

## Article

# Biobased and Eco-Compatible Beauty Films Coated with Chitin Nanofibrils, Nanolignin and Vitamin E

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**Abstract:** A stable water-based suspension containing chitin nanofibrils (CN), chitin nanofibrils complexed with nanolignin and the latter containing Vitamin E was prepared starting from CN nanosuspension and nanostructured powders. The water-based coating was deposited by a spray technique on three different renewable and biodegradable films consisting of biodegradable polyesters and starch to prepare possible beauty mask prototypes. After drying, the films were extracted with water to control their potential release on the wet skin and different amounts of released materials were obtained. The results were discussed considering the composition and morphology of the adopted substrates and their interactions with the coating. The eco-compatibility of these films is related to the absence of preservatives and their easy biodegradability in several environmental conditions, decreasing their burden on solid waste management with respect to fossil-based versions.

**Keywords:** chitin nanofibrils; nanolignin; biopolyesters; starch; beauty masks; biodegradable films; poly(hydroxy alcanoate)



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## 1. Introduction

The pursuit of aging and skin diseases prevention and wellbeing together with respect for the environment are driving innovations in cosmetics [1]. On the one hand, consumers are seeking personalized products respecting nature and obtained through smart technologies [2]. On the other hand, they are also reallocating their interests to high-performance products that could better fulfill their needs and priorities [3]. In this contest, beauty masks represent for the consumer the possibility to access a treatment with the same skin benefits obtainable from beauty center treatments. The development of dry beauty masks, that do not contain preservatives, emulsifiers, colors and other chemicals, therefore being more skin-friendly and respectful of nature, consisting of biopolymers or natural fibers able to strictly bind and release the entrapped active ingredients at different doses and times, is an effective answer to these needs [4]. Thanks to the selected carrier substrate and functional ingredients applied on it, this innovative product can be used as an antibacterial, anti-inflammatory, sun-protective, whitening, or anti-aging cosmeceutical, depending on the effectiveness of the selected ingredient(s).

Beauty masks are currently produced using wet non-woven tissues, often prepared with petrol-based fibers, packed in sealed total barrier packaging. After their use, landfill or incineration are the main beauty masks' end-of-life options. Biopolymers, being both biobased and biodegradable, having the capacity for a rapid release of molecules beneficial for skin and easily compostable after usage, represent highly eco-sustainable options. From among biobased polymers already available on the market, poly(hydroxyalkanoates) (PHAs), obtained from bacteria, are particularly advantageous for this application because of their very high biocompatibility [5], the lower Green House Gas emissions [6]

and compostability both in soil and marine environment [6,7]. Wu and Liao prepared arrowroot starch/polyester-based membranes using a flexible PHA and demonstrated that this membrane promotes cell viability [8]. Starch is also a cheap biopolymer that can be released on the wet skin, acting as an emollient and hydration promoter on it [9,10].

Two kinds of smart and sustainable beauty masks can be distinguished. The first group includes those that dissolve in water, thus releasing the active molecules on the skin and in this case, the post-consumer mask material follows the wastewater stream and thus the biodegradability in water of the selected materials is important. The second group includes those that remain solid, and are then disposed in solid waste, but the high biodegradability of the constituent materials can allow a plurality of waste management options, including composting or anaerobic digestion. Both the approaches seem interesting at the moment, as it is important to avoid excessive burdens both on management of wastewater and solid waste [11–13].

Beauty masks developed starting from pullulan [14], as an example of biopolymers easily suspendable in water, belong to the first category. The advantage is the high release capacity obtained thanks to the dissolution of the pullulan matrix, and hence the active ingredient can be released efficiently. Recently, Teno et al. [15] have produced an electrospun pullulan mask that resulted effective in decreasing area, length and depth of forehead and crow's feet wrinkles, and significantly increased moisturizing levels in the skin. Moreover, it increased skin firmness, while it did not show skin irritation after the test.

Regarding the solid beauty masks, some materials were investigated as substrates, such as collagen [16] or biocellulose [17]. PHA/starch-based film substrates were developed in a previous work of our group through compression molding or extrusion [18]. The films were highly cyto-compatible with skin, enabled immune modulation by keratinocytes and allowed starch release in water up to 49% by weight in 30 min. To overcome the issue of the narrow processability window of PHA and its high melt viscosity, the partial replacement of PHA with poly(butylene adipate-co-terephthalate) (PBAT) was successively investigated [19]. This strategy resulted successful and several differences were highlighted between compression molded and extruded films in phase morphology to modulate their properties and release kinetics. Some more research is required to modify the beauty masks with active molecules, thus allowing them to release not only starch but also these specific functional agents.

Several antioxidants were encapsulated to enhance their solubility or bioavailability or to protect them from external factors, and several systems were investigated allowing a controlled release of specific molecules, especially designed mainly for biomedical applications [20]. Electrospinning has proven to be an excellent option for applications in nanotechnology, as electrospun nanofibers can provide the necessary environment for antioxidant encapsulation [21]. Taepaiboon et al. [21] prepared mats of electrospun cellulose acetate nanofibers as carriers for delivery of the model vitamins, all-trans retinoic acid or vitamin A acid (Retin-A), and  $\alpha$ -tocopherol or vitamin E (Vit-E). The kinetic release of these mats was compared with that of cast film, and it was found that for release time lower than 200 min, the cumulative released functional agent was higher for the cast system than for the electrospun mat, whereas the electrospun mat released more for longer time. This study suggests that the preparation of films incorporating functional molecules can be effective in beauty mask applications.

Chitin nanofibrils have shown skin regenerating and anti-microbial activity [22,23]. Moreover, chitin nanofibrils–nanolignin complexes (CN-LG) can be prepared by gelation method, incorporating selected molecules [4]. Examples are complexes incorporating glycyrrhetic acid (GA) [24] or niacinamide [25], that can be selected for their anti-inflammatory properties.

In a beauty mask, the anti-aging functionality is highly desired. Despite that nanolignin is reported to have this property [26], the production of CN-LG complexes incorporating Vitamin E seems promising for this application. Vitamin E was applied in the past to cotton- [27] and fossil-based textiles [28] for skin-contact applications. As it is not very

soluble in water, the entrapment by the gelation method, exploiting the specific interactions of lignin towards the aromatic portion of Vitamin E molecule, is particularly promising as a carrying strategy.

