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Production of a Polylactic Acid-Based, Chitosan- and TiO_2-Modified Biodegradable Antimicrobial Coating Material and Investigation of Its Physical Properties

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ABSTRACT

Polymer wastes are increasingly threatening the environment. The industry is interested in the use of biodegradable coatings for sustainability and the environment. The aim of this study is to produce an antibacterial coating material based on polylactic acid (PLA) synthesized with chitosan (CS), and titanium dioxide (TiO_2). PLA and CS are biodegradable biopolymers. This study tests the surface properties of the coating using scanning electron microscopy, chemical reactions using ATR-FTIR, surface roughness, antimicrobial activity, air permeability, contact angle, and printing suitability of the coated paper in accordance with the standards. It has been shown that the coatings have antimicrobial activity against *Y. enterocolitica*, *S. aureus*, and *C. albicans* bacteria and reduce bacterial growth. SEM images show the dissolution of TiO_2 nanoparticles in the coatings and pilling in the mixtures with CS. Data obtained with ATR-FTIR confirm the chemical effects of PLA, TiO_2, and CS. PLA, and TiO_2 reduced the porosity on the paper surface. It was concluded that the mixtures formed with CS increased the wettability in contact with liquid and that PLA formed a good barrier property with TiO_2. The coating proved to be an environmentally friendly study with its printability properties on disposable food contact materials.

1 | Introduction

Plastics, which we use a lot in our daily life, are among the most widely used packaging materials in the world. The intensive use of plastics has led to a number of environmental problems such as excessive use of oil and microplastic pollution of marine and land systems [1]. Nonbiodegradable coatings used on paper cups and cardboard packaging are responsible for pollution of the soil, atmosphere, and marine systems, prompting governments to introduce plans to limit plastic use [2]. The increasing waste problem caused by the use of fossil-based coatings makes it necessary to find rational solutions for single-use products. Some companies, such as Starbucks, have recently started using alternative products to plastic by using straws made from disposable paper [3]. In the packaging and distribution sectors, its recyclability, dependence on renewable raw materials, and low cost have made paper a preferred material [4]. Due to its hydrophilic structure, the scope of its application in the packaging sector is restricted. Hence, these disposable packaging materials and utensils are laminated with petroleum-based coating in order to increase their hydrophobic properties. Therefore, creating paper-based biodegradable coatings that are nonpolluting and effective liquid-resistant is an environmentally friendly way to replace single-use plastics.

Within the concept of sustainability, the reduction of fossil-based materials and the development of biodegradable materials will eliminate the threat to nature. Biodegradable polymers already have a great impact in various areas. In this respect, the lower mechanical strength, thermomechanical properties, and high costs of biodegradable materials compared with petroleum-based materials limit their use. It is possible to overcome the limitations by

producing biodegradable polymer mixtures with desired properties by including a suitable compatibilizer during mixture preparation [5]. Polylactic acid (PLA) is a promising biodegradable plastic easily obtained from natural sources such as corn, cassava, sugar cane, or sugar beet pulp, upon condensation polymerization process [6, 7]. Blends prepared with chitosan (CS) can also ensure biodegradability and reduce the contact of the coated paper with water while maintaining its biorenewability [8]. Coatings made with CS not only enhance the antimicrobial and gas barrier properties required for food contact packaging but also improve water resistance [9]. One strategy to overcome these disadvantages is to combine CS with another biopolymer while ensuring that the disposable material is biocompostable. Among the many biodegradable materials being tested, PLA is a suitable material for use with CS. Studies have been conducted to develop blends of CS and PLA by improving the hydrophilicity and water-soluble nature of CS [10]. Nano-sized titanium dioxide (TiO_2) is a naturally occurring, oxidized form of titanium. TiO_2 can absorb ultraviolet radiation and also prevent the passage of radiation, thanks to its photocatalytic properties, to be antibacterial in coated materials [11]. TiO_2 nanoparticles exhibit hydrophilic properties in addition to their antimicrobial properties [12]. Many researchers have conducted research on PLA/TiO_2 nanocomposites and PLA/CS, mainly on their compostability, antibacterial activity, and mechanical properties [13, 14].

