see the red arrows in Figure 8a) can be noticed on the fiber–matrix interfaces of the fractured surface of untreated samples. These gaps can be ascribed to the triggering and propagation of pull-out and debonding phenomena. As a consequence, this morphology clearly confirms that a scarce fiber–matrix adhesion is achieved [57,58] due to the weak adhesion between the hydrophilic untreated flax fibers and the hydrophobic epoxy matrix. Furthermore, the poor mechanical properties shown by composites reinforced with untreated fibers is fully justified (i.e., R batch).

On the contrary, A5 composites evidence better morphologies than R composites (i.e., untreated), as shown in Figure 8b. Indeed, more compact structures characterized by good fiber–matrix adhesion indicated by blue arrows, without evidence of wide cracks can be identified in this image. A progressive increase in the number of cracks and defects (red arrows) is noticeable in the fracture surface of A10 and A20 composites: i.e., fiber–matrix interfaces are characterized by evident detachment areas. These findings evidence the effectiveness of the proposed treatment on the adhesion between fibers and matrix if the solution weight concentration does not exceed 5%. On the contrary, the morphology of A10 and A20 specimens (Figure 8c,d) clearly indicates that the proposed treatment is not effective when the sodium acetate concentration in the solution is too high. The presence of large voids due to the absence of some fiber bundles as consequence of pull-out phenomena can be noticed. The poor fiber–matrix compatibility can be considered the main responsible for the low mechanical performance experienced by these composites. These findings clearly confirm that the 5% weight content of sodium acetate in the proposed solution represents the best condition to reinforce the fiber–matrix adhesion, with positive effects on the mechanical response of the composites.

The main findings of the morphological analysis are confirmed by the evaluation of the void content (Table 1). Voids are the most common defects due to the manufacturing process, which deeply influence the overall properties of composites [59]. The composites' quality can be assessed as a function of the void content [60]: i.e., composite materials are classified as excellent (i.e., void content lower than 1%), good (i.e., void content in the range between 1% and 5%) or poor (i.e., void content higher than 5%). Table 1 data show that the sodium acetate treatment slightly influences the fiber volume fraction (i.e., in the range 34.3–38%). Moreover, the investigated composites evidence a noticeable variation of their void content after the proposed treatment. In detail, the sodium acetate treatment lowers the void content of composites, since A5 composites exhibit the lowest value (i.e., 1.2%).