In the present paper, the coating of selected starch/biopolyester films, able to release starch in water and having different morphologies, was performed by applying a water-based treatment by spray technique and drying the films. The water-based treatment was prepared including chitin nanofibrils, and also complexes of chitin nanofibrils with nanolignin (CN-LG) prepared by spray-drying and including Vitamin E. The releasing properties in the coated films were then studied to compare the effect of the same coating on the different substrates, correlating with surface composition, morphology and releasing mechanism of the different systems.

## 2. Materials and Methods

### 2.1. Materials

CN suspension in water (2 wt%) were kindly provided by TEXOL (Pescara, Italy). CN-LG and CN-LG-Vit-E were supplied by Mavi Sud, Aprilia (LT, Italy). CN-LG and CN-LG-Vit-E were prepared in powder by using a Buchi Mini B-190 spray-drier (Flawil, Switzerland) [29] by adding 2% with respect to CN-LG of poly(ethylene glycol) having a molecular weight of 8000 (PEG8000) from Sigma-Aldrich (Milan, Italy). Complexes CN-LG and CN-LG-Vit-E were thus prepared in accordance with previous works [30,31]. The ratio between CN and LG is 2:1 by weight. The content of Vitamin E in CN-LG-Vit-E is 0.2% by weight.

PHA (Ecomann EM F5400 F) was supplied in pellet form from Shenzhen Ecomann Biotechnology Co., Ltd., Shandong, China. Wheat native starch was supplied by Sacchetto SPA (Lagnasco, CN, Italy). Poly(ethylene glycol) with  $M_n = 400$  (PEG400) and Glycerol were purchased from Sigma-Aldrich (Milan, Italy). PBAT (Ecoflex C1200) was purchased in pellet form from BASF, Germany, company. It is a statistical, aromatic-aliphatic copolymer based on the monomers 1,4-butanediol, adipic acid and terephthalic acid. Specifically, PBAT C1200 has a density of  $1.26 \text{ g/cm}^3$  and molecular weight (MW) = 126,000 g/mol.

Treated calcium carbonate (further indicated as CC) (OmyaSmartfill 55—OM) was supplied from Omya SPA, Switzerland, and is characterized by 55% of particles with a diameter less than  $2 \mu\text{m}$ .

Pre-plasticization of starch was performed by mixing wheat starch (Relative Humidity 75%), PEG400 and glycerol in a 60:10:30 ratio into a mortar. The mixture was kept overnight in a ventilated oven at  $80 \text{ }^\circ\text{C}$  to obtain the starch gelatinization. Pre-plasticized starch (P-PLS) was then mixed with the powder of PHA or PBAT into a mortar.

The BMSMART, EBM1 and EBM5 films were prepared according to our previous papers [18,19]. BMSMART is a film substrate consisting of 46.5% of PHA, 46.5% of plasticized starch (P-PLST) and 7% of calcium carbonate, and prepared by compression molding, hence its morphology is coarse. EBM1 film has the same composition but is extruded and compression molded, hence the starch is dispersed more homogeneously in the PHA. EBM5 film is extruded and compression molded. It consists of 46.5% of P-PLS, 23.25% of PHA and 23.25% of PBAT, hence it also contains this latter polymer, that makes the extrusion simpler, determining a decrease in the melt viscosity [19].

### 2.2. Methods

The complex and the other ingredients were suspended in water according to the following composition: 2% CN, 2% CN/LG, 0.3% CN/LG/Vitamin E. Concentration refers to the ratio between molecules' weight and total weight of liquid suspension. The suspension remains stable for days and is easily re-suspendable by manual stirring.

Six  $20 \times 20 \text{ mm}^2$  squares were cut out from each formulation of beauty masks and placed in a petri dish. The squares were treated by spraying technique with the same suspension volume and dried at room temperature.

The morphology of the materials' samples was investigated by field emission scanning electron microscopy (FESEM) using a FEI FEG-Quanta 450 instrument (Field Electron and Ion Company, Hillsboro, OR, USA). The CN suspension (2 wt%) was diluted 1:1000 and the CN-LG and CN-LG-Vit-E were suspended in water (concentration = 80 ppm), then one drop of diluted suspension was poured and dried on a glass window, where the analysis of the particles was carried out. The coated film samples were fractured in liquid nitrogen and the fractured surface was sputtered with Gold (Gold Edwards SP150B, England) before analysis.

The powders, as provided by MAVI company (Turkey), and the coated films were characterized by infrared spectroscopy using a Nicolet T380 Thermo Scientific instrument equipped with a Smart ITX Attenuated Total Reflection (ATR) accessory with a diamond plate.

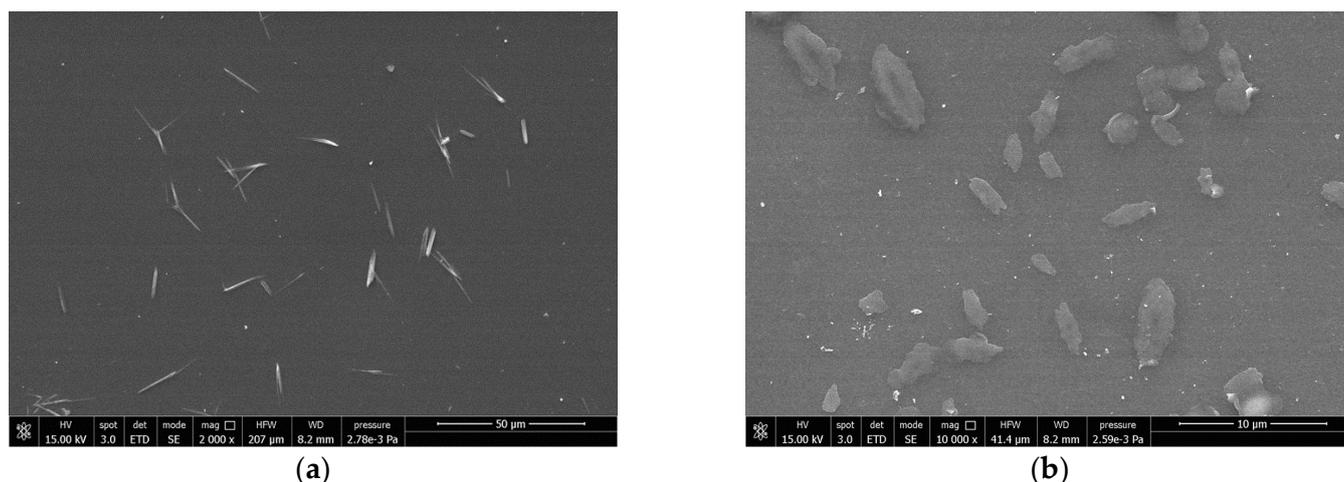
Thermogravimetric analysis (TGA) onto the powders were performed on 4–10 mg of sample using a Mettler-Toledo Thermogravimetric Analysis/Scanning Differential Thermal Analysis (TGA/SDTA) 851 instrument operating with nitrogen as the purge gas (60 mL/min) at 10 °C/min heating rate in the 25–800 °C temperature range.

