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Aleksandra Ježo , [Faksawat Poohphajai](#) , [Rene Herrera Diaz](#) , [Grzegorz Kowaluk](#) *

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Article

Incorporation of Nano-Zinc Oxide as a Strategy to Improve the Barrier Properties of Biopolymer-Suberinic Acid Residues Films—A Preliminary Study

Aleksandra Ježo ¹, Faksawat Poohphajai ^{2,3,4}, Rene Herrera Diaz ^{2,3} and Grzegorz Kowaluk ^{1,*}

¹ Institute of Wood Sciences and Furniture, Warsaw University of Life Sciences - SGGW, Nowoursynowska St. 159, 02-776 Warsaw, Poland

² InnoRenew CoE, Livade 6a, 6310 Izola, Slovenia

³ University of Primorska, Faculty of Mathematics, Natural Sciences and Information Technologies, Koper, Slovenia

⁴ Department of Bioproducts and Biosystems, Aalto University School of Chemical Engineering, Aalto, Finland

* Correspondence: grzegorz_kowaluk@sggw.edu.pl

Abstract: Finishing coatings in the wood-based composites industry not only influence the final appearance of the product but also serve to protect against fungi, and molds, and reduce the release of harmful substances, particularly formaldehyde and volatile organic compounds (VOCs). Carbon-rich materials, such as those derived from birch bark extraction, specifically suberin acids, can fulfil this role. Previous research has demonstrated that adding suberin acid residues (SAR) at 20% and 50% by weight significantly enhances the gas barrier properties of surface finishing materials based on poly(lactide) (PLA) and polycaprolactone (PCL), particularly in terms of Total VOC (TVOC) and formaldehyde emissions. This study aims to explore whether these properties can be further improved through the incorporation of nano-zinc oxide (nano-ZnO). Previous research has shown that these nanoparticles possess strong resistance to biological factors and can positively affect the characteristics of nanofilms applied as surface protection. The study employed PLA and PCL finishing layers blended with SAR powder at 10% w/w and included 2% and 4% nano-zinc oxide nanoparticles. The resulting blends were milled to create a powder, which was subsequently pressed into 1 mm thick films. These films were then applied to raw particleboard surfaces. TVOC and formaldehyde emission tests were conducted. Additionally, the fungal resistance of the coated surfaces was assessed. The results showed that PLA/SAR and PCL/SAR composites with the addition of nano-zinc oxide nanoparticles exhibited significantly improved barrier properties, offering a promising avenue for developing biodegradable, formaldehyde-free coatings in the furniture industry with enhanced features. Furthermore, by utilizing SAR as a post-extraction residue, this project aligns perfectly with the concept of upcycling.

Keywords: barrier properties of nanofilms; nano-zinc oxide nanoparticles; suberic acid-residues; biodegradable finishing coatings; biological resistance

1. Introduction

Surface finishing technologies in the furniture industry aim to ensure both aesthetic appeal and functional safety, including resistance to hydrolysis [1], biological factors [2], fire retardance [3] and minimizing environmental emissions, depending on the furniture's intended use. Breakthroughs in green nanotechnology are revolutionizing processes and products, benefiting the environment, reducing pollution, and conserving resources [4,5].

Poly(lactic acid) (PLA) polymers, derived from renewable resources like corn starch or sugarcane [6], offer an eco-friendly alternative for wood finishing coatings [7], combining sustainability with a durable finish [8,9]. However, due to some drawbacks of PLA, further modifications are implemented, including fiber reinforcement [7–16], blending [17] or plasticization [18]. The findings by OKSMAN et al. indicate that PLA serves as an effective matrix material for

natural fiber composites, demonstrating promising improvements in the mechanical properties of PLA and flax fiber composites [19].

Aside of PLA, another promising biodegradable polymer is polycaprolactone (PCL), showing good compatibility with other polymers [20–25]. It has also been proven beneficial to incorporate lignocellulosic particles/fibers into PCL to enhance its properties [16,21,26,27] or other compounds like kaolin [28] or bioactive glass [29].

The incorporation of nanoparticles into polymers, also PLA and PCL, is an area of research that holds promise for enhancing the properties and functionality of these biodegradable materials. Incorporating nanoparticles like SiO₂, Al₂O₃, TiO₂, and Fe₂O₃ into Poli-L-lactide (PLLA) significantly improves the barrier properties of the resulting nanocomposites, reducing water vapour permeability by up to 18% and wet oxygen permeability by up to 9% [30]. By applying CaCO₃ nanoparticles up to 5 wt% the gas permeability results of N₂, O₂, and CO₂ revealed an improvement in final barrier properties [31]. CeO₂ nanoparticles deposition on wood surfaces with chitosan and cationic starch as building blocks proved to offer a significant UV protection effect while being a fully biodegradable and durable product [32]. Also, nano-ZnO deposited on wood by KONG et al. [33], forming dense and uniform arrays of nanorods provided UV protection, improved photostability, enhanced flame retardancy, and water repellency when modified with stearic acid. Cellulose nanocrystals (CNC) and lignin nanoparticles (LNP) enabled the creation of PVC-based composites with improved barrier properties, limiting gas migration and enhancing the UV-shielding [34]. Incorporating nanoparticles into polymers can improve barrier properties due to two main factors: 1. reduction in available diffusion area, achieved by replacing permeable polymer with impermeable nanoparticles; 2. increased path length for the permeant to traverse the film, as it follows a convoluted route around the impermeable nanoparticles [35].

