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# Almonds By-Product Microcrystalline Cellulose as Stucco for Wooden Artifacts

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**Abstract:** Over the years in the field of conservation of cultural heritage, a wide use of traditional products for the plastic reintegration of wooden artifacts has been seen. However, they are usually not designed for this purpose. The present study also shows, in terms of material compatibility, the material most suited for wood restoration, cellulose pulp, from the perspective of a new green approach of reusing waste. Indeed, microcellulose was obtained by simple alkaline treatment from softwood almond shells. In particular, *Prunus dulcis* Miller (D.A.) Webb. was considered an agro-industrial waste largely available in southern Italy. To value the possibility of using this material in a circular economy framework, a microcellulosic material was used, by adding different binders, to manufacture several stuccos to utilize as wood consolidants. Successively, in order to obtain stuccos with biocidal properties against fungal colonization or insect infestation, to which wooden artifacts are often exposed, cellulose pulp was combined with the essential oil of *Thymus capitaus* (L.) Hoffmanns. & Link., whose biological properties have been largely reported. The physical flexion properties of all new materials were tested.

**Keywords:** nuts; by-products; microcellulose; wood conservation; *Thymus capitatus*; essential oil



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## 1. Introduction

Nuts have always been the staple diet of people living in temperate climate areas. Moreover, the Mediterranean Basin represents an important area of dissemination and production of nuts based very often on local cultivars related to established gastronomic use with significant health implications [1–3]. Sicily, at the center of the Mediterranean, boasts a great biodiversity of almond (*Prunus dulcis* Miller (D.A.) Webb.) thanks to naturalization processes still studied today [4] that have been followed by centuries of cultivation and selection, delivering us great genetic variability [5–7].

Recently, almond cultivation has attracted renewed interest [8], pushing for biodiversity conservation models of the *Prunus* genus [9,10] and is one of the fastest growing nut crops in terms of surface area and yield [11]. Almond production in the world remains consistently well-diversified; in the Mediterranean Basin, there has been increased interest in higher fatty acid almonds with shelling yields ranging from 30 to 40%, especially when grown specialized intensive orchards. These are semi-hard- or hard-shelled almonds, not always totally or partially self-fertile, which are often part of large germplasm pools with an established destination for product use. In contrast, in California and Australia, the

types of almonds cultivated refer to soft-shelled cultivars with high shelling yields (up to 80 percent) intended mainly for snack production [12].

This diversification also results in the production of extremely different waste, both in quantitative and qualitative terms. In quantitative terms, Mediterranean almonds produce a large amount of shell (about 60 percent of the total), while in qualitative terms, these shells are more consistent due to the higher amount of lignin, cellulose, and hemicellulose, which are the main components [13–15]. This knowledge is closely related to studies on the topic of a circular economy [16], which has received great attention in the European arena thanks to the spread of EU legislation and regulations [17]. Nowadays, the possibility of using alternative heating sources, more based on natural products and supported by circular economy policies, appears to be highly topical due to the effects of the socio-political crises that are straining civil society on a global scale. In these directions, there is growing interest in the application of biobased reuse of waste from agri-food matrices in order to reduce disposal interventions and increase the sustainability of production [18]. In nuts, this process is made even more interesting because of the possible applications in the reuse of hulls [19], shells, and seed skins [4,20], which represent the main waste products in post-harvest processing along with the residue of pruning in the field [21].

Almond shells are attributed a high industrial potential both for a number of specific applications and components of particle boards and for opportunities related to calorific value, especially when used as a heating fuel capable of producing fewer negative effects of combustion [22,23]. More specific interest is now being highlighted in the cellulose content found in the shell as it represents a component with multiple potential applications. The value of cellulose depends not only on its biodegradability, renewability, strength, and stiffness characteristics but also on the different sizes in which it can be extracted and consequently its versatility as a commercial product [24,25]. Cellulose can be distinguished into elemental fibrils, fibrillar cellulose, and crystalline cellulose [8], and its value is directly related to its potential for strength and stiffness but also to biodegradability and intermini variability in size post extraction. In this sense, it is interesting to note that microcrystalline cellulose (MCC), one of the cellulose derivatives, exhibits many of these characteristics, as it represents a micrometric, biodegradable powder with high mechanical strength. Recent studies have pointed out that the contribution of waste from agro-food matrices to the production of MCC can be very relevant. There are many fruits that have shown the possibility of effectively extracting MCC, evidencing its application as a filler for the PBAT matrix [26].

In our previous work [14], MCC particles were successfully extracted from softwood almond (*Prunus dulcis*) shells via an alkaline treatment, and recently, these MCC particles were used as fillers for a PBAT matrix. PBAT-based biocompostable composites were prepared by the melt mixing processing. In particular, the materials were characterized in order to find correlations between the processability, structural properties, thermal behavior, and mechanical properties of the PBAT-based biocompostable composites [15].