Small square specimens, of about 20 mm in size, were cut out from the films in two replicates. The samples were immersed at room temperature (RT) in water for 16 h. After soaking with water, the specimens were dried in an oven at 60 °C until constant weight. The replicates were left in water for 16 h and then washed and dried in the same way.

### 3. Results

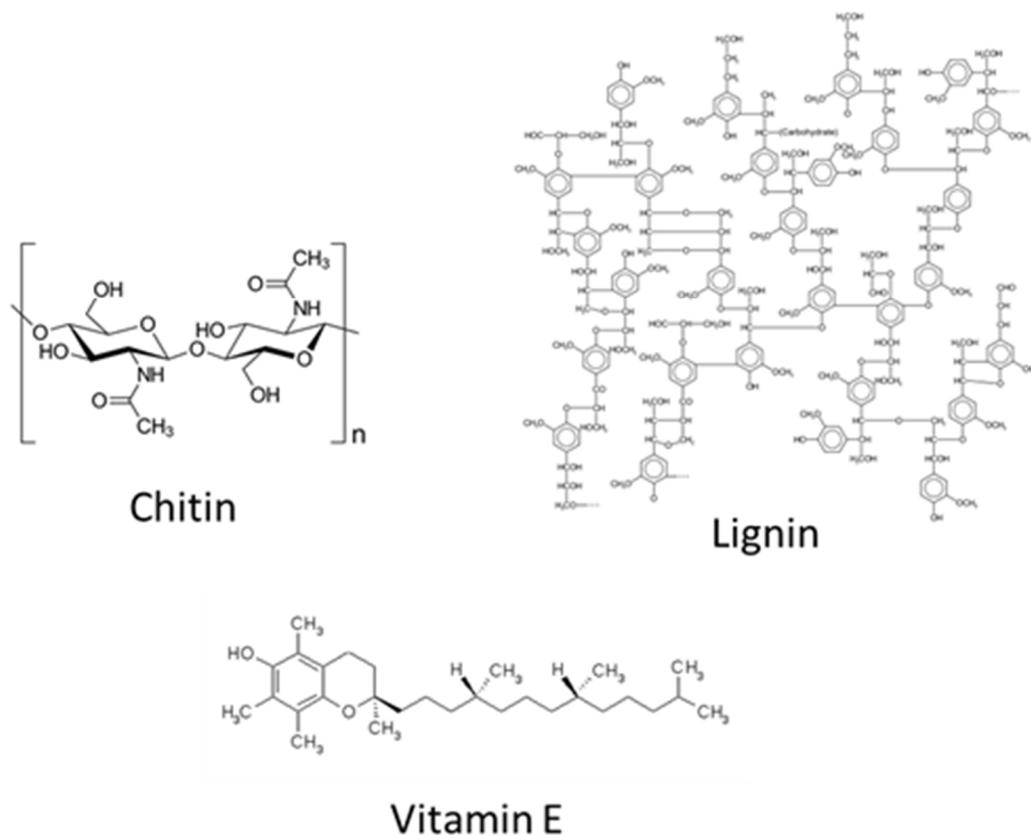
#### 3.1. Characterization of Powders

Through the FESEM analysis, CN appeared as almost straight fibrils having a nanometric thickness and a micrometric length (Figure 1a). The spray-dried complex CN-LG showed a completely different morphology, consisting in micrometric disks having a round or ellipsoidal shape (Figure 1b). These disks consist of agglomerated chitin nanofibrils and lignin nanoparticles [24]. During their preparation in diluted water solution, the slightly positive chitin nanofibrils are complexed with slightly negative nanolignin, hence these discoidal complexes including several nanofibrils and lignin nanoparticles are formed and they are able to entrap molecules that may be present in the solution, like Vitamin E, niacinamide or glycyrrhetic acid [24].



**Figure 1.** Field emission scanning electron microscopy (FESEM) micrographs on diluted powder suspensions deposited on glass: (a) chitin nanofibrils (CNs), (b) chitin nanofibrils–nanolignin complex (CN-LG).