One of the other potential improvements that the implementation of nanoparticles can bring, is making the composite bioprotective. It has been proven, that the addition of metal-based particles, such as copper [36,37] and silver [15,38,39], into polymers is a versatile route to take advantage of their strong antimicrobial properties, producing novel biocide materials [40]. Moreover, as WU et al. found out in the example of organoclays, the introduction of nanofillers leads to a significant enhancement in phase morphology, primarily due to their strategic localization that effectively prevents the merging of discrete domains and encourages the breakup of droplets [25].

Carbon-rich natural substances, like those found in birch bark extraction products, such as suberic acids (SA) and their residues (SAR), have significant potential for reducing emissions of harmful substances into the environment. The findings of Ježo and Kowaluk [16] indicate a positive influence of 20% and 50% addition of SAR into PLA and PCL blends regarding TVOC and formaldehyde emission from plywood. This can be attributed to the high lignin content in SAR particles. Furthermore, SAR addition enhances the relative hardness and scratch resistance of PLA- and PCL-based surface finishing materials. This paper investigates whether adding nano Zinc-oxide (nano-ZnO) can improve the barrier properties and biological resistance of nanocomposites created by blending PLA/PCL, SAR, and nanoparticles. Since it has been shown, that the addition of nano-ZnO to PLA/PCL has potential in medical applications [41,42], it is to be found if such potential lays also in the wood composites industry. Both the effects of SAR addition and nanoparticle incorporation will be investigated.

2. Materials and Methods

2.1. Materials

Surface finishing layers were fabricated using two distinct matrices: laboratory-purpose PLA (Sigma-Aldrich, Saint Louis, MO, USA, product no. 38534) and PCL (Sigma-Aldrich, product no. 704105) in drops with a diameter of 3 mm. Suberinic acid residues (SAR) used in the research, that have been utilized to prepare the blends, have been described in detail by Rizikovs et al. [43]. The following are the basic chemical properties of SAR: cellulose 9.0 wt%, aromatic suberin, lignin 21.4 wt%, ω -hydroxy acids 17.5%, and α , ω -diacids 11.9%. The nanoparticles used in the study were nano

zinc-oxide (nano-ZnO), hereafter called “nano” obtained from ASTON Chemicals, Warsaw, Poland, with a diameter of 265 nm. Methylene chloride (CH₂Cl₂) (Sigma-Aldrich, product no. 34856), toluene (C₆H₅CH₃) (Sigma-Aldrich, product no. 320552), Potato Dextrose Agar (Sigma Aldrich, product no. 70139).

2.2. Blends Processing Methods

(1) PLA finishing layer, made by mixing methylene chloride (CH₂Cl₂) solution for PLA, 21% dry matter content, with SAR powder, 10% w/w, respectively, hereafter called “PLA/SAR” and with nano-ZnO particles, 2% and 4%, w/w, respectively, hereafter called “PLA/SAR nano 2%” and “PLA/SAR nano 4%”. Samples with the addition of nano-ZnO but without SAR are hereafter called “PLA nano 2%” and “PLA nano 4%”. A pure PLA surface finishing layer has also been tested (hereafter called “PLA”) as a reference. All the prepared blends have been spread on Polytetrafluoroethylene (PTFE) sheets under a fume hood in order to evaporate the solvent, and then milled to attain a powder size smaller than 0.1 mm. Such a powder has been formed in a hot press (as mentioned above), as described by Gumowska et al. [44]. The prepared film has been pressed in a hot press (pressing time 75 s, temperature 185 °C, and pressure 0.8 MPa) onto the unfinished particleboard surface described above.

(2) PCL finishing layer, obtained by toluene (C₆H₅CH₃) solution for PCL, 25% dry matter content. The remaining steps of surface finishing preparation are the same as those described above for PLA. Using this method, the subsequent samples have been attained: PCL (hereafter called “PCL”; no SAR/nano-ZnO addition, reference sample) “PCL/SAR”, “PCL/SAR nano 2%”, “PCL/SAR nano 4%”, “PCL nano 2%”, “PCL nano 4%”.

According to the research plan, the surface finishing layers created on the particleboard base were exposed to ambient conditions (20 °C; 65% R.H.) until a constant weight was achieved over a span of seven days before tests. All the variants and their composition have been presented in Table 1.

From each variant, one sample has been grinded and pressed on the surface twice, to investigate the effect of repeated processing on the relative hardness.

Table 1. The composition of tested surface finishing layers.

Variant label	Matrix	SAR filler content (w/w of dry matter)	Nano ZnO content (w/w of dry matter)
PLA	PLA	0	0
PLA nano 2%		0	2
PLA nano 4%		0	4
PLA/SAR		10	0
PLA/SAR nano 2%		10	2
PLA/SAR nano 4%		10	4
PCL	PCL	0	0
PCL nano 2%		0	2
PCL nano 4%		0	4
PCL/SAR		10	0
PCL/SAR nano 2%		10	2
PCL/SAR nano 4%		10	4

2.3. Relative Hardness

Relative hardness was measured according to the procedure described in the ISO 1522 standard [45]. As many as 2 repetitions per tested sample type were performed.

2.4. Cold Liquids Resistance

Cold liquid resistance was measured according to the procedure described in the EN 12720+A1 standard [46]. As many as 2 repetitions per tested sample type were performed. The following cold liquids were employed: acetone, citric acid, ethanol, and distilled water. The exposition time equaled 24 hours.

2.5. Total VOC and Formaldehyde Emission

The Total VOC and formaldehyde emission tests were completed in the emission test chamber at a temperature of 23 °C $\pm$ 0.5 °C and relative air humidity of 44% $\pm$ 1%. Other parameters of sample conditioning were performed following the EN 717-1 standard [47]. The TVOC and formaldehyde emission tests were carried out after 24 h of conditioning of the samples by analyzing the chamber air over three repetitions after 20 min each using a JD-3002 Air Quality Tester (Dongguan Jinlide Electronic Technology Co., Ltd., Dongguan City, Guangdong Province, China). We adhered to the standards regarding air conditioning conditions for samples during the emission test.