In this study, coating materials consisting of PLA, CS, and TiO_2 were prepared and applied to the paper surface as coating. Then, the air permeability and surface roughness of the paper coated with the prepared mixtures were determined by Lorentzen & Wettre (L&W). Additionally, water contact angles and surface energies were measured and compared to see the interaction of these materials with the liquid. The chemical structure of the coating material, surface morphology, and antibacterial activity results were examined. Considering the biodegradable nature of the coating materials and the food and beverage product contact, this production strategy can be seen as an environmental gain toward water-resistant coated paper.

2 | Materials and Methods

2.1 | Materials

PLA granules, obtained in a laboratory setting, were utilized in the fabrication of biofilms. The material is transparent, with a density of 1.24 g/cm^{-3}, a melt flow index of 6.0 g/10 min (2.16 kg and 210°C), a glass transition of ~55°C, and a melting temperature of ~150°C. CS (molecular weight Mn = 50,000–100,000 g/mol, the degree of deacetylation > 95%) was purchased from Nurbal natural food industry trade limited company. White color uncoated 80 g/m^2 paper was used in the study. It was purchased from UPM Turkey. All chemicals—chloroform ($CHCl_3$) and TiO_2 nanopowder, with particle sizes < 100 nm and 99.5% purity—were obtained from Merck.

2.2 | Preparation of PLA/CS/TiO_2 Coating Solutions

PLA pellets were dissolved with $CHCl_3$ at 600 rpm with a heated magnetic stirrer. The dissolution process was carried out with a magnetic stirrer for 1 h under laboratory conditions. The solutions containing 10 wt % PLA were weighed and added to the solution to form 1 wt %, 2 wt % TiO_2 solution by weight. The solutions containing 10 wt % PLA were weighed and added to the solution to form 5 wt %, 10 wt % CS solution by weight. Stirring was continued for at least 1 h after the addition of the post-added mixtures to the PLA solution. Different solutions were prepared while producing the coatings. These solutions are shown in Table 1.

White uncoated office papers were cut into 100 × 100 mm dimensions and placed on the coating table. The formulation was applied to the paper surface under laboratory conditions using a Mayer bar on a laboratory-type paper coating machine. The process was executed with Mayer stick no. 2, yielding a theoretical wet film deposit of 20 μm on the paper surface. The coating was permitted to dry for 1 min after the application of each layer. The coating bar was set to a speed of 2 m/min. The drying of the coated samples was carried out in a laboratory oven with air circulation at 105°C for 3 min. These steps were repeated between one and 10 times, with the objective of placing a layer of 0.1 g/m^2 on a surface of the obtained formulations on paper samples.

2.3 | Printability Properties of Coating Paper With PLA/CS/TiO_2

CIE *L*a*b** color values of biodegradable material coated and uncoated surfaces were determined using an X-Rite handheld spectrophotometer. Spectrophotometer D50 was used under light source conditions, in the spectral range of 400–700 nm, with 2° observers and 45° geometry. To calculate the color differences between the coatings, the CIE DE ΔE_{ab} Euclidean color difference Formula (1) ISO 11664-6:2014 was used. For an accurate calculation, measurements were made from five different areas of the coating. The *L* axis gives the brightness, the *a* axis the red–green area, and the *b* axis the yellow–blue area. ΔL^*, Δa^*, Δb^* are the differences between the initial and final color values.

$$\Delta E^*_{ab} = \sqrt{\left(L^*_2 - L^*_1\right)^2 + \left(a^*_2 - a^*_1\right)^2 + \left(b^*_2 - b^*_1\right)^2} \quad (1)$$

The surface gloss of the coated papers was measured with the BYK-Gardner gloss measuring device in ISO 8254-1 75° geometry.

Surface roughness value was determined according to TAPPI T555 om-99 using L&W pps roughness Tester (1000 kPa). Air

TABLE 1 | Paper coating formulations.

Solution no.	Solution parameters		
	PLA (%)	TiO_2 (%)	CS (%)
P10	10		
P10/T1	10	1	
P10/T2	10	2	
P10/C10	10		10
P10/T1/C10	10	1	10

Permeability value was determined according to Tappi T 460 om-88 using L&W Air Permeance Tester.