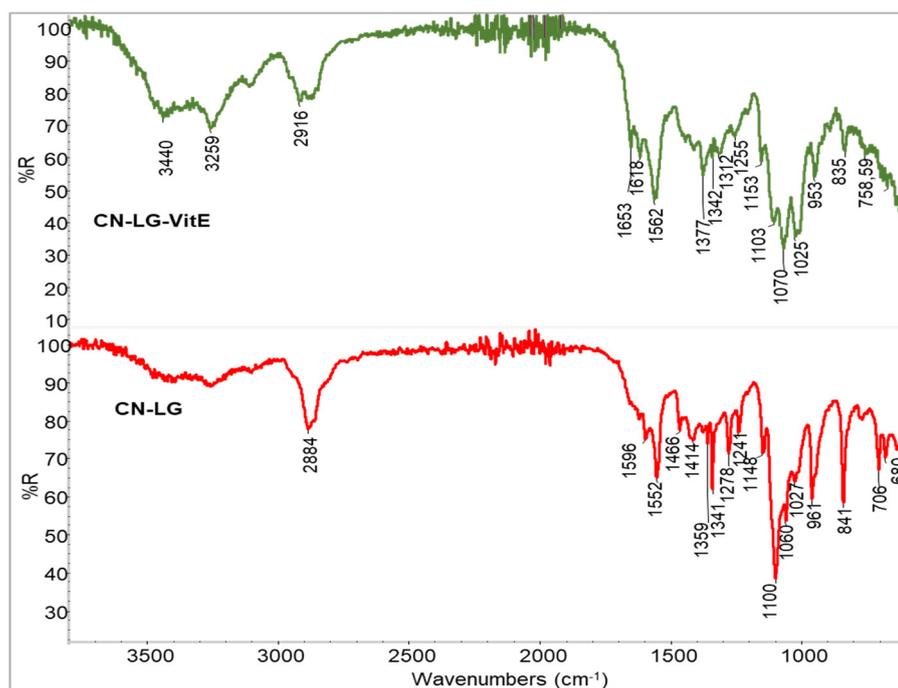
Chitin is a polysaccharide, whereas lignin has an aromatic structure. Vitamin E is a lipophilic molecule including a phenolic ring and an aliphatic 16 carbon atoms chain (Figure 2).



**Figure 2.** Chemical structure of chitin, lignin and Vitamin E.

The complexes CN-LG and CN-LG-Vit-E were characterized by infrared spectroscopy. As discussed in our previous work [24], CN showed characteristic amide I and Amide II bands at about  $1620$  and  $1550\text{ cm}^{-1}$ , respectively. The most intense bands at about  $1020$  and  $1070\text{ cm}^{-1}$  are characteristic of C-O stretching and agree with the polysaccharidic nature of this biopolymer. The band at  $3440\text{ cm}^{-1}$  is attributable to O-H stretching, and the bands at  $3259$  and  $3200\text{ cm}^{-1}$  to N-H stretching of amine and amide groups, respectively. The band at about  $2880\text{ cm}^{-1}$  is associated to C-H stretching. LG shows bands at  $1030$ ,  $1120$  and about  $1240\text{ cm}^{-1}$ . The band at  $1240\text{ cm}^{-1}$  can be associated with C-C plus C-O plus C=O stretching.

The complex CN-LG and the same complex entrapping Vitamin E showed quite similar spectra, and they showed the described bands of CN and LG (Figure 3). The presence of poly(ethylene glycol) can be responsible for the peak at  $840$  and  $950\text{ cm}^{-1}$ , characteristic of this polymer [32]. The presence of Vitamin E can be revealed despite its low concentration in the sample ( $0.2\% w/w$ ). The Vitamin E ( $\alpha$ -tocopherol) spectrum exhibited an absorption band at about  $3470\text{ cm}^{-1}$  for OH,  $2930$  and  $2870\text{ cm}^{-1}$  for asymmetric and symmetric stretching vibrations of the  $\text{CH}_2$  and  $\text{CH}_3$ ,  $1460\text{ cm}^{-1}$  for phenyl skeletal and methyl asymmetric bending,  $1377\text{ cm}^{-1}$  (intense peak because of the high number of methyl groups in the molecules (Figure 2)) for methyl symmetric bending,  $1260\text{ cm}^{-1}$  for  $-\text{CH}_2-$ ,  $1100\text{ cm}^{-1}$  for plane bending of phenyl and  $919\text{ cm}^{-1}$  for trans,  $\text{CH}_2$  stretching [33]. In the CN-LG-Vit-E spectrum, the more intense peaks at  $2916$ ,  $1377$  and  $1100\text{ cm}^{-1}$  can thus be referred to the presence of Vitamin E on the spray-dried sample.



**Figure 3.** ATR spectra of chitin nanofibrils–nanolignin–Vitamin E complex (CN-LG-Vit-E) and chitin nanofibrils–nanolignin complex (CN-LG).

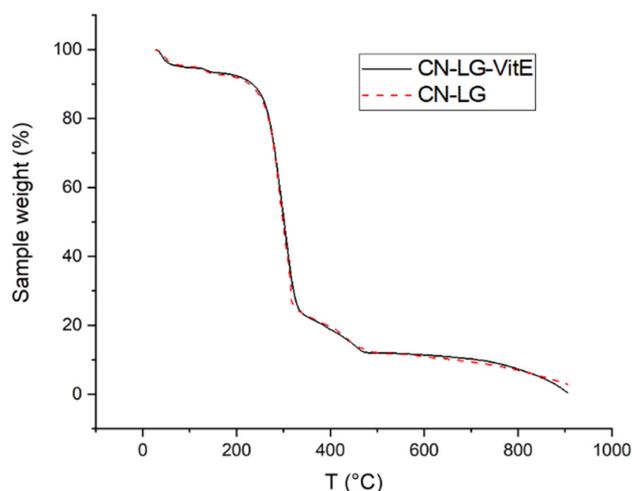
The thermogravimetric analysis (TGA) in nitrogen flow of the two complexes was investigated as well as the one of pure dried chitin nanofibrils CN (Table 1). Interestingly, CN show a very high amount of residue after the thermal degradation. The dried nanofibrils, agglomerated, represent a sample that cannot be easily degraded and thus it forms a high amount of carbonaceous residue during thermal heating in nitrogen flow. On the contrary, the spray-dried powder, consisting of micrometric particles having a discoidal shape, show a lower amount of residue. The spray drying in the presence of PEG is a process that highly affects the morphologic features of these nanostructured materials, thus also influencing their thermal behavior [24].

**Table 1.** Thermogravimetric data related to CN, CN-LG and CN-LG-Vit-E (Vitamin E).

Entry	Onset 1 <sup>3</sup> (°C)	Step 1 (%)	Onset 2 (°C)	Infl. 2 <sup>4</sup> (°C)	Step 2 (%)	Onset 3 (°C)	Step 3 (%)	Residue (%)
CN <sup>1</sup>	45; 140	−2.4; −2.6	277	349.1	−21.2	387	−9.5	58.08
CN-LG-PEG <sup>2</sup>	114	−2.59	266	287	−69.25	406	−10.39	12.37
CN-LG-Vit-E <sup>2</sup>	125	−2.54	264	301	−70.99	435	−10.90	11.56

<sup>1</sup> Analysis performed on dry CNs. <sup>2</sup> Analysis performed on spray-dried particles, containing 2% of PEG. <sup>3</sup> Step 1 is the loss of volatile molecules (for instance water), step 2 is the main degradation step and step 3 is the secondary degradation step. <sup>4</sup> Inflection point of the main peak.