2.6. Antifungal Test

In the antifungal study, the disc diffusion method was employed to assess the growth inhibition of the materials on specific mold fungi. A 90 mm Petri dish containing Potato Dextrose Agar was centrally inoculated with a 100 μ L spore suspension of two common Molds species, namely *Aspergillus niger* and *Cladosporium cladosporioides*. The spores were evenly spread using a sterile plastic spreader. Subsequently, one test disc of each type of test material was placed in the center of the plate and three replicas of each material were employed for each mold species. The plates were incubated in a growth chamber in the dark under a control temperature of 25°C. After 10 days of incubation, the growth of fungi was visually evaluated using a Keyence VHX-6000 digital microscope (Keyence, Osaka, Japan). The growth of mold was assessed based on the percentage of mold coverage on the surface. To ensure uniform evaluation of the test, the following six-grade assessment scheme was applied in this experiment:

- Grade 0 = no infestation of the surface.
- Grade 1 = 1–20% infestation of the surface.
- Grade 2 = 21–40% infestation of the surface.
- Grade 3 = 1–60% infestation of the surface.
- Grade 4 = 61–80% infestation of the surface.
- Grade 5 = 81–100% infestation of the surface.

2.7. The Effect of Repeated Processing of Polymer Blends on Their Hardness

The samples have been pressed onto the board surface, as described in 2.1. and then subsequently recovered from the surfaces by scratching off. Then, recovered blends were ground and pressed onto the surfaces again. One sample of each type has been processed this way, and then the relative hardness has been examined as described in 2.2.

2.8. Statistical Analysis

Analysis of variance (ANOVA) and t-test calculations were used to verify significant differences ($\alpha = 0.05$) between factors and levels where appropriate, using the RStudio software (R Foundation, Vienna, Austria).

3. Results and Discussion

3.1. Cold Liquids Resistance

The cold liquids resistance evaluation results of the tested surface finishing layers have been presented in Table 2. When it comes to pure PLA, only in the case of citric acid and distilled water was there slight cloudiness found. There was no significant influence of the addition of SAR to PLA regarding the resistance to cold liquids. The pure PCL layer has been more resistant when referred to PLA. No changes in the surface have been found. The addition of SAR to PCL did not significantly lead to lowering of the resistance of the tested blends. Only in case of PCL/SAR nano 4% sample there has been slight change observed when affected by ethanol. To compare the results with the

commercial coatings, let us regard waterborne coatings (acrylate-based and polyurethane-based). Pavlic *et al.* [48] found out that the best resistance to cold liquids was performed in the case of exposure to water and citric acid, while the fastest changes were observed after acetone application. The coatings that were acrylic-based performed better resistance compared to the polyurethane-based ones. It was also stated by Lis *et al.* [49] that most of the agents had caused no changes on waterborne UV acrylic coatings even after 24 h. Only the ethyl alcohol showed negative impact on evaluated surfaces, causing slight changes.

Table 2. Resistance to cold liquids performed by the tested finishing layers.

Variant label	Acetone	Citric acid	Ethanol	Distilled water
mg m ⁻³				
PLA	A*	B	A	B
PLA nano 2%	B	C	C	B
PLA nano 4%	C	C	B	A
PLA/SAR	B	B	A	A
PLA/SAR nano 2%	C	C	B	C
PLA/SAR nano 4%	B	B	C	C
PCL	A	A	A	A
PCL nano 2%	A	A	A	A
PCL nano 4%	A	A	B	A
PCL/SAR	A	A	A	A
PCL/SAR nano 2%	A	A	A	A
PCL/SAR nano 4%	A	A	A	A

3.2. Total VOC and Formaldehyde Emission

Table 3 shows the results of testing the emission of free formaldehyde (HCHO) and (VOCs) in samples covered with coatings on both sides. A particleboard not covered with any coating was used as a control sample (REF). There has been a significant reduction of TVOC and HCHO emission when the investigated surface finishing layers have been applied. The addition of SAR reduces the revealed emissions. However, the lowest emissions values have been obtained for the samples with nano-ZnO incorporated with the PCL nano 2% and 4% performing the strongest gas barrier properties. The polymer matrix was the only significant factor in this test. The mentioned reduction of TVOC and formaldehyde emission from particleboard covered with different surface finishing layers can be an effect of the scavenger nature of lignin, which is the main component (over 21 wt%) of SAR. The SAR-containing surface finishing layers act as a bi-functional barrier layer, which can avoid the gas transfer from the core of the composite to the environment, as well as can fix the formaldehyde and other emitted compounds in the finishing layer structure [50]. According to [51] and [52], the blends of PLA, as well as PCL can be recognized as extremely promising for the development of bio-based and biodegradable polymeric materials with low oxygen permeation, that is, for the development of suitable alternatives to conventional and highly pollutant oil-based plastics. It can be concluded, that the tested surface finishing materials, based on biopolymers with SAR incorporation, have promising features regarding the gas barrier layer on wood-based material surfaces. It is moreover notable, that nanoparticles exhibit great advantages since they can reduce formaldehyde emissions through indirectly increasing the curing degree of the resins, thus resulting in improved hydrolytic stability, due to the increased chemical bonds of the resin components with free formaldehyde. Furthermore, the reaction of hydroxyl groups that occur on the nanomaterial surface with free formaldehyde, and such coatings are able to perform barrier properties or “shielding effect” [53]. As [54] found out, the application of 8% zinc results a reduction in formaldehyde emission by an average of 44%.

Table 3. The TVOC and HCHO emissions of the tested finishing layers.