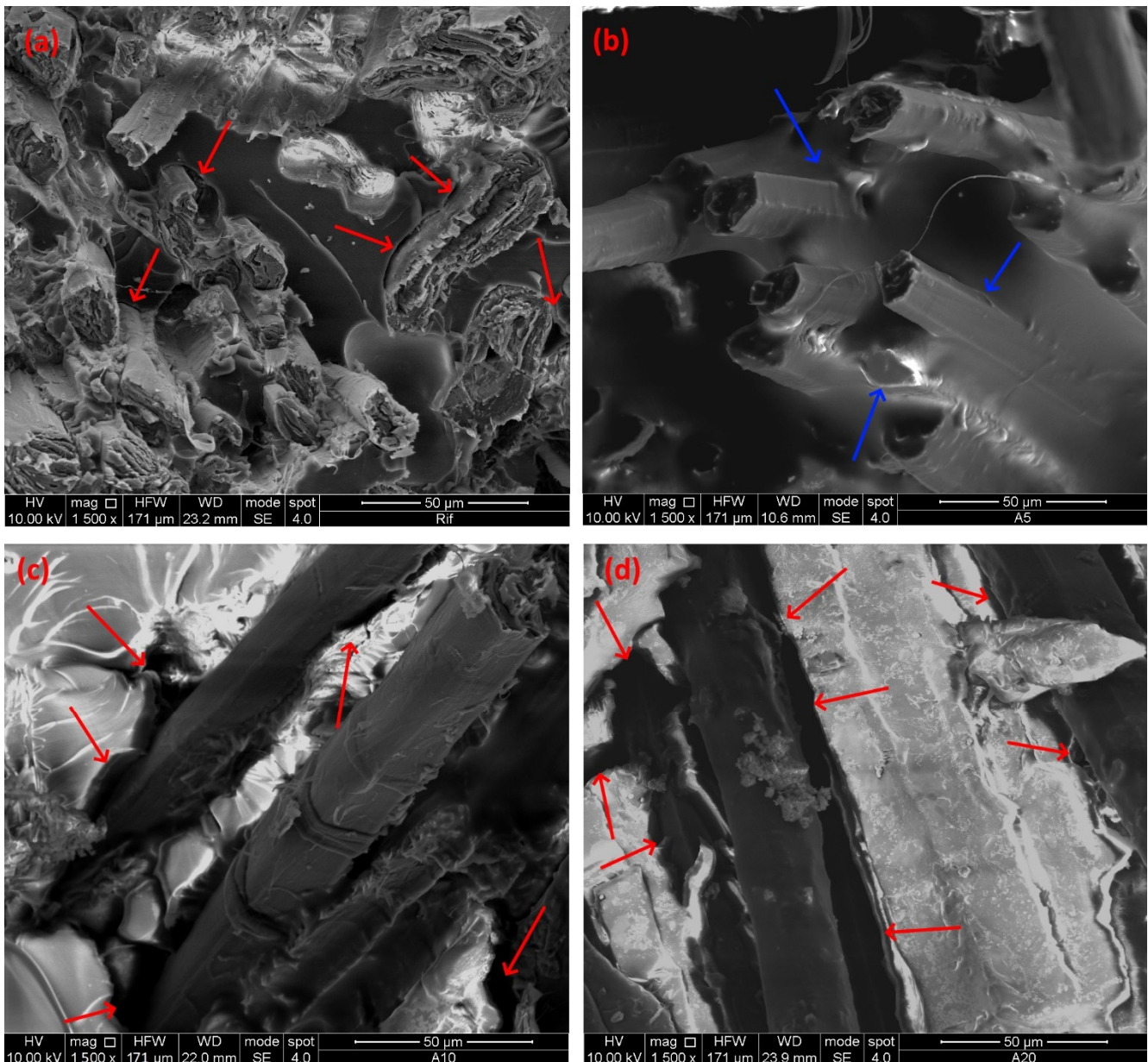


Figure 8. SEM micrographs at high magnification (1500×) of tensile fractured surfaces: (a) R, (b) A5, (c) A10 and (d) A20 composites.

Table 1. Main physical properties of composites for each treatment condition.

Sample	R	A5	A10	A20
Thickness [mm]	4.07 ± 0.02	4.45 ± 0.05	4.64 ± 0.03	5.21 ± 0.07
Theoretical density [g/cm ³]	1.318 ± 0.001	1.297 ± 0.002	1.314 ± 0.002	1.336 ± 0.002
Experimental density [g/cm ³]	1.229 ± 0.001	1.281 ± 0.004	1.268 ± 0.003	1.261 ± 0.003
Fiber volume content [%]	36.8 ± 0.2	34.3 ± 0.4	36.8 ± 0.2	38.0 ± 0.5
Void content [%]	6.8 ± 0.1	1.2 ± 0.2	3.5 ± 0.1	5.7 ± 0.1

Moreover, the void content of A5 and A10 composites is in the range of 1–5%, meaning that these materials can be considered as good quality composites. Conversely, R and A20 composites are poorly made materials because they show high void content (i.e., more than 5%). These defects easily tend to form micro-cracks and, hence, to reduce the mechanical properties of such composites. As previously stated, the experimental density

values of flax fibers were measured through a helium pycnometer for each treatment condition. In particular, the average density value of untreated fibers is 1.5020 g/cm^3 whereas fibers treated in 5%, 10% and 20% sodium acetate solutions present densities equal to 1.5048 g/cm^3 , 1.5066 g/cm^3 and 1.4981 g/cm^3 , respectively. As a consequence, the fiber density slightly increases with the concentration of the solution up to 10% concentration. This finding is strictly correlated to the modifications induced by the fiber treatment on fiber thickness as well as on the chemical structure of the fiber surface. In more detail, the fiber diameter is reduced after the treatment due to fiber fibrillation, when the weight concentration of the solution is 5% (Figure 9).