The thermograms of CN-LG and CN-LG-Vit-E were similar (Figure 4). By the addition of Vit-E, the stability of the complex was slightly improved. In fact, the Onset 1 temperature and the inflection temperature of the main peak were slightly increased (Table 1). This could reasonably be due to the radical scavenger activity of Vit-E [34]. In fact, a reduced reactivity of radicals thanks to this scavenging action, can contrast, at least partially, the thermal degradation mechanism [35].



**Figure 4.** TGA thermograms of chitin nanofibrils–nanolignin–Vitamin E complex (CN-LG-Vit-E) and chitin nanofibrils–nanolignin complex (CN-LG).

In general, all the tested materials showed a high thermal stability. These considerations were considered pivotal for correctly preparing coatings and applying them on biobased substrates as well as for storing them in the correct way.

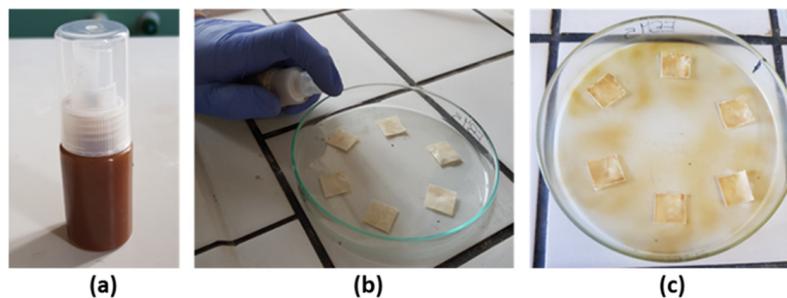
### 3.2. Coating Preparation and Characterization of the Coated Substrates

The 2 wt% suspension of CN was the starting point to obtain a water suspension containing 2 wt% of CN, 2 wt% of CN-LG and 0.3 wt% of CN-LG-Vit-E. This suspension resulted brown in color (Figure 5) and it was stable for days and is easily re-suspendable by manual stirring. Hence, the presence of the suspended CN-LG complexes did not result in any significant sedimentation. Several techniques can be applied for coating biobased substrates. The spray methodology was selected for its easy up-scalability and reduced costs.

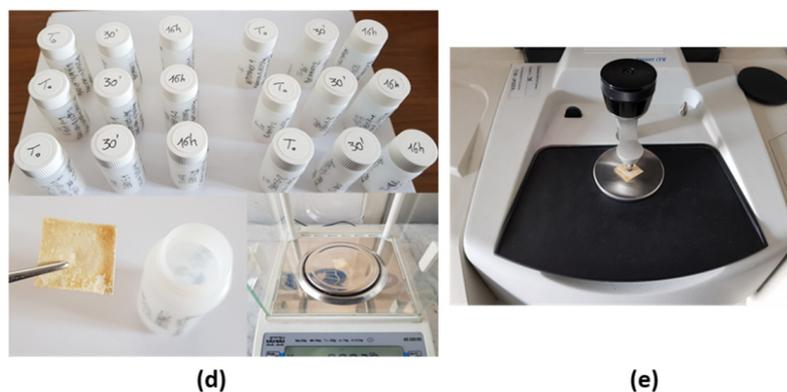
The selected substrates were BMSMART, EBM1 and EBM5, consisting of starch, biopolyesters and calcium carbonate. The films had different morphological properties. The BMSMART is fully produced by compression molding, whereas EBM1 was prepared from extruded pellets and had a more homogenous morphology. The last film, EBM5, contains not only PHA as biopolyester, but also PBAT, allowing an improved melt processability, hence its composition is different with respect to the other ones and its morphology was also the most homogeneous. Films were treated with water-based suspension and then the samples were dried.

Generally, CN have shown an effective film-ability from 2 wt% solution [36], hence each drop that arrives on the surface through the spray methodology forms a millimetric solid film after water evaporation. The continuity of the film would be granted by controlling the spraying technique in terms of drop size and effective suspension quantity applied on the surface. The reproducibility of the spray technique was investigated with a preliminary test. A known quantity of suspension was poured in the sprayers and after ten sprays, the remaining quantity was weighted. This procedure was repeated ten times. An average value was thus obtained for the weight and the standard deviation was calculated. This procedure allowed to verify that the variation of weight in spray application was only 0.7%.

## Sample preparation by spraying



## Characterization



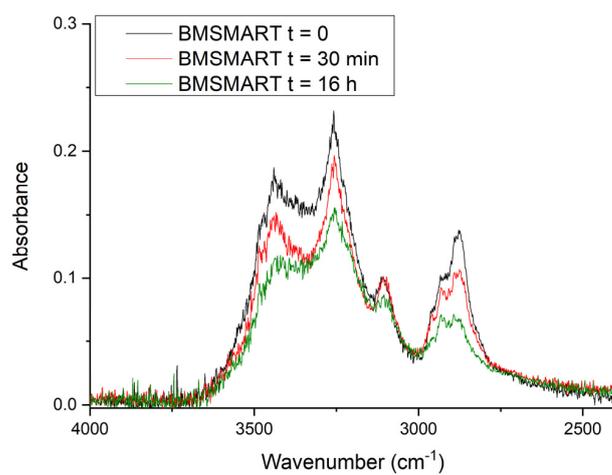
**Figure 5.** Pictures related to: (a) water-based suspension containing CN-LG-Vit-E, (b) application of CN-LG-Vit-E onto the films, (c) films after the CN-LG-Vit-E application, (d) water extraction, drying and weight of samples and (e) ATR-infrared analysis of dried films.

The adopted spray methodology was repeated in exactly the same way for all the films, to allow a comparative study. Moreover, 6 specimens, treated on both sides, were investigated for each sample.