Variant label	TVOC	HCHO
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	mg m ⁻³	
REF	0.245	0.044
PLA	0.220	0.039
PLA nano 2%	0.172	0.030
PLA nano 4%	0.179	0.031
PLA/SAR	0.222	0.041
PLA/SAR nano 2%	0.218	0.039
PLA/SAR nano 4%	0.216	0.040
PCL	0.264	0.045
PCL nano 2%	0.068	0.012
PCL nano 4%	0.065	0.012
PCL/SAR	0.080	0.014
PCL/SAR nano 2%	0.078	0.013
PCL/SAR nano 4%	0.077	0.016

2.3. Relative Hardness

The figure 1. shows the results of testing the relative hardness of the produced coatings. In coatings made on a PLA matrix, the sample made of pure polymer without additives (0.52) showed the highest hardness. For the sample with a 2% addition of nano-ZnO, a decrease in hardness to 0.43 was observed, while when the share of nanoparticles was increased, there was a slight increase in hardness (0.45). PLA-based samples containing SAR showed significantly lower hardness, 0.33, 0.30 and 0.33 for the PLA/SAR variants, PLA/SAR nano 2% and PLA/SAR nano 4%, respectively. As for the samples produced on the basis of the PCL matrix, the pure polymer showed a hardness of 0.42. The nano-ZnO tax resulted in an increase in hardness to 0.45 and 0.47, respectively. For the PCL/SAR sample, a decrease in hardness to 0.39 was observed, while for the PCL/SAR nano 2% and PCL/SAR nano 4% variants, an increase in hardness to 0.50 and 0.48 was observed, respectively. Statistical analysis showed that in the case of the tested samples, statistically significant differences were related to the addition of SAR, the type of matrix, as well as the interaction between the matrix and SAR. The addition of nanoparticles did not have a statistically significant impact on the obtained results.

Previous research conducted by Ježo and Kowaluk [16] on PLA and PCL blends with SAR showed that the addition of 20% and 50% SAR causes an increase in hardness. However, [55] stated in their study that the mechanical properties of PLA/IFR (intumescent flame retardant (IFR)-graphene oxide (GO)) blend when incorporated by nano-ZnO were diminished seriously, the tensile strength decreased by 67%, the impact strength decreased by 69% and the elongation at break was off by 70%. The authors explain their findings with nano-ZnO catalyzing PLA, which decomposed into small chains with low molecular and then was destroyed easily. Also [56] stated that addition of ZnO nanoparticles introduced an accelerated degradation of the PLA/PCL blends. Rheological results showed that with increasing nanoparticles, the elastic modulus and the complex viscosity decreased, which was correlated to the degradation and chain scission of polymeric chains induced by nano-ZnO. The mentioned references are applicable since an approximately linear correlation between the hardness and elastic modulus has been established [57]. Moreover, the tensile strength and the hardness of a material are highly correlated [58]. The large size of the nanoparticles could also have influenced the negative results. As shown by [59], big size and aggregates/agglomerates weaken the positive attributes of nanoparticles in nanocomposites. Small nanoparticles and thick interphase present high levels for the B parameter (interfacial parameter which shows the level of interfacial adhesion), tensile strength, interphase volume fraction, and an interphase parameter. [60] confirm that by decreasing the particle size from 300 nm to 10 nm, the SiO2 nanoparticles become drastically harder (~39×), stiffer (~15×), and tougher (>3.5×).

Since SAR showed statistical significance for the obtained results, the decrease in hardness of samples containing PCL and PLA can also be attributed to its addition. Because improved mechanical properties, including hardness, are known from the literature after adding natural fibers to polymers[16,54], the authors intend to take a closer look at the observed phenomenon and link it with

manufacturing parameters and further processing. The result for worsening of relative hardness by incorporation of SAR can be due to its alkaline form. It has been confirmed by [61], that alkali treatment can cause a depolymerization of polymers. Also [62] reported that at a lignin content of 10 wt%, heterogeneous morphology was observed, suggesting phase separation between PLA and alkali lignin. Similar observations were shown in PLA/kraft lignin blends with lignin concentrations higher than 10 wt% [63,64]. This heterogeneity might be an indication of weak mechanical properties of the investigated system at concentrations higher than 10 wt%.

Comparing the obtained results with different polymer matrixes, it is worth mentioning that by increasing nano-ZnO up to 0.3% in a polystyrene polymer matrix, there is a remarkable increment of approximately 47% in the hardness [65], while the hardness can be decreased by 5.73% when added into natural rubber [66]. Incorporation of ZnO–Ag hybrid nanoparticles into the acrylate epoxy matrix increases its pendulum hardness [67], while compared with neat polyurethane acrylate (PUA), the hardness in films increases from 0.03 to 0.05 GPa when ZnO in share of 5% is incorporated [68].

Degradation causes changes in mechanical properties, particularly when the molecular weight importantly decreases. Reinforcements could attenuate the loss in mechanical properties, depending on its structural integrity and the state of interfacial adhesion [69].