The measurements were performed with Pocket Goniometer Model PG-X. Surface energies were calculated from the contact angle using the ASTM D5946-17 standard test method. Distilled water was used as the standard for contact angle and surface energy measurements.

2.4 | Scanning Electron Microscopy

The morphological properties of film-coated papers containing control PLA, micro, and nano TiO_2, and CS were analyzed by field emission scanning electron microscopy (ZEISS EVO MA10). Before the analysis, the films were cut into small pieces and coated with gold to impart conductivity to the films. Surface images were obtained at 1000× magnification under low vacuum and at a voltage of 10 kV and working distances of 8–13 mm.

2.5 | ATR-FTIR Analysis

Film-coated papers containing control PLA, micro and nano TiO_2, and CS were further characterized with an ATR-FTIR spectrometer (model: JASCO FT/IR-4000). The measurements were conducted within the spectral range from 4000 to 400 cm^{-1}, with a total of 32 scans collected at a resolution of 4 cm^{-1}.

2.6 | Antimicrobial Testing of Coated Samples

TS EN ISO 20743 adapted in-house method was used to test the antibacterial activity of the paper samples. *Escherichia coli* (ATCC 25922), *Staphylococcus aureus* (NCTC-13552), *Yersinia enterocolitica* (ATCC 9610) bacteria, and *Candida albicans* (ATCC 10231) yeast were prepared in 1 mL of 5×10^6 CFU/mL, and 1 × 1 cm samples of paper samples were added. The 5×10^5 CFU/mL culture prepared without samples was used as a positive control. Eppendorf tubes containing the samples polymer were shaken at 150 rpm for 4 h. To remove microorganisms adhering to the surface of the samples, the tubes containing the samples and the tubes prepared as positive controls were kept in an ultrasonic water bath for 30 s and then vortexed. 100 µL suspension was transferred into 900 µL physiological saline (FTS) and 6 dilutions were made. Petri dishes containing Mueller–Hinton Agar (MHA) were divided into six, and 25 µL of each dilution was inoculated. After incubation at 37°C for 24 h, the antimicrobial activity value was counted as colonies forming units (CFU). The difference in growth between the positive control and polymer-treated culture was evaluated logarithmically.

3 | Results and Discussion

The measurement results of the coatings produced under the specified experimental conditions using the solutions in Table 1 and applied to the paper surface are shown in Figures 1 and 2.

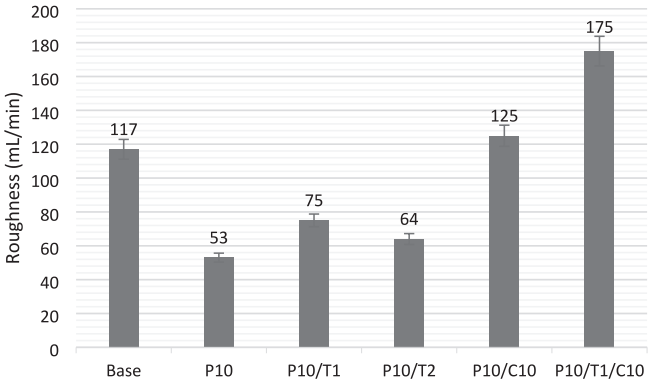


FIGURE 1 | Surface roughness results of coated paper samples.

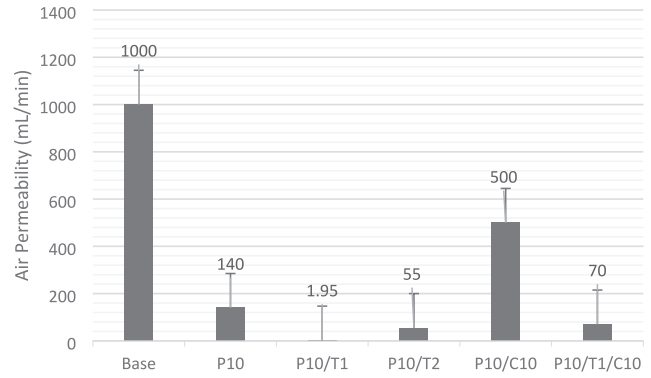


FIGURE 2 | Air permeability results of coated paper samples.