For a long time, essential oils (EOs) have been applied in several medicinal fields, as well as in the food and pharmaceutical industries [27–29]. In recent years, EOs have also been used to contrast the biodeterioration of cultural heritage, and consequently they can be considered a powerful tool in green conservation strategies [30]. In particular, recently, the essential oil (EO) of *Thymus* ssp. has been utilized to fight the biodeterioration processes induced by fungal colonization (*Aspergillus flavus*) or insect infestation (*Anobium punctatum*) in wooden art crafts [31]. The compatibility with artwork constitutive materials and the lack of negative effects on human health and environmental pollution have indicated essential oil as a valid alternative method with respect to traditional synthetic biocides [32].

Consequently, some mixtures have been prepared, such as wood consolidants and biocidal stuccos, by utilizing, first, the MCC, obtained from *P. dulcis*, and some binders commonly used for the reintegration and consolidation of wooden artworks, and successively, other stuccos by also adding the essential oil of a Sicilian accession of *Thymus capitaus* (L.) Hoffmanns. & Link., whose biological properties have been largely reported [33–35]. The

stucco, as a cellulose-based mixture, is extremely compatible with wooden artifacts due to the chemical structure of wood. The addition of the essential oil is expected to reduce samples' mechanical strength, however foreseeing negligible results that allow operators to use and spread this new mixture in the field of conservation of cultural heritage.

## 2. Materials and Methods

### *2.1. Materials*

#### 2.1.1. Plant Material

Almond shells were produced by a local farmer and originated from almond trees (*P. dulcis*) of Agrigento (Sicily, Italy) belonging to the Casteltermini variety. Aerial parts of *Thymus capitatus* (L.) Hofmgg. & Lk. were collected at Salinelle Beach, Lascari, Palermo (38°01′48″ N, 13°18′40″ E, 6 m s/L), 50 km east of Palermo, Sicily (Italy), in June 2022.

The first collection (TC1) occurred on 14 May 2014, followed by a second collection (TC2) on 19 June 2014, and a third collection (TC3) on 16 July 2014. All three were identified by Emanuele Schimmenti and then stored in the STEBICEF Department at the University of Palermo, Palermo, Italy [34].

#### 2.1.2. Binders

Aquazol 500 and Plextol B 500 crystals, m.w. 500,000, were both supplied by CTS Europe (36077 Altavilla Vicentina (VI), Italy), while hydroxylproprylcellulose—Klucel G—crystals, m.w. 60,000, were supplied by Sigma Aldrich (Sigma Aldrich, St. Louis, MO, USA).

### *2.2. Methods*

#### 2.2.1. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) was carried out on the samples using a DMA Q800 (TA Instruments, New Castle, DE, USA). Flexion tests were conducted under a controlled force ramp (0.010 N $min^{-1}$). Based on the analysis of the stress vs. strain curves, the stress values at breaking points, the ultimate elongation, and the derivatives of strain percentages were determined. All data reported are an average of the results collected with a three-repeated analysis for each type of sample.

#### 2.2.2. Gas Chromatography–Mass Spectrometry

In order to determine essential oil chemical composition, gas chromatography-mass spectrometry was performed at the University of Naples "Federico II", Department of Pharmacy. A Perkin Elmer Sigma 115 gas chromatograph was used, furnished with a HP 5MS capillary column (0.25 µm film thickness, 30 mm × 0.25 mm), a flame ionization detector (FID) at 280 °C, and a split-splitless injector warmed up to 250 °C. The column temperature was originally maintained at 40 °C for 5 min, then progressively increased to 250 °C at 2 °C/min., and finally elevated to 270 °C at 10 °C/min. Ten microliters was the injection volume (split ratio 1:20); a HP Innowax fused silica polyethylenglycol capillary column (0.25 µm film thickness, 50 m × 0.20 mm) was also employed. In both cases, the carrier gas was helium (1 mL/min). Gas chromatography-mass spectrometry analysis was conducted on a Serie II Agilent 6850 apparatus, equipped with a fused silica HP 5 capillary column (0.25 µm film thickness, 30 m × 0.25 mm), connected with an Agilent MSD 5973 Mass selective detector; multiplier energy of electrons 2000 V; ionization voltage 70 eV; source temperature 250 °C. Mass spectra were set with a scan time of 5 scans/s, in the range of 35–450 amu. The majority of essential oil compounds were identified through gas chromatography by comparing their retention indices (Ri) with either those of authentic compounds accessible in our laboratories or taken from Sigma-Aldrich Co. To obtain retention indices, a corresponding series of n-alkanes (C8–C30) was employed under the same conditions. Furthermore, essential oil compound identification was accomplished by comparing the mass spectra of both columns with those kept in Wiley 275 and NIST02 libraries or with those from our personal library. The concentration of each compound was estimated using GC peak areas without any correction factors. The outcomes are presented in Table 1 [34].