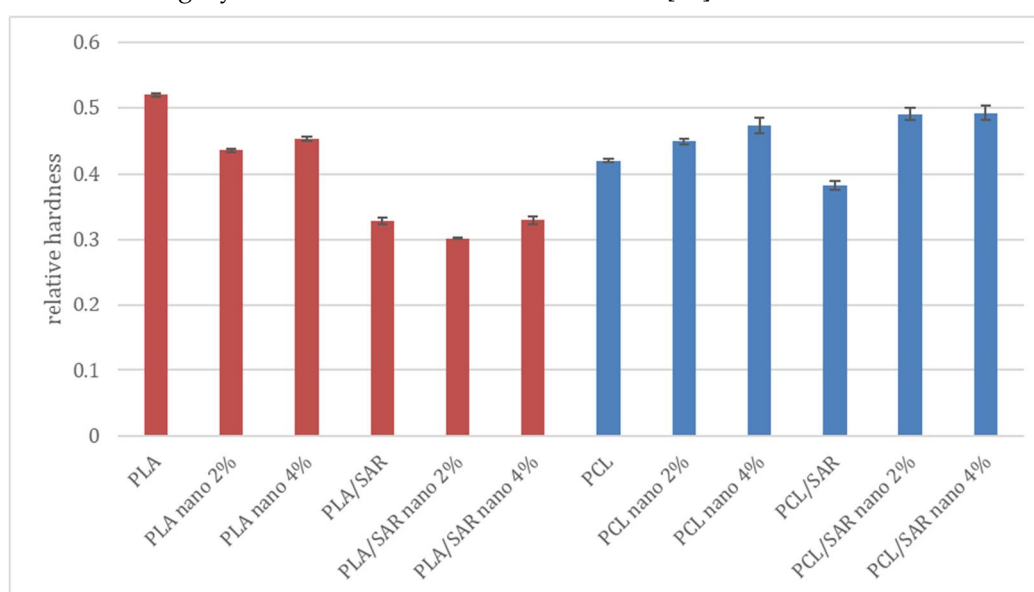


Figure 1. The results of the relative hardness of the examined coatings.

2.4. Antifungal Test

In the figure 2. the results of the antifungal tests have been illustrated, with demonstration of average mold grade values. In figures 3-6 the photos of the infected samples have been shown. In the case of samples containing PLA and additives, specifically PLA/SAR nano 2%, PLA/SAR nano 4%, and PLA nano 4%, a higher antifungal effect was observed, with no contact between the fungal spores and the material, in contrast to the PLA control. Additionally, PLA/SAR nano 2% and PLA/SAR nano 4% demonstrated an inhibition zone against *A. niger*, indicating their ability to prevent or impede fungal growth. Similar antifungal effects were observed in PLA samples against *C. cladosporioides*, with the highest activity in samples PLA/SAR nano 2%, PLA/SAR nano 4%, and PLA nano 4%. An exception was found in PLA/SAR samples, which proved to be the most susceptible to *A. niger* and *C. cladosporioides*. Conversely, samples containing PCL and additives generally exhibited better performance, particularly against *C. cladosporioides*, notably in samples PCL/SAR nano 4%, PCL nano 2%, and PCL nano 4%. However, even the PCL control showed some inhibitory effect against *C. cladosporioides*. In the case of *A. niger*, PCL samples displayed similar performance in PCL/SAR nano 2%, PCL/SAR nano 4%, and PCL nano 2%, where few spores were observed, unlike the control sample (PCL) and PCL/SAR, where the samples were colonized by *A. niger*.

As other studies confirm, the silane modified ZnO hybrid embedded Poly(methyl methacrylate) (PMMA) offer resistance against fungal growth when infected with *Aspergillus niger* and *Aspergillus*

flavus [70]. Nano-ZnO shows antifungal activity against *Aspergillus niger* with an MIC of 2.5 mg/mL. Thus nano-ZnO is twice as potent in killing *Aspergillus*, as compared to its non-nano-counterpart (micro ZnO) [71].

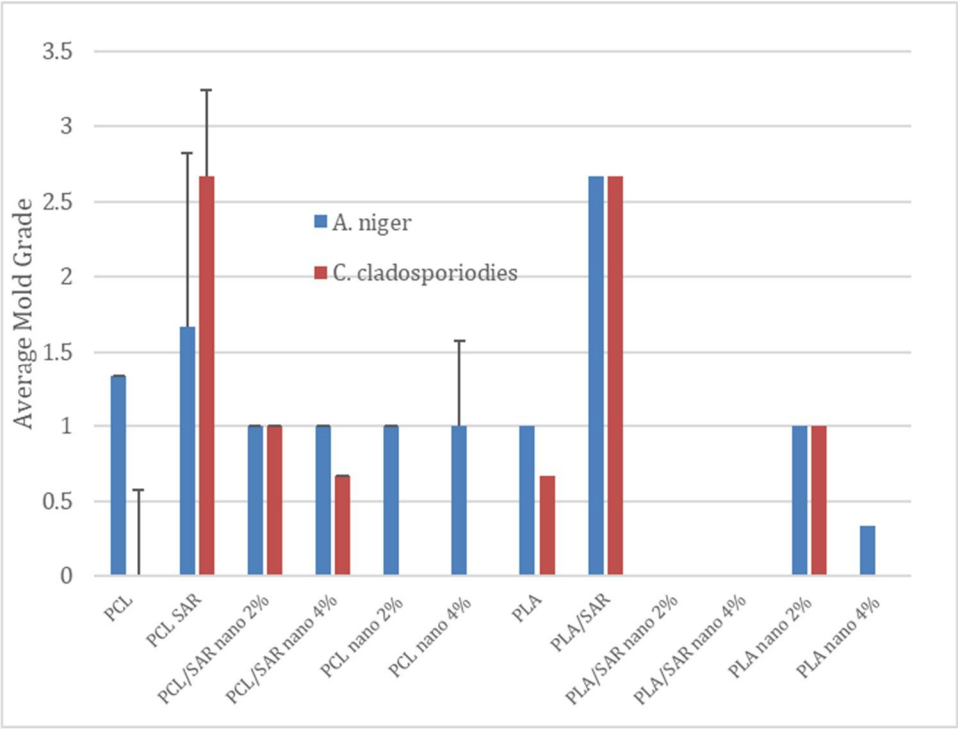


Figure 2. The average mold grade of the examined coatings exposed to *A. niger* and *C. cladosporioides*