When the values in Figures 1 and 2 are examined, it is seen that the roughness and air permeability of the paper decreased only in P10, P10/T1, and P10/T2 samples. The coating reduced porosity by closing the pores on the surface of the paper, made the paper more compact, and increased printability by reducing the air permeability of the paper. CS used in samples P10/C10 and P10/T1/C10 did not reduce surface roughness and air permeability. This is because the CS added during the preparation of the mixture did not dissolve well. The data obtained are consistent with previous studies [15].

SEM images of the base paper and the 100% PLA (10% PLA) coated paper sample (Figure 3a,b) clearly support the air permeability and surface roughness results, along with the contact angle data. The SEM image clearly shows that the PLA coating forms a good surface on the paper and reduces the surface roughness [16]. The image of the high porosity structure of the paper is shown by SEM (Figure 3a). In the other image, the porosity of the paper coated with PLA was significantly reduced (Figure 3b). The SEM images of Figure 3c,d show that TiO_2 is homogeneously dispersed and does not cause pilling on the fibers. It is important that TiO_2 is homogeneously dispersed with PLA and provides the desired fiber formation. SEM images of Figure 3d,e show that CS does not provide the desired homogeneous fiber formation and causes pilling. These results coincide with the results of air permeability and surface roughness.

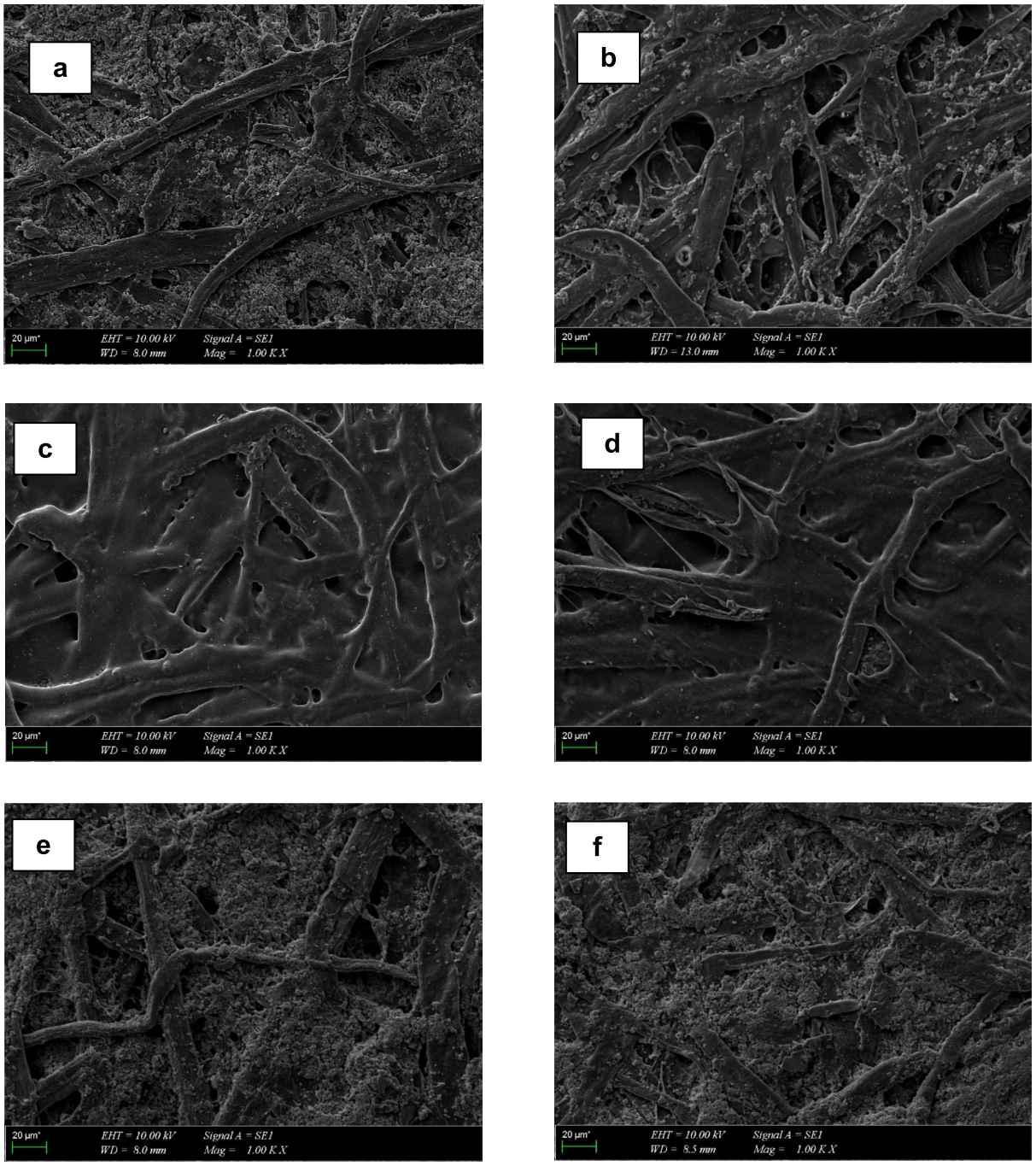


FIGURE 3 | Scanning electron microscopy images of (a) base paper (b) 10% PLA-coated paper (c) 10% PLA-1% TiO_2 coated paper (d) 10% PLA-2% TiO_2 coated paper (e) 10% PLA-%10 CS coated paper (f) 10% PLA-10% CS-1% TiO_2 coated paper, respectively. [Color figure can be viewed at wileyonlinelibrary.com]