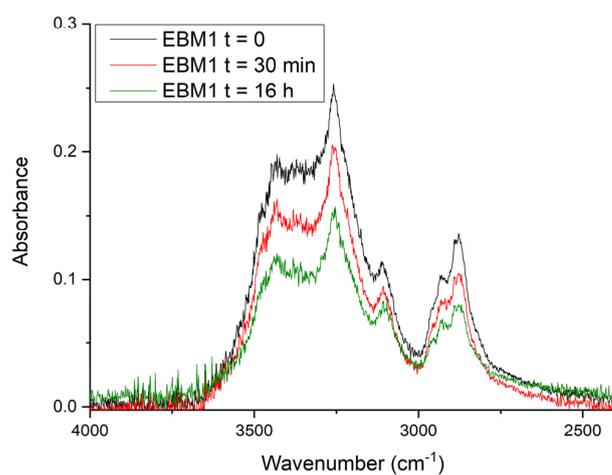
The coated specimens were immersed in water and 3 of them were left there for 30 min, whereas the other 3 specimens were left in water for 16 h. After these treatments, the specimens were dried, weighted and characterized by ATR infrared analysis (Figure 6). The infrared spectra showed the surficial composition of the samples.

Interestingly, by normalizing on the carbonyl band of biopolyesters (not extractable by water), we could observe that the characteristic bands of starch, at  $3250\text{ cm}^{-1}$ , attributable to -OH stretching, decreased after 30 min and 16 h, initiating the release of the starch from the films. Similar results were observed for the uncoated substrates, characterized with an identical methodology [18,19]. A similar trend was observed for BMSMART- and EBM1-coated films, whereas, in the case of EBM5, a less evident decrease in bands' intensity was noticed (Figure 6c).

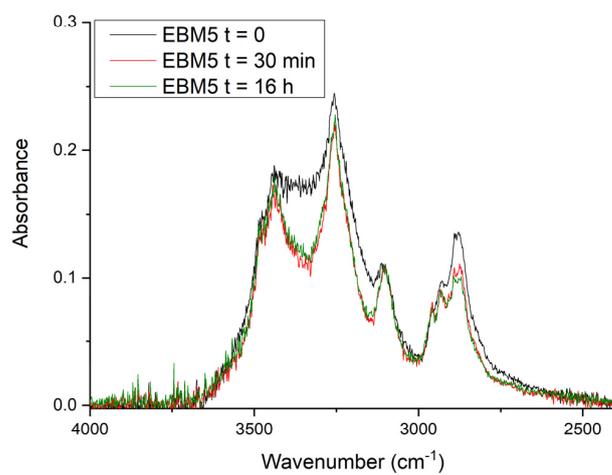
The data regarding the extracted fraction (Table 2) showed that the released percentage of weight was decreased in the coated film with respect to the uncoated ones. The observed differences are reported in Table 2 as  $\Delta 30\text{ m}$  and  $\Delta 16\text{ h}$ , indicating the percentage of decreased release due to coating, and these values were significant for all the films, but they resulted extremely high for the EBM5 sample at 30 min. In this case, the release of starch was strongly reduced both after 30 min and after 16 h, indicating that the coating had almost inhibited the release of starch from the film.



(a)



(b)



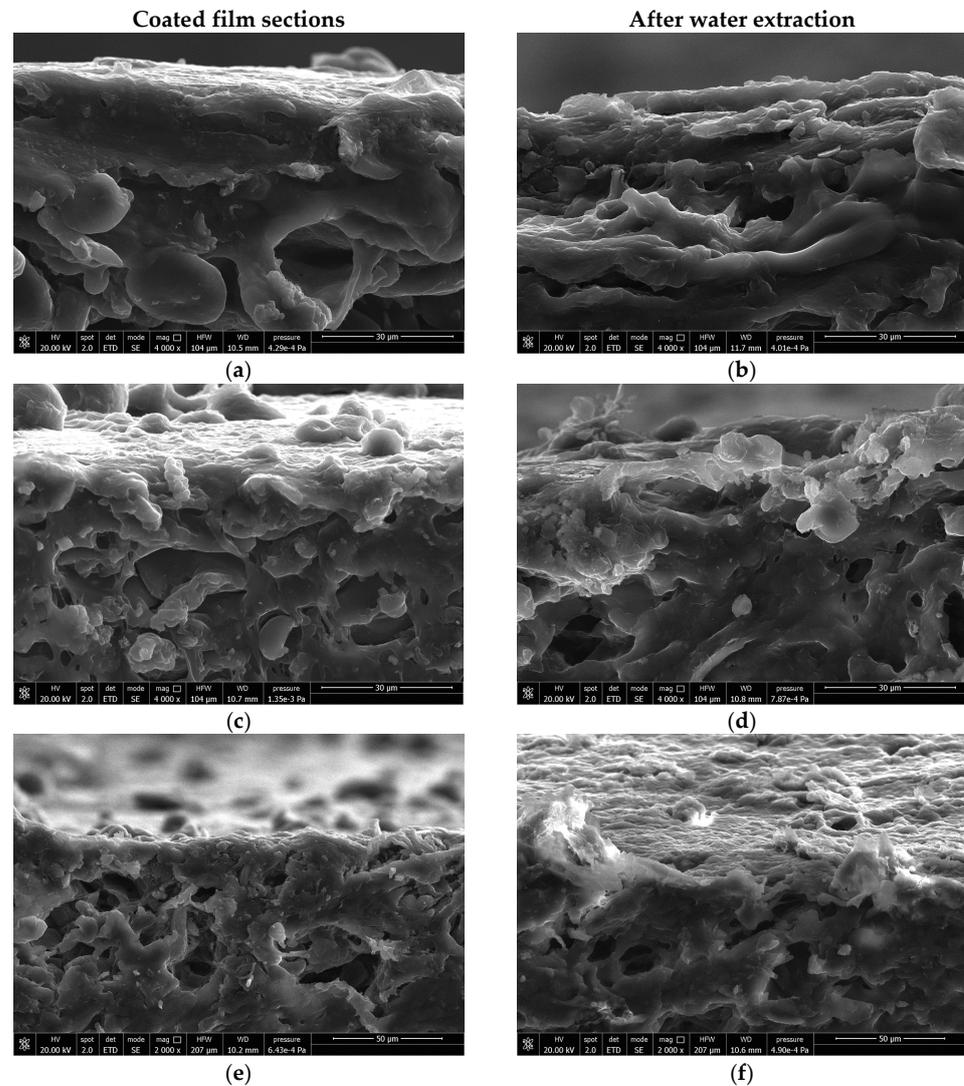
(c)

**Figure 6.** Infrared ATR spectrum related to the surface composition of: (a) coated BSMART, (b) coated EBM1, (c) coated EBM5.