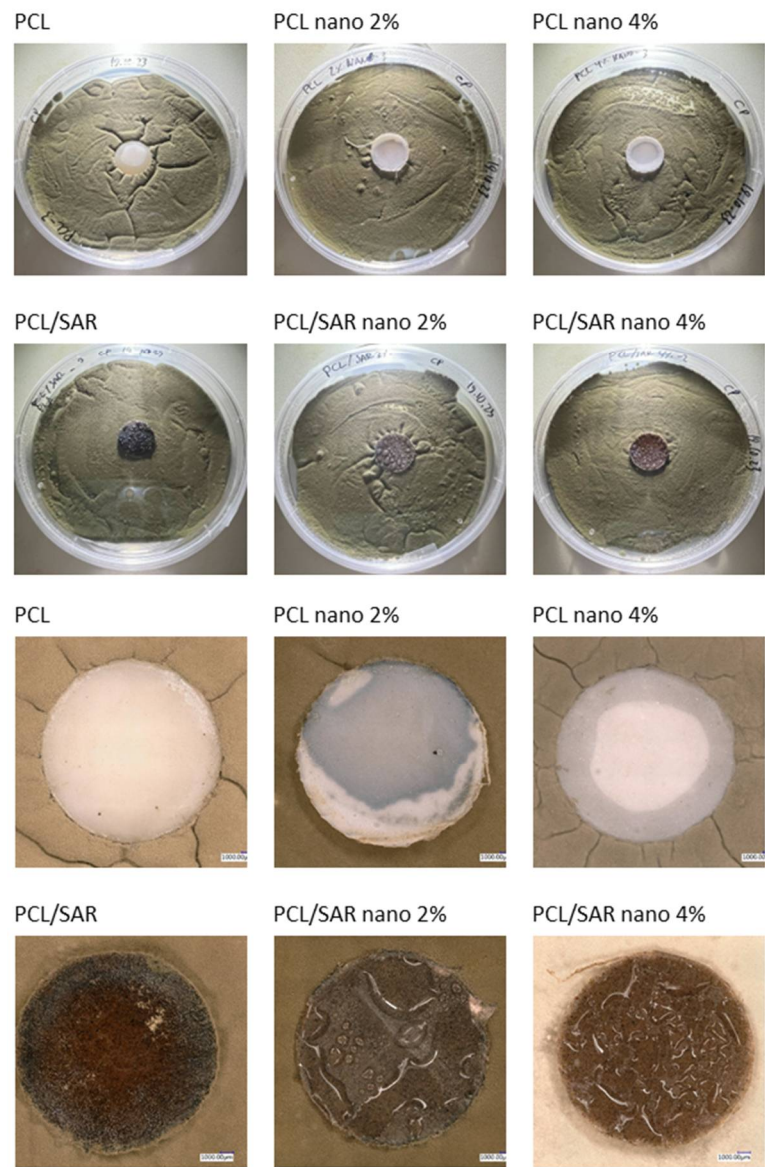


Figure 3. PCL tested with *Cladosporium cladosporioides*

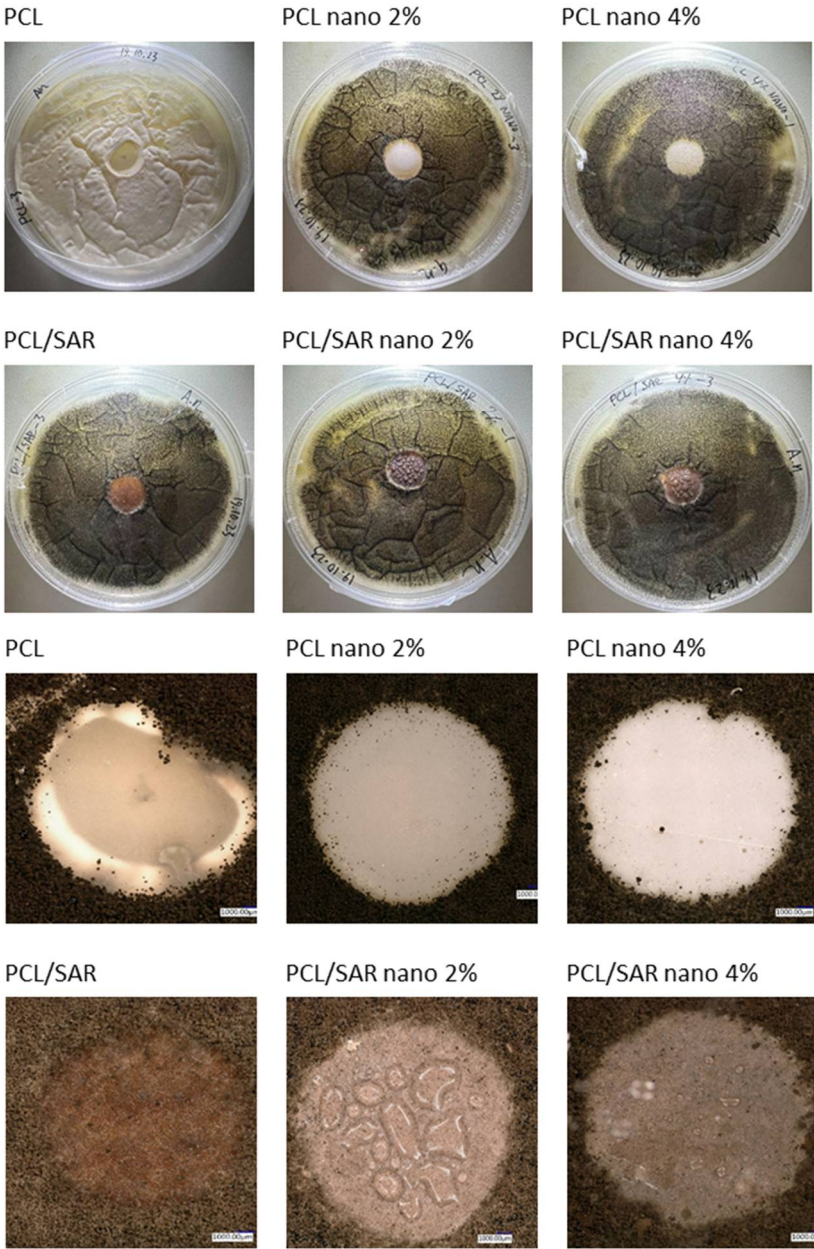


Figure 4. PCL tested with *Aspergillus niger*

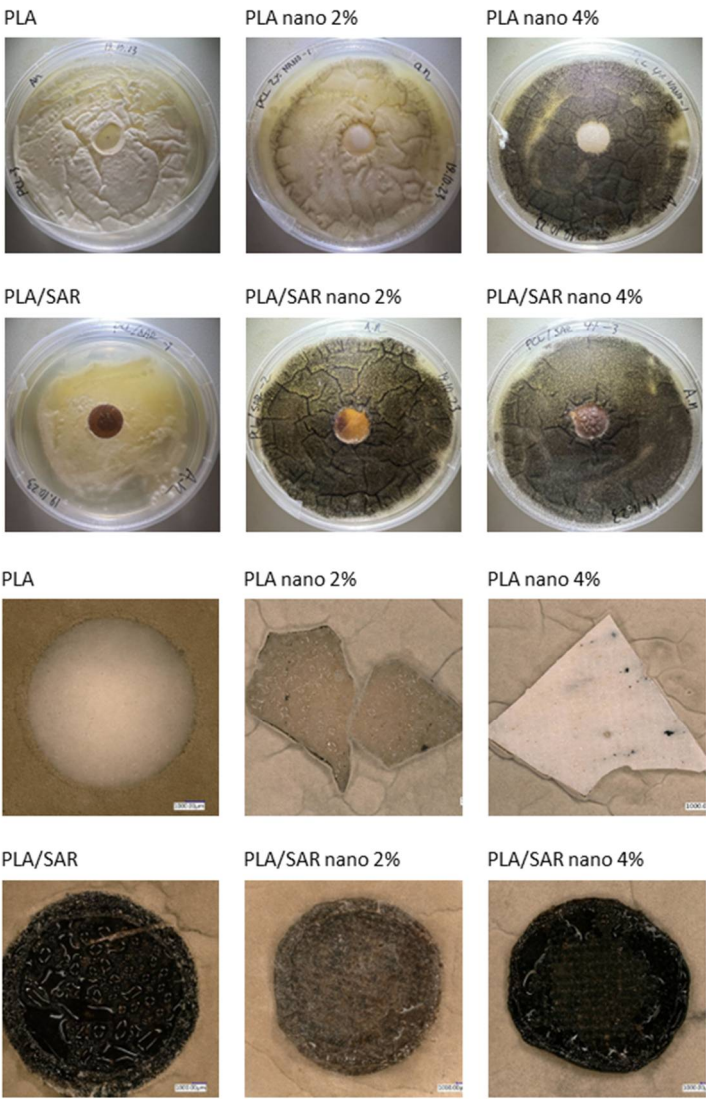


Figure 5. PLA tested with *Cladosporium cladosporioides*

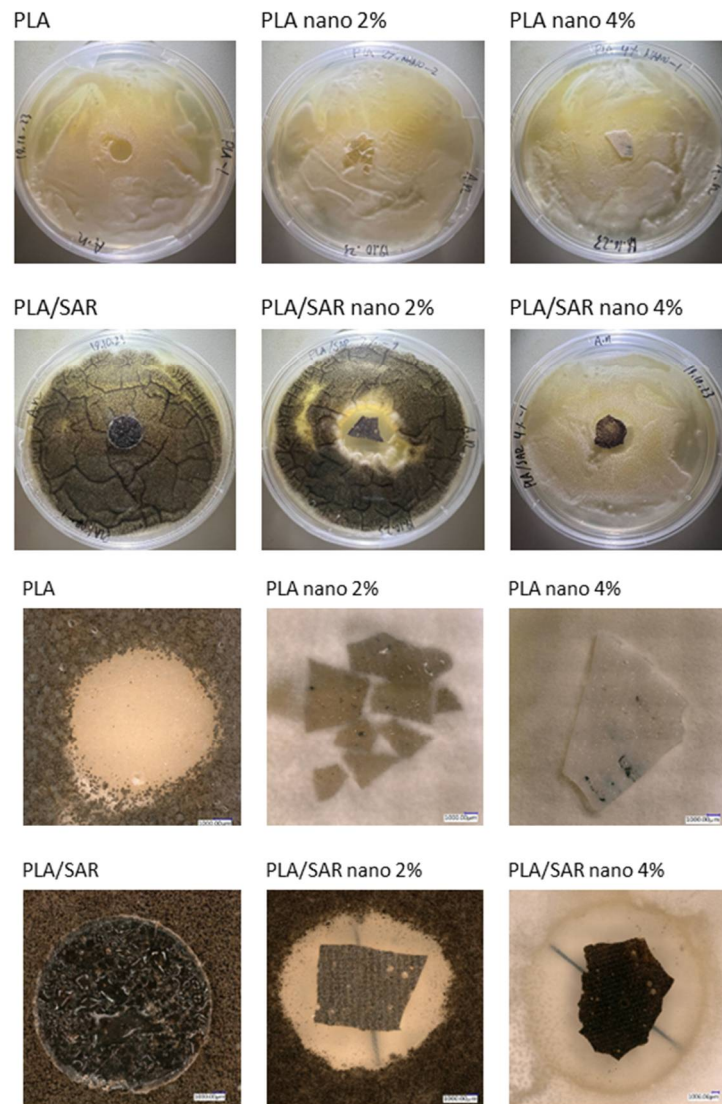


Figure 6. PLA tested with *Aspergillus niger*

2.5. Relative Hardness after Repeated Processing of the Samples

Figure 7 shows a comparison of the relative hardness of the tested coatings ground and pressed once and twice. A decrease in the value of the tested parameter can be noticed for samples whose coating was reprocessed after ironing. The decrease in hardness recorded for the samples is shown in the table. Greater differences were observed in the case of samples made on the basis of the PLA matrix than on the basis of the PCL matrix. As a result of the re-processing of PLA-based blends, the polymer degraded, which significantly affected its mechanical properties, an example being the loss of hardness. [72] report similar observations for PLA blends with starch, where the degradation of PLA was confirmed by SEM tests. The authors observed a decrease in the flexural modulus and impact strength values as a result of repeated processing of the blends. The degradation of PLA due to repeated processing is also confirmed by [73], who investigated the impact of repeated extrusion on the properties of PLA/HDPE and PLA/PC blends. As demonstrated by [74], mechanically recycled PLA has lower mechanical properties compared to virgin PLA, with impact strength and hardness decreasing by 50% and 4%, respectively.