**Table 1.** *Thymus capitatus* Hoff. Et Link. (L.) essential oil composition growing wild, Sicily.

| Ki [a] | Ki [b] | Ident. [c] | Compounds | TC1 | TC2 | TC3 |
|---|---|---|---|---|---|---|
| | | Monoterpene hydrocarbons | | 65.8 | 13.9 | 13.5 |
| 930 | 1014 | 1, 2 | α-Thujene | 2.4 | 1.0 | 1.5 |
| 938 | 1032 | 1, 2, 3 | α-Pinene | 2.6 | 0.5 | 0.7 |
| 953 | 1076 | 1, 2, 3 | Camphene | 0.2 | 0.1 | 0.1 |
| 973 | 1132 | 1, 2 | Sabinene | 0.3 | | |
| 978 | 1118 | 1, 2, 3 | β-Pinene | 0.5 | 0.1 | 0.2 |
| 993 | 1174 | 1, 2, 3 | Myrcene | 2.1 | 1.1 | 1.4 |
| 1005 | 1150 | 1, 2, 3 | α-Phellandrene | 0.3 | 0.1 | 0.3 |
| 1009 | 1157 | 1, 2 | $\delta^3$-Carene | t | 0.1 | 0.1 |
| 1012 | 1189 | 1, 2, 3 | α-Terpinene | 0.2 | 0.8 | 1.0 |
| 1025 | 1278 | 1, 2, 3 | *p*-Cymene | 22.8 | 5.8 | 5.0 |
| 1029 | 1218 | 1, 2 | β-Phellandrene | | 0.3 | 0.4 |
| 1049 | 1262 | 1, 2 | (*E*)-β-Ocimene | | | 0.1 |
| 1057 | 1256 | 1, 2, 3 | γ-Terpinene | 34.4 | 3.8 | 2.6 |
| 1086 | 1265 | 1, 2, 3 | Terpinolene | | 0.2 | 0.1 |
| | | Oxygenated monoterpens | | 0.2 | 0.6 | 1.7 |
| 1097 | 1553 | 1, 2, 3 | Linalool | | | 0.4 |
| 1063 | 1555 | 1, 2 | (*Z*)-Sabinene hydrate | t | 0.1 | t |
| 1098 | 1475 | 1, 2 | (*E*)-Sabinene hydrate | t | | |
| 1167 | 1718 | 1, 2, 3 | Borneol | | 0.1 | 0.1 |
| 1176 | 1611 | 1, 2, 3 | Terpineol-4 | 0.1 | 0.3 | 0.5 |
| 1189 | 1706 | 1, 2, 3 | α-Terpineol | | | 0.1 |
| 1195 | 1624 | 1, 2 | *cis*-Dihydrocarvone | 0.1 | | |
| 1238 | 1694 | 1, 2 | Neral | | 0.1 | 0.2 |
| 1243 | 1752 | 1, 2 | Carvone | | | 0.1 |
| 1268 | 1741 | 1, 2 | Geranial | | | 0.3 |
| | | Sesquiterpene hydrocarbons | | | | |
| 1363 | 1492 | 1, 2 | Cyclosativene | 2.5 | 3.3 | 2.1 |
| 1407 | 1538 | 1, 2 | α-Gurjunene | 0.2 | | |
| 1415 | 1612 | 1, 2, 3 | (*E*)-β-Caryophyllene | t | 2.3 | 1.7 |
| 1437 | 1628 | 1, 2 | Aromadendrene | 0.6 | 0.1 | |
| 1455 | 1689 | 1, 2 | α-Humulene | | 0.1 | 0.1 |
| 1463 | 1667 | 1, 2 | allo-Aromadendrene | | t | |
| 1487 | 1679 | 1, 2 | α-Amorphene | t | | |
| 1489 | 1743 | 1, 2 | Eremophilene | 0.1 | | |
| 1508 | 1746 | 1, 2 | (*Z*)-α-Bisabolene | 0.7 | 0.3 | 0.1 |
| 1511 | 1743 | 1, 2 | β-Bisabolene | 0.5 | 0.4 | 0.2 |
| 1513 | 1709 | 1, 2 | Ledene | | t | |
| 1526 | 1773 | 1, 2 | δ-Cadinene | 0.2 | 0.1 | |
| 1494 | 1687 | 1, 2 | Viridiflorene | 0.2 | | |
| | | Oxygenated sesquiterpenes | | 3.2 | 1.5 | 0.5 |
| 1578 | 2150 | 1, 2, 3 | Spathulenol | | 0.2 | t |
| 1580 | 2008 | 1, 2, 3 | Caryophyllene oxide | 2.2 | 1.3 | 0.5 |
| 1612 | 2018 | 1, 2 | Humulene oxide II | 0.3 | | |
| 1615 | 2324 | 1, 2 | Caryophylla-4(12),8(13)-dien-5α-ol; Caryophylladienol II | 0.3 | | |
| 1640 | 2158 | 1, 2 | *t*-Cadinol | t | | |
| 1642 | 2209 | 1, 2 | *s*-Muurolol | 0.1 | | |
| 1716 | 2478 | 1, 2 | 14-Hydroxy-a-humulene | 0.3 | | |
| | | Diterpenes | | 1.1 | 0.1 | |
| 1896 | 2147 | 1, 2 | Rimuene | | | t |
| 1908 | 2176 | 1, 2 | Isopimara-9-(11),15-diene | 0.7 | | |
| 2054 | 2524 | 1, 2 | Abietatriene | 0.4 | 0.1 | |