Untreated paper was used to understand the color differences that the coating applied onto the paper. Looking at the color values between the coatings, it was determined that the P10, P10/T1, P10/T2, P10/C10, and P10/T1/C10 coatings shifted the color to a small amount of blue (−*b* value) compared with the base paper (Table 2). The color change (ΔE_{ab}) range is about 1.32–2.46, and it is well accepted that $\Delta E_{ab} \leq 1$ is unable to be distinguished by the human eye [17]. The minimum ΔE_{ab} value to be perceived by an untrained or inexperienced observer is approximately 2 [18, 19]. $\Delta E_{00} \geq 3$ is considered significant for industrial applications [17].

The results of the gloss measurement of biodegradable coatings are given in Table 2. The print gloss was higher in coated papers than in uncoated papers. High-print gloss values were obtained in papers coated with PLA and TiO_2 mixtures. In coatings using CS, gloss decreased compared to other coatings. It was seen as a result of the data that all applied coatings were at least two times brighter in terms of gloss value compared with the base paper. The smoothness created by the coating on the surface caused the gloss value to be higher. In particular, the prevention of diffuse reflection on the surface was effective. These results are consistent with the literature.

TABLE 2 | CIE $L^*a^*b^*$ and ΔE_{ab} color and gloss values of surface treatments according to ISO 8254-1.

Process	L^*	a^*	b^*	ΔE_{ab}	Gloss (75°)
Base paper	94.73	2.56	−12.41	Ref.	4.5
P10	93.86	2.97	−14.16	1.99	6.84
P10/T1	93.91	2.74	−13.44	1.32	8.46
P10/T2	93.59	2.9	−14.09	2.05	7.5
P10/C10	94.31	2.88	−13.62	1.32	5.16
P10/T1/C10	93.56	3	−14.54	2.46	7.56

The results of the study showed (Table 3) that samples P10 and P10/T1 of the biodegradable coatings had antimicrobial activity on *Y. enterocolitica* bacteria and reduced the growth of the bacteria by $\log_3$ from 10^6 to 10^3, sample P10/C10 reduced the growth of the bacteria by $\log_2$ up to 10^4. Sample P10/C10 reduced the growth of *S. aureus* bacteria by $\log_2$ up to 10^4. Sample P10 had antimicrobial effect on all test microorganisms; *S. aureus* up to 10^4, that is, by $\log_2$. Sample number P10/T1/C10 had antimicrobial effect on all test microorganisms. Sample number P10/T1 reduced the growth of *C. albicans* yeast up to 10^4, that is, by $\log_2$. As seen in the results, no activity against *E. coli* bacteria was found in all coatings.