Although the literature lacks examples of a decrease in hardness after regrinding for PCL, researchers have considered many other polymers - polyoxymethylene (POM) [75], thermoplastic polyurethane elastomers [76] or polypropylene [77] - which may confirm a similar trend for PCL as demonstrated in this study. However, there have been found polymers that increased their hardness after couple of cycles of processing, like high impact polystyrene [78].

Statistical analysis showed statistically significant differences between the values obtained for hardness after one and two processing, which confirms that repeated grinding and pressing of polymer blends statistically reduces their relative hardness. Moreover, the only factor that had a statistically significant impact on the percentage decrease in hardness after reprocessing was the type of polymer matrix.

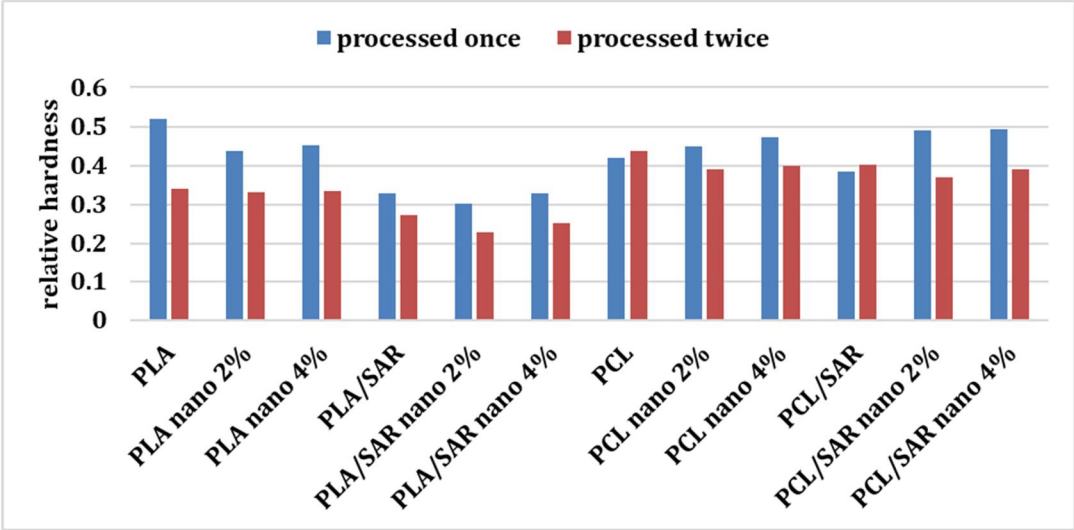


Figure 7. The relative hardness of the samples after one and after repeated processing.

Table 4. Percentage decrease of relative hardness of the examined samples after the second processing.

Variant label	Hardness decrease after the second pressing
PLA	34.60%
PLA nano 2%	23.72%
PLA nano 4%	26.14%
PLA/SAR	16.57%
PLA/SAR nano 2%	24.62%
PLA/SAR nano 4%	23.32%
PCL	-3.81%
PCL nano 2%	13.28%
PCL nano 4%	15.49%
PCL/SAR	-5.00%
PCL/SAR nano 2%	24.66%
PCL/SAR nano 4%	20.73%

5. Conclusions

The following study aimed to investigate some preliminary examinations on the surface finishing coatings containing suberinic acid residues (SAR) with nano zinc-oxide (nano-ZnO). The tests performed included: resistance to cold liquids, relative hardness, formaldehyde and VOC emissions as well as antifungal tests. The results revealed no worsening when exposed to cold liquids in the case of samples based on the PCL matrix with slight changes in some samples based on PLA polymer. The relative hardness tests showed a decrease in hardness regarding PLA-based samples when incorporated nanoparticles and PCL-based samples performed a decrease in hardness in case of SAR incorporation. This phenomenon needs to be further investigated, however, the authors

suggest that the reason of this worsening might have been the alkali character of the SAR incorporated. It has been concluded that the incorporation of SAR and nano-ZnO allowed to minimize both the emissions of free formaldehyde as well as TVOC. The investigated samples with fillers incorporated exhibited moreover good antimicrobial properties. Moreover, the impact of repeated processing on the relative hardness has been regarded, leading to an observation of a decrease in this parameter for both PLA and PCL. The authors see great potential in the findings obtained and the topic will be continuously investigated.

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