**Table 1.** *Cont.*

| Ki [a] | Ki [b] | Ident. [c] | Compounds | TC1 | TC2 | TC3 |
|---|---|---|---|---|---|---|
| | Phenolic compounds and derivatives | | | 19.8 | 76.7 | 81.5 |
| 1245 | 1975 | 1, 2, 3 | Carvacrol methyl ether | 1.9 | 0.5 | 0.2 |
| 1297 | 2239 | 1, 2, 3 | Carvacrol | 14.2 | 76.1 | 81.2 |
| 1298 | 1956 | 1, 2 | Carvacrol ethyl ether | 0.7 | | |
| 1353 | 2186 | 1, 2, 3 | Eugenol | 0.8 | 0.1 | 0.1 |
| 1367 | 1885 | 1, 2, 3 | Carvacryl acetate | 1.5 | | |
| 1472 | 1985 | 1, 2 | Carvacryl isobutyrate | 0.7 | t | |
| Total | | | | 92.6 | 96.2 | 99.8 |

[a] $K_i$: linear retention index: on HP 5MS column. [b] $K_i$: linear retention index: on HP Innowax column. [c] $K_i$: linear retention index: (1) retention index identical to the literature, (2) MS: comparison of mass spectra with MS libraries, (3) Co-GC: co-injection with authentic compound; t, trace, less than 0.05%. TC1: first collection, 14 May 2014; TC2: second collection, 19 June 2014; TC3: third collection, 16 July 2014.

#### 2.2.3. Treatment of Almond Shells

The MCC samples used were obtained by alkaline treatment from softwood almond (*P. dulcis*) shells, as reported in a previous work [14]. Before cellulose extraction, unprocessed dried almond shells were ground in a mortar until they reached the size of approximately 5 mm. The ground substance (400 g) was then subjected to reflux using a 200 mL of 7.5% *w*/*w* NaOH solution for 24 h in order to remove hemicelluloses and an amount of lignin. The resulting mixture of clear fibers, coming from the vascular bundle, and shells was filtered and repeatedly washed with distilled water to decrease the pH to 7. A part of the obtained mixture composed by cellulosic fibers (30 g, yield 7.5%) was treated with 50 mL of 2.5% *w*/*v* NaClO solution between 60–70 °C for 1 h, then washed with distilled water, filtered, and air dried; then, it was ready to be used to fabricate paper. The excess material (200g) underwent the same process of refluxing, was treated again with 100 mL of NaClO solution (2.5% *w*/*v*) for 1 h at 70 °C, was left under mechanical stirring, was washed three times using 50 mL of distilled water, and was filtered one more time. The results of these treatments yielded a light powder (50 g with a yield of 12.5%) and several shell fragments [14].

#### 2.2.4. Preparation of Binders

In order to give the cellulose pulp-based stucco good filler properties, the three following binders were tested:

- Klucel-G (K): hydroxypropyl cellulose with high surfactant properties, used as a thickener for aqueous solutions and to gel solvents or solvent mixtures. For the stucco preparation, it is used at 5% in $H_2O$ or at 5% in $H_2O$/EtOH (1:1) [36].
- Aquazol 500 (A): thermoplastic polymer made of two poles (2-ethyl-2-oxazoline). It has good thermal stability and broad solubility in water and polar organic solvents and maintains a neutral pH. It has applications as an adhesive, painting medium, consolidant, and binder [37].
- Plextol B500 (P): thermoplastic acrylic resin (acrylate and methacrylate copolymer) with good chemical resistance and viscosity in aqueous dispersion. It is used for relining paintings and as a consolidant for painted layers [38].

Klucel G at 5 wt% was slowly added to a 100 mL aqueous solution under magnetic stirring. The addition of the cellulose ether was completed before the appreciable increase in liquid viscosity. Once the desired amount of Klucel G was reached, the rate of agitation was reduced but continued until the gel was obtained. Aquazol 500 at 20 wt% and Plextol B500 at 40 wt% were added to a 100 mL ethanol solution and to a 100 mL aqueous solution, respectively, for 5 min at room temperature under magnetic stirring.