Contact angle and surface energy measurements were performed to show the interaction of the paper with water. As seen in the results, the contact angle for PLA coated paper increased compared with the base paper (Figure 4). It shows that there is an increase in the contact angle of PLA coatings with TiO_2 compared with the coatings using CS. The obtained data again complement the results obtained from air permeability and SEM analysis. As the pores in the base paper are filled by the coating, there are no pores left on the paper surface. This leads to an increase in the surface smoothness and therefore the contact angle values decrease and increase with different coating concentrations. In particular, PLA can be considered a moderately hydrophobic material as it is insoluble in water and has a surface contact angle with water of 74.5°–85°.

Mixtures were prepared using PLA, CS, and TiO_2 in different ratios and coated on the paper surface. The chemical structure analyses of the coated papers were explained with ATR-FTIR results. Figure 5 shows the ATR-FTIR spectra of the base paper, P10, P10/T1, P10/T2, P10/C10, and P10/T1/C10. Shown in Figure 5 is the ATR-FTIR spectrum of the untreated paper. When the spectrum is examined, O—H stretching at 3335 cm^{-1}, stretching of C—H vibration at 2898 cm^{-1}, ring stretching at 1161 cm^{-1}, and C—O peak at 1030 cm^{-1} are observed in the untreated paper belonging to cellulose. The data obtained are consistent with previous studies [20].

According to FTIR analysis results examined, the broad peak at 3273 cm^{-1} belongs to O—H stretching, C—C and C—O stretching peaks at 1416 and 1151 cm^{-1} were observed [21]. The absorption peak at 2932 cm^{-1} belongs to C—H stretching. The increase in the absorbance value from 500 to 900 cm^{-1} indicates that TiO_2 enters the polymer matrix. These peaks are due to Ti—O and O—Ti—O bond vibrations. The results are consistent with the literature [22].

TABLE 3 | Antimicrobial activity of different coated papers against *E. coli* and *S. aureus*, *Y. enterocolitica*, and *C. albicans* (TS EN ISO 20743 adaptation in house method).

Bacteria	Control	P10	Log_{10}— reduction	P10/T1	Log_{10}— reduction	P10/T2	Log_{10}— reduction	P10/C10	Log_{10}— reduction	P10/T1/C10	Log_{10}— reduction
E. coli	5×10^6	5×10^6	0	5×10^6	6.69	5×10^6	0	5×10^6	0	5×10^6	0
S. aureus	5×10^6	2.8×10^5	1.25	2.4×10^5	1.31	1.2×10^5	1.61	1.2×10^5	1.61	2.4×10^4	2.31
Y. enterocolitica	5×10^6	7.2×10^3	2.81	4.0×10^3	3.09	4.4×10^3	3.05	2.2×10^4	2.35	5×10^6	0
C. albicans	5×10^6	5×10^6	0	8.8×10^4	1.75	2.4×10^5	1.31	5×10^6	0	2.0×10^5	1.39

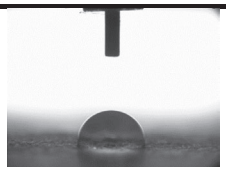
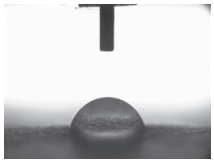
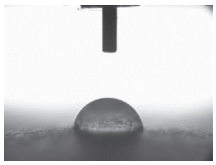
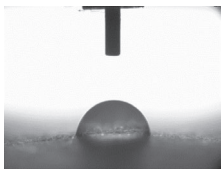
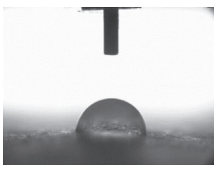
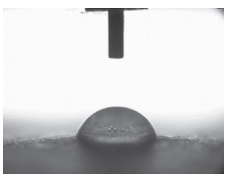
Process	Contact angle	Surface energy(mL/m^2)	Contact angle images
Base Paper	69.8	39.8	
P10	74.5	38.1	
P10/T1	75.7	37.7	
P10/T2	84.3	34.6	
P10/C10	82.8	35.1	
P10/T1/C10	75.5	37.7	

FIGURE 4 | Surface energy and contact angle values of different paper coatings.