**Table 2.** Extracted fraction in water.

Entry	wt% after 30 min	wt% after 16 h	$\Delta_{30\text{ m}}$	$\Delta_{16\text{ h}}$
COATED BMSMART BMSMART	−12.0 −17.2	−16.4 −23.5	30.2%	30.2%
COATED EBM1 EBM1	−11.7 −19.3	−16.5 −20.8	39.4%	20.7%
COATED EBM5 EBM5	−5.6 −17.6	−5.9 −22.2	68.2%	73.4%

The use of FESEM on cryo-fractured films, before and after extraction in water for 16 h, allowed to analyze the film and surface morphology. The BMSMART film showed a complex morphology, where the starch granules in the film bulk could be noticed (Figure 7a). The surface resulted homogenous (Figure 7a), in agreement with a good film-ability of CN and other particles on the surface. In fact, the deposition of a CN suspension by casting on a glass surface allow to produce films (Figure 8).



**Figure 7.** FESEM micrographs of the cryo-fractured films consisting of: (a) coated BMSMART, (b) coated BMSMART after water extraction, (c) coated EBM1, (d) coated EBM1 after water extraction, (e) coated EBM5 and (f) coated EBM5 after water extraction.



**Figure 8.** Film of pure CN obtained through casting.

After the release in water, the surface resulted less smooth, because the water significantly corroded the surface, removing the starch particle near the surface (Figure 7b). The morphology of the EBM1 film resulted more homogenous in the bulk, and the surface resulted smooth, despite some round particles emerging from it (Figure 7c). After the release in water, the smoothness of the surface decreased because of the surficial loss of starch, leaving cavities on the surface (Figure 7d). The last film, EBM5, was only slightly affected by the treatment with water and, in agreement with release gravimetric determinations and with infrared analysis results, the loss of starch seemed almost inhibited (Figure 8e,f).

#### 4. Discussion

The release of active compounds is a subject fundamental in drug delivery, hence kinetic aspects are considered pivotal in this field, where several models were applied mainly considering the diffusion fundamentals [37]. However, in our specific case, the release of mostly insoluble macromolecules of starch are considered, hence simply diffusive laws are probably not fully suitable. Generally, the release of starch from films was only considered to investigate migration into food simulants from starch-based films used in food packaging [38].

Korsmeyer and Peppas [39] developed an empirical equation to analyze both Fickian and non-Fickian release of drug from swelling as well as non-swelling polymeric delivery systems. The kinetic of release is described by Equation (1):

$$\frac{M_t}{M_\infty} = kt^n \quad (1)$$

where  $M_t/M_\infty$  is the fraction of drug released at time  $t$ ,  $k$  is the rate constant (having units of  $t^{-n}$ ) incorporating structural and geometric characteristics of the delivery system and  $n$  is the release exponent indicative of the mechanism of transport of drug through the polymer. The  $n$  value is used to characterize different release mechanisms [40].

As for each coated and uncoated film, data of weight release and correspondent time were available as well as film composition, neglecting the weight of the coating because it was enormously thinner than the substrate, and it was possible to evaluate by calculation  $k$  and  $n$  values for all the samples (Table 3). The values of  $n$  are all lower than 1, and this indicates a quasi-Fickian diffusion typical of non-swelling matrix diffusion.

**Table 3.**  $k$  constant and  $n$  exponent in the Kormeyer–Peppas equation calculated for the different coated and uncoated films.

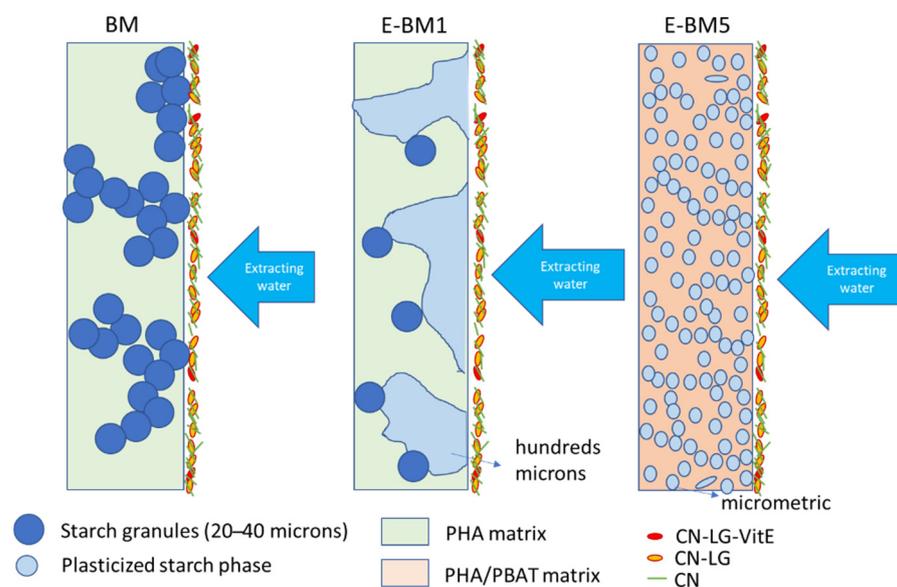
Entry	$k$	$n$
COATED BMSMART	0.131	0.0904
BMSMART	0.188	0.0901
COATED EBM1	0.119	0.0992
EBM1	0.353	0.0217
COATED EBM5	0.107	0.0152
EBM5	0.229	0.0669

The results suggest that EBM1 has a high value of  $k$ , but  $n$  is quite low, indicating that there is a low growth of release as a function of time. The coated EBM1 represents the most convenient releasing device, as it shows the highest value of  $n$ . The coated and uncoated BMSMART resulted efficient in releasing starch, and the coating of the substrate has not highly modified the release kinetic. The most evident peculiarity is represented by the low values of both  $k$  and  $n$  for the coated EBM5 sample, indicating, in good agreement with the results of Section 3, that the release of starch from this film has a terribly slow kinetic. This requires to better deepen the release mechanism of the coated films.