2.2.5. Preparation of Samples

All samples were obtained by maintaining a constant ratio between the cellulose pulp and binder of 23.4 wt% and 76 wt%, respectively. For each binder, two samples were prepared, one with the addition of *T. capitatus* EO and one without. The following protocol was employed to obtain all mixtures: three samples (Ce_A; Ce_K; Ce_P) were prepared b slowly adding the almond cellulose pulp (Ce) to the binder (K, A, or P), then blended in a mortar until a thick mixture was obtained; three samples (Ce_A_EO; Ce_K_EO; Ce_P_EO) were prepared, as mentioned above, blending the cellulose pulp with the binder and, after reaching an homogeneous mixture, adding 0.6 wt% of *T. capitatus* EO with the auxile of a micropipette and blending all three compounds in a mortar. Subsequently, in order to produce six samples of equal size (36.1 mm × 17.6 mm × 2.6 mm) (Figure 1), a preformed parallelepiped plastic mold was filled with the obtained mixtures and then dried outdoor for 48 h. This operation was repeated three times for each sample in order to obtain more statistically correct analyses of the variables analyzed.

(**a**) (**b**)

**Figure 1.** Samples within (**a**) and without (**b**) the addition of *T. capitatus* EO after 48 h of drying.

## 3. Results

### *3.1. Composition of Almond Shell Cellulose Pulp*

The lignocellulosic material obtained from almond shell (P. dulcis) was characterized by NMR spectroscopy, and the composition of ca. 22 wt% of lignin and 78% of holocellulose was found based on the protocol provided in our recent work [14]. Moreover, the fibrous morphological feature of the obtained material was promising in terms of tensile performance for its composites.

### *3.2. Sample Flexion Properties and Structure*

Cellulose-based reintegration with different binders and with the addition of the essential oil were tested in order to find a reintegration protocol for wooden artifacts that could also have some disinfection effects. The mechanical properties of the composites were investigated by observing their behavior under flexural stress and analyzed according to the procedure described by R. N. Haward [39]. As shown in Figure 2, the stress vs. strain curves of all samples did not present a linear increasing trend (elastic region). We detected that the addition of the essential oil in each case increased the strain percentage, warping samples at lesser strain values. Within this, the sample mechanical strength was slightly decreased due to the presence of liquid-like regions where the oil was accumulated. This behavior was due to the complex mesoscopic structure, which can be simplified as cellulose bundles that can be stretched from a globular to a straight fiber conformation under stress. Accordingly, a first derivative of the stress vs. strain curve was calculated for each composite, as it represents the modulus variation upon increasing the deformation. In particular, the elastic modulus changes can be interpreted by considering the morphological changes sketched in Figure 3. In particular, the minimum in the modulus represents the deformation needed to obtain an almost fully stretched conformation of the fibers.