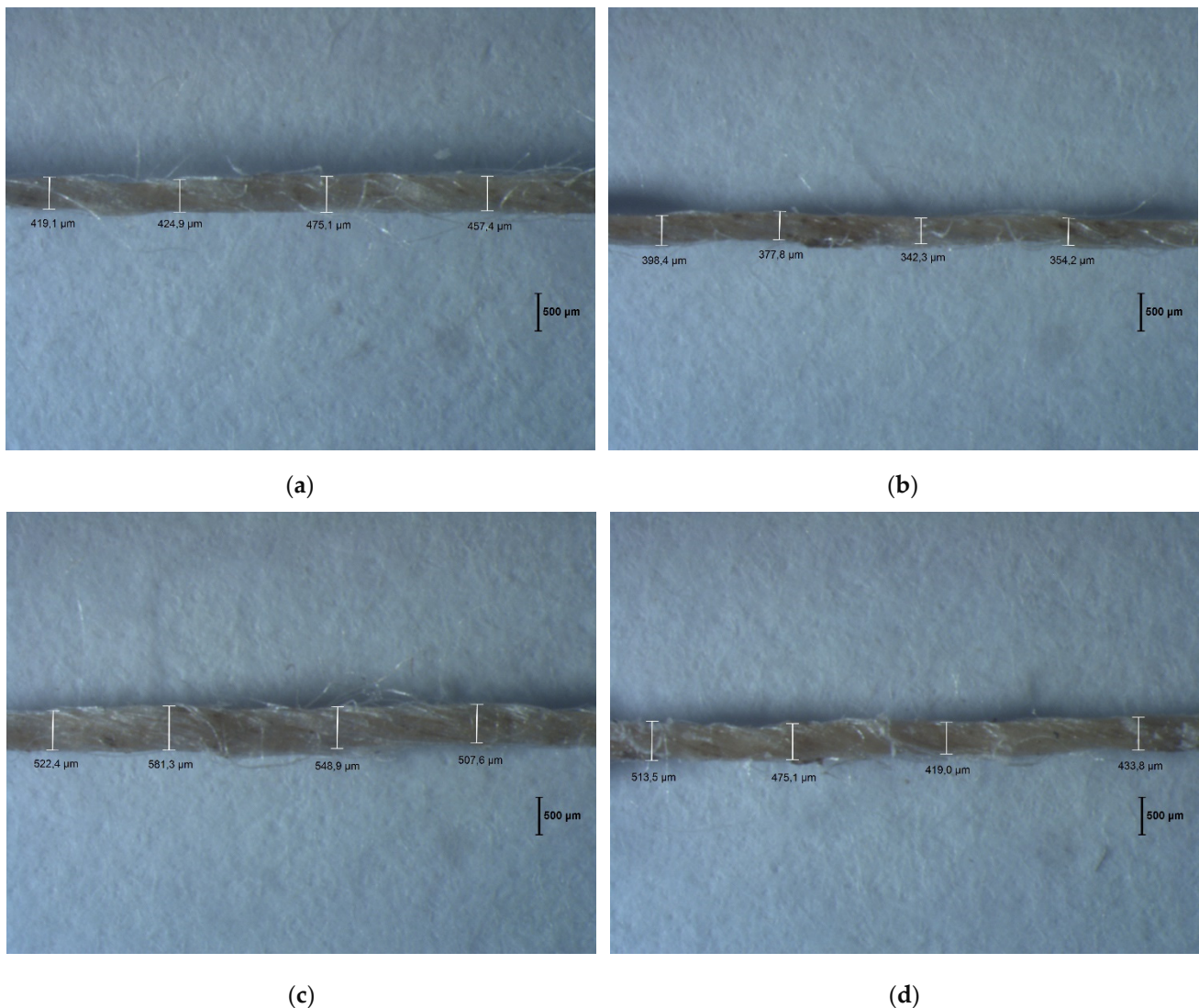


Figure 9. Optical images of flax fibers for each treatment condition: (a) R, (b) A5, (c) A10 and (d) A20 fibers.

On the contrary, the higher diameters of fibers treated in 10% and 20% sodium acetate solutions are due to the fiber swelling in addition to the deposition of salt crystals over the fiber surface. This means that the proposed treatment has detrimental effects on the fiber structure if the concentration of the sodium acetate solution exceeds 5%.