For the preparation of beauty mask prototypes, the selected substrates were BMSMART, EBM1 and EBM5, consisting of starch, biopolyesters and calcium carbonate. The films had different morphological properties. The BMSMART is fully produced by compression molding, whereas EBM1 was prepared from extruded pellets. The latter methodology is simpler to upscale in a flat die extrusion device, widely diffused in industry and for this reason, was investigated. However, in our previous work, it was shown that the capability of releasing starch in water from uncoated substrates is decreased for EBM1 more than for BMSMART [18], because the phase distribution of BMSMART resulted coarser: starch round granules of tens of microns [41] were present in the biopolyesters matrix. On the contrary, the EBM1 film consisted of a matrix consisting of both biopolyesters and plasticized starch, with the presence of a few residual starch granules.

Successively, for optimizing the extrusion by decreasing the melt viscosity, half the PHA was replaced with PBAT, and thus the EBM5 film was produced [19]. This specific film showed the most homogeneous morphology consisting of a matrix of biopolyesters and dispersed micrometric particles of plasticized starch. The latter film showed the lowest capability for releasing starch. The different morphologies of the three formulations are schematized in Figure 9.

The application of the coating by the spray technique allowed to deposit on the surface CNs, CN-LG and CN-LG-Vit-E, that formed a film thanks to the good film-ability of CNs and their high compatibility with the CN-LG and CN-LG-Vit-E complexes (Figure 9). The water interacted with this coating layer and penetrated in the film bulk where the starch could be removed, thus creating cavities in the film. The obtained data showed that the starch release in water is decreased thanks to the application of the coating with respect to uncoated films. This means that there was a strong interaction and adhesion between the coating and all the substrate materials, making the interaction between water and the film surface more difficult. Reasonably, the high interaction of chitin and starch, both being polysaccharides, can explain this “cap effect” well, as shown by the coating applied on the films.



**Figure 9.** Scheme considering the different species and morphologies of the three potential models of beauty masks for explaining the results of release tests in water.

The different amount of released starch can be explained considering the different morphology. As the morphology of the BMSMART film is coarser, the surface is also more irregular, and it is rich in starch granules. The application of the coating has a shielding effect towards water. In the case of EBM1, the presence of plasticized starch big domains can result in a similar release of starch, despite the high adhesion between the coating and this smooth starch-rich surface being certainly high. In the case where starch is homogeneously dispersed as micrometric domains in the biopolyesters matrix (EBM5), the release is less efficient. The high hydrophobic effect of the matrix, combined with a lesser hydrophobic superficial layer, makes the release of starch more difficult. However, a strong decrease in starch release was observed comparing the uncoated EBM5 and the coated one. Hence, an enhanced interaction between the coating and the materials of the film, including PBAT, can be reasonably hypothesized. Lignin was reported to have a better compatibility with PBAT, because of specific interactions between aromatic groups, than with poly(lactic acid) (PLA), and thus it was used as a compatibilizer in these blends [42]. Lignin was added to PBAT in several works as a reinforcing agent, and this was explained considering the good interactions occurring between PBAT and lignin [43–45]. Moreover, more specifically, lignin was reported to favor PBAT crystallization thanks to nucleation induced by its phenolic rings [46]. All these works suggest the occurrence of significant interactions between lignin of the coating and the aromatic units of PBAT inducing an increased adhesion between the coating and the surface, that can hinder the effective extraction of starch from the surface operated by water.

## 5. Conclusions

Raw materials were characterized in terms of their morphology, chemical composition and thermal stability. Chitin nanofibrils consist of whiskers, whereas chitin nanofibrils–nanolignin complexes have a discoidal shape. All the materials show a high thermal stability and the presence of Vitamin E in the chitin nanofibrils–nanolignin complex could be revealed by infrared analysis. Stable water-based suspension containing chitin nanofibrils (CN), chitin nanofibrils complexed with nanolignin (CN-LG) and the latter containing Vitamin E (CN-LG-Vit-E) was prepared starting from CN nanosuspension and nanostructured powders. The water-based coating was deposited by a spray technique on three different renewable and biodegradable films consisting of biodegradable polyesters and starch to prepare possible beauty mask prototypes. After drying, the films were extracted with water to control their potential release on the wet skin and different quantities of re-

leased materials were obtained. In particular, the compression-coated compression-molded film (BMSMART) and the extruded film (EBM1) consisting of a poly(hydroxyalcanote) (PHA) and starch showed a slightly lower release of starch than the uncoated films, but they are potentially exploitable for beauty masks' applications. On the contrary, the films containing starch and a mixture of PHA and poly(butylene adipate-co-terephthalate) (PBAT) had a release almost inhibited if coated. These interesting results were discussed in terms of kinetics aspects by using the Korsmeyer and Peppas equation. The differences were then explained considering the mechanism of action of water on the surface of the films, considering their specific morphologies and also considering the instauration of high adhesive forces between the lignin in the complexes and the PBAT, supported by literature studies.

In general, the spray-coating of this water-based functional lotion on the films decreased the amount of released starch, but certainly, the functional molecules are released together with emollient starch to confer to the treatment anti-microbial and skin-regenerative (chitin nanofibrils) and antioxidant (nanolignin and Vitamin E) properties. The possibility of including the functional molecules in the starch domains could be studied in the future to compare its effectiveness with the present strategy.

The eco-compatibility of these films is related to the absence of preservatives because they can be commercialized in the dry state and can be wet before their application on the skin. Their easy biodegradability, granted by the formulation consisting of biodegradable materials in several environmental conditions, decreases their burden on solid waste management with respect to fossil-based versions, as composting or anaerobic digestion can be potentially adopted. As only starch or functional biopolymers are released from the mask (and they can potentially reach the wastewater net where they are biodegradable), this product, disposed in the solid waste, will not pollute water and sea.

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