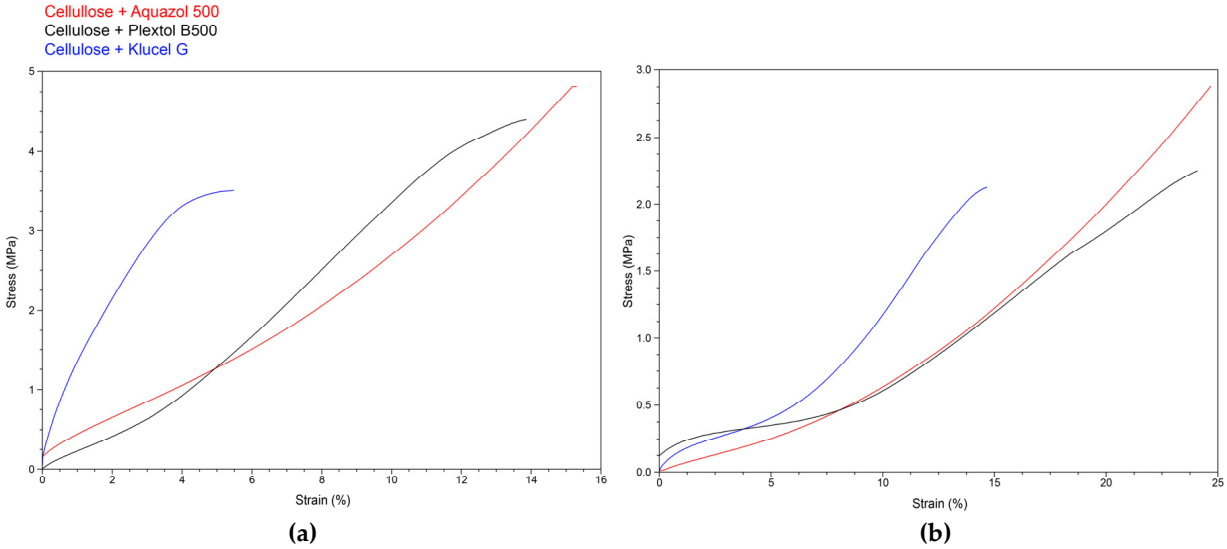


**Figure 2.** Stress vs. strain curves for cellulose samples without EO (**a**) and within EO (**b**).

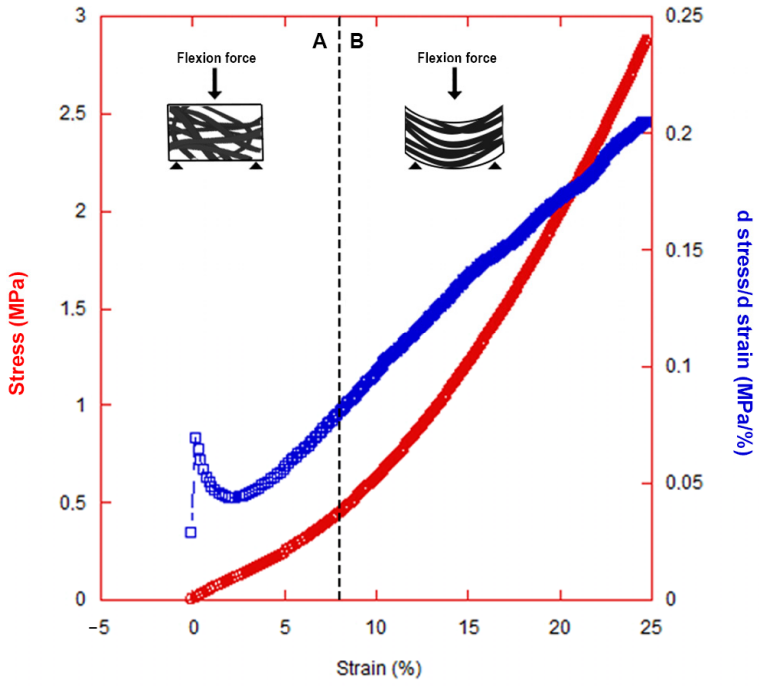


**Figure 3.** Morphological changes of sample fibers from coil (**A**) to stretched conformation (**B**).

These observations were supported by the results obtained with digital microscope analysis (Figure 4). It was clearly evidenced that the samples became less homogeneous after the addition of the EO, and single droplets of EO were not well emulsified and were rather large inside the composite. Contrary to these results, the sample prepared with Aquazol 500 as the main binder generated negligible variations after the addition of the EO (Figure 5).