The reduction in the diameter of 5% treated flax fibers can be ascribed to the alteration of the chemical structure of fiber surface after sodium acetate treatment, as evidenced by the FTIR spectra of treated and raw fibers (Figure 10). The spectra were baseline corrected to the peak centered at 3337 cm^{-1} , attributed to the O-H stretching vibration and hydrogen

bond of the hydroxyl groups [61–63]. Similar to NaOH treatment (i.e., mercerization), the innovative treatment leads to the removal of a certain portions of lignin and hemicellulose from the fiber surface. In fact, the peak centered at 1732 cm^{-1} related to the carbonylic group C=O stretching vibration of the linkage of carboxylic acid in lignin or ester group in hemicellulose disappears for treated fibers [21,64]. Moreover, the peak at 1240 cm^{-1} , attributed to the C-O stretching vibration of the acetyl group in lignin, is reduced in the spectra of treated fibers [45,65]. No additional evident alterations can be observed in the spectra of treated fibers.

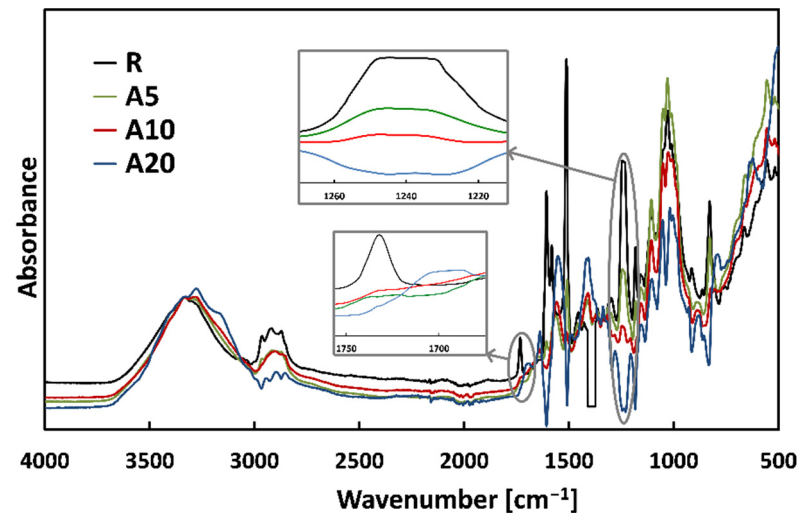


Figure 10. FTIR spectra of untreated and treated flax fibers.

Furthermore, the partial removal of hemicellulose and lignin due to the proposed treatment improves the number of available reaction sites of cellulose, thus favoring adhesion with the surrounding matrix [66].

4. Conclusions

The effect of a new, cheap and eco-friendly treatment on the morphology and mechanical properties of natural fiber-reinforced epoxy composites was investigated by soaking fibers in sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$) solutions at varying the weight concentration (i.e., 0–20%).

The mechanical behavior of composites was evaluated through quasi-static tensile and flexural tests, dynamical mechanical thermal tests and Charpy impact tests, whereas their morphology was analyzed by means of SEM (scanning electron microscope) observations and helium pycnometry. Furthermore, Fourier transform infrared analysis (FTIR/ATR) was performed for evaluating the chemical changes on the flax fiber surface due to the proposed treatment.

It was found that low concentrations of the treating solution led to alterations in the surface properties of flax fibers, which resulted in a strengthening of the fiber–matrix interface. As a consequence, composites reinforced with flax fibers treated with 5% sodium acetate solution evidenced the best mechanical performance in addition to the lowest porosity. Conversely, solutions with salt content equal to 10% and 20% led to fiber swelling, with detrimental effects on the morphology of composites as well as on their mechanical properties.

These promising results clearly indicate that this innovative treatment can be considered as a promising alternative to harmful and more expensive treatments in the manufacturing of natural fiber-reinforced composites with enhanced properties.

Author Contributions: Conceptualization, V.F. and A.V.; methodology, V.F.; validation, V.F. and D.B.; formal analysis, V.F. and A.V.; investigation, D.B., C.S.; data curation, C.S.; writing—original draft preparation, C.S. and D.B.; writing—review and editing, V.F.; visualization, D.B.; supervision, A.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data has been obtained from the experimental results.

Conflicts of Interest: The authors declare no conflict of interest.

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