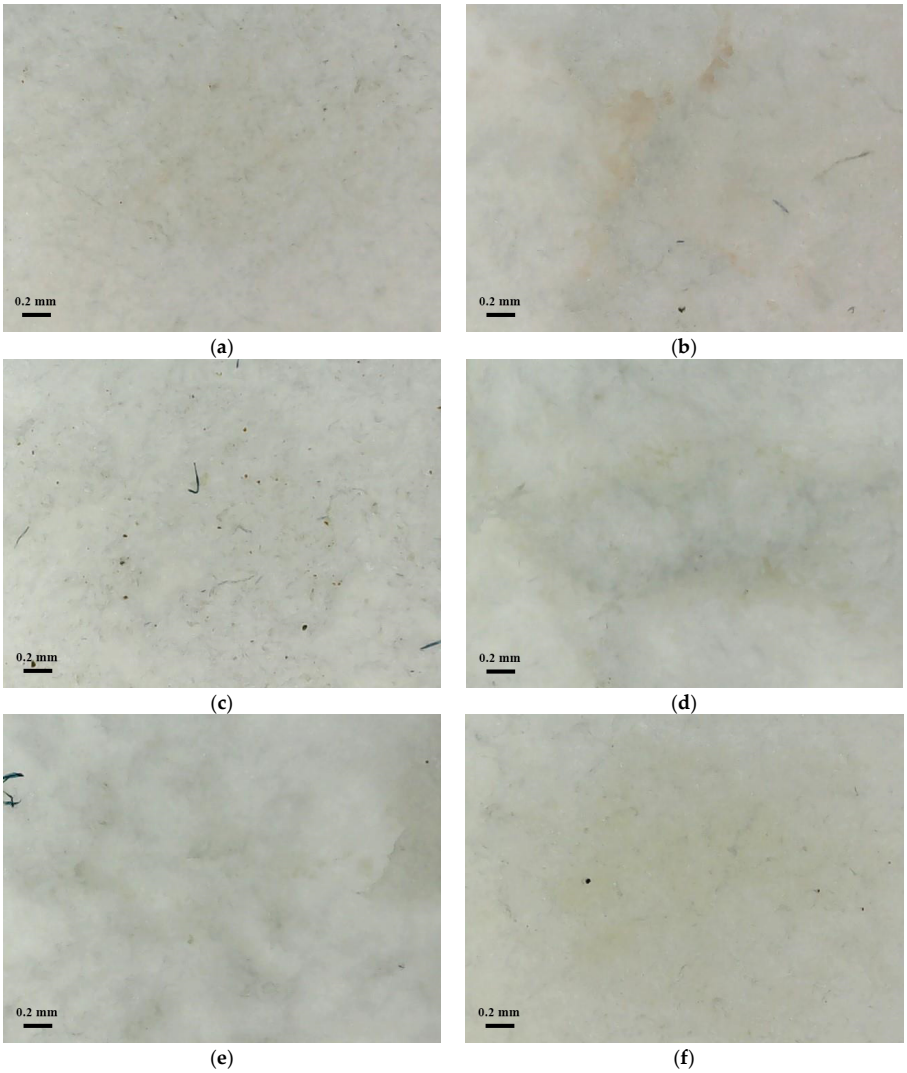


**Figure 4.** Digital microscope analysis of samples without EO−Ce_A (**a**), Ce_P (**c**), Ce_K (**e**), and within EO–Ce_A_EO (**b**), Ce_P_EO (**d**), Ce_K_EO (**f**).

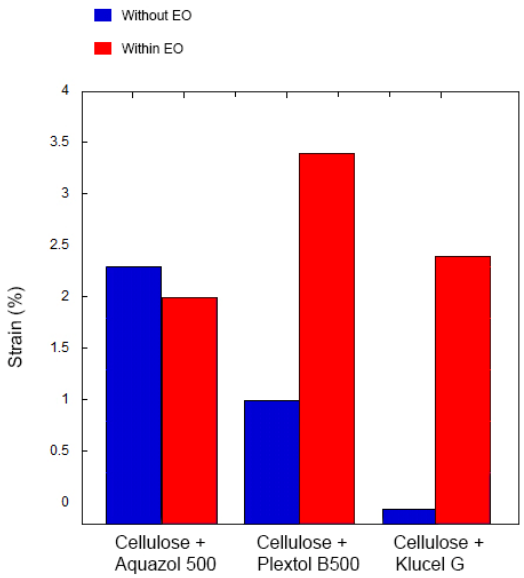


**Figure 5.** Strain obtained from stress–strain curve derivatives of samples with and without EO.

## 4. Discussion

Some authors demonstrated that cellulose-based materials are suitable for the conservation of cultural heritage due to the wide presence of several cellulosic artifacts, mainly composed of paper and wood [40]. In particular, cellulose pulp is largely applied for artifact restoration, especially for salt removal from stone surfaces [41]. Recent advances have demonstrated the suitability of cellulose as a filler material for the reintegration of wooden artifacts [42]. In this study, cellulose pulp extraction from natural sources and waste materials has been demonstrated, enhancing its properties by adding an EO whose antibacterial properties have been previously tested [35].

The mechanical analyses conducted under flexural stress showed that in each case, the addition of the essential oil always reduces the mechanical strength, especially for those samples prepared with Plextol B500 and Klucel G as binders. Indeed, as can be observed by digital microscope analysis, in each case, there are regions of essential oil accumulations suggesting not-homogeneous dispersion of the oil inside the cellulose pulp. In this area, there is a presence of liquid-like regions that globally decrease the mechanical strength of the mixture. As a matter of fact, analyzing Plextol B500 and Klucel G samples' mechanical properties, a huge difference in strain values before and after the addition of the essential oil was recorded: after the addition of the EO, samples start deforming at lower values of stress applied, also recording an increasement of the maximum strain percentage. An exception was represented by Aquazol 500 samples, for which negligible stress variations between samples before and after the addition of the essential oil were recorded.

Hansen solubility parameters can be used to determine the affinity of a solvent with a given polymer [43]. The variation between samples was due to distinct preparation protocols that also differ for the solvent employed in the binder solubilization. Namely, Aquazol 500 was solubilized in ethanol, while Plextol B500 and Klucel G were solubilized in water. Indeed, the ethanol Hansen parameter was more similar to cellulose than water (Table 2). Closer values of the Hansen solubility parameter indicate a compatibility between the polymer and a given solvent, and therefore can be related to a compact/extended polymer structure. Therefore, the Aquazol 500-based samples are the only ones that did not reach a breaking point, most likely because the compatibility of the binder and specifically its solvent to cellulose, whose fibers are mostly aligned (Figure 4). Differently, the water-based binders (Plextol B500 and Klucel G) generate a more compact cellulose conformation that is consistent with the mechanical performances. Speaking about cellulose fiber order, as already shown in Figure 2 but also in Figure 5, Klucel G samples, both with and without EO, show lower strain values. These samples' cellulose fibers are the most aligned, due to the compatibility of cellulose pulp to cellulose ether.

**Table 2.** Hansen solubility parameters.

| Material | Hansen Solubility Parameter $(j/cm^3)^{1/2}$ |
|---|---|
| Cellulose | 18.03 |
| Ethanol | 24 |
| Water | 36.2 |

## 5. Conclusions

A new reintegration protocol for the conservation of wooden artifacts, able also to evidence some disinfection effects, is proposed. A stucco was made by mixing microcellulose, obtained by simple alkaline treatment from softwood almond shell, and *T. capitatus* EO. In order to determine the samples' mechanical properties, DMA analysis under flexural stress was conducted on all the samples. The only samples not to reach the breaking point were the ones whose binder was Aquazol 500, both within and without the addition of the EO. A schematic representation of the procedure is highlighted in Figure 6.

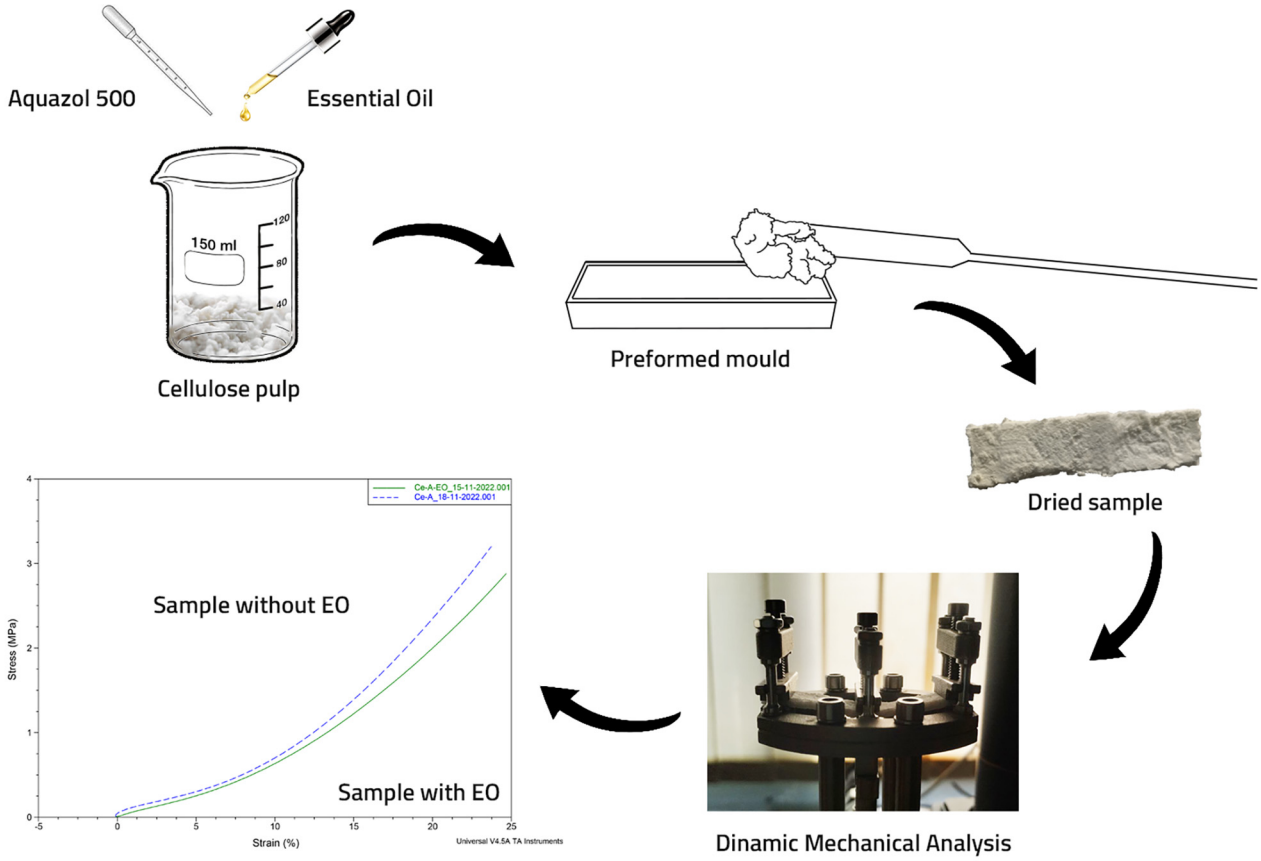


**Figure 6.** Scheme of the followed procedure with an attention for Aquazol 500 samples.

According to the DMA results, the addition of the essential oil in each case increased the strain percentage, decreasing the sample mechanical strength, with the exception of the Aquazol 500 sample. Confirming the interpretation of samples stress vs. strain curves, digital microscope analysis evidenced that each sample was less homogeneous after the addition of the *T. capitatus* EO, showing single particles of EO visibly not well emulsified inside the mixture. Besides having reached the breaking point, all other samples also showed remarkable strain variations before and after the addition of the EO.

On this basis, the almond by-product microcrystalline cellulose can be considered as effective as stucco for wooden artifacts if mixed with Aquazol 500 as the main binder. Moreover, this work demonstrates that stucco may be charged with antimicrobial features by adding *T. capitatus* EO without affecting its mechanical properties. The knowledge can be helpful for designing new reintegration protocols.

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