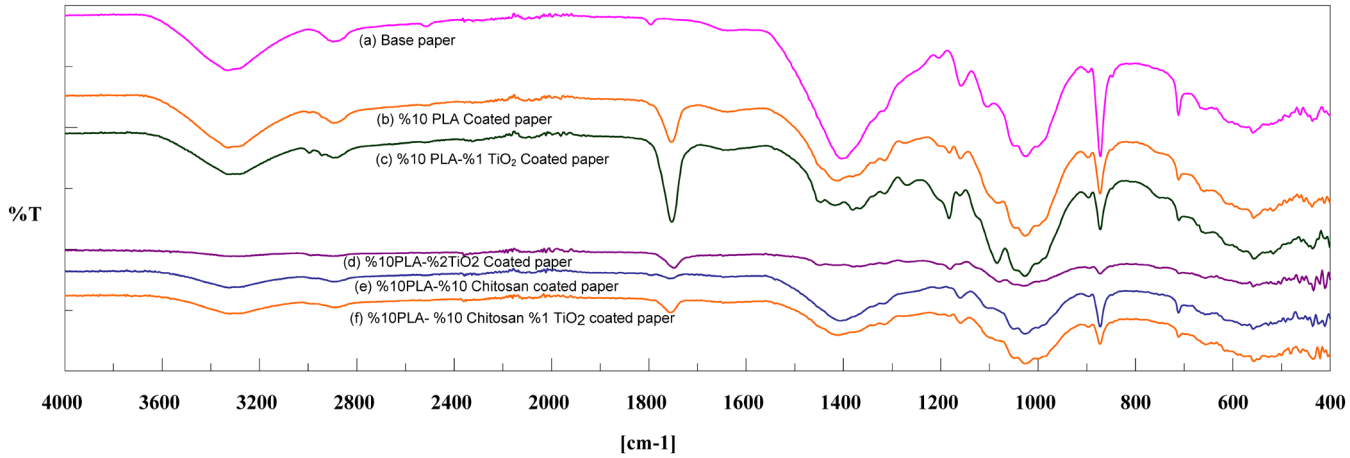


FIGURE 5 | ATR-FTIR spectra of (a) base paper, (b) 10% PLA-coated paper, (c) 10% PLA-1% TiO_2 coated paper, (d) 10% PLA-2% TiO_2 coated paper, (e) 10% PLA-10% CS coated paper, and (f) 10% PLA-10%CS 1% TiO_2 coated paper, respectively. [Color figure can be viewed at wileyonlinelibrary.com]

When the FTIR results of the coatings containing PLA are examined, it can be said that the peaks in the 3000–2900 cm^{-1} band range are due to the C—H stretching of the methyl group and the O—H stretching of the carboxylic acid [23]. The peak at 1758 cm^{-1} originating from the C—O stretching of the carbonyl group is seen. The other characteristic appearance of PLA is between 1454 and 1370 cm^{-1}; the first one was due to the asymmetric deformation of the $—CH_3CH$ stretching, and the second one was due to the symmetric deformation of the $—CH_3CH$ stretching. The stretching band formed by C—O is seen in the 1200–1000 cm^{-1} range. It is in accordance with the literature that these four peaks belong to the characteristic appearance of PLA [24–26].

When the FTIR spectrum of the CS film is examined, it shows peaks belonging to strong O—H and N—H stretching at 3353–3295 cm^{-1} (Figure 5). In addition, the vibrations occurring in the range of 2921–2867 cm^{-1} are attributed to symmetric CH_3 stretching and asymmetric CH_2 stretching. Again, the peaks at 1650 and 1587 cm^{-1} are the peaks showing the stretching vibrations of the characteristic carbonyl groups of CS (νC═O amide I) and the bending vibrations of the amino groups at the C2 position of glucosamine (νNH2 amide II) [27, 28]. The peaks observed at 1313 cm^{-1} are attributed to the amide III band. The peaks observed at 1375 cm^{-1} are attributed to the symmetric CH_3 deformation. The strong absorption region at 1150 and 1019 cm^{-1} is due to the saccharide structure of CS. Similar peaks were observed by groups working on CS [29].

4 | Conclusions

In this study, PLA was successfully synthesized with TiO_2 and CS as antibacterial agents for a biodegradable paper coating material that will not pose a threat to the environment. Air permeability and surface roughness of the coated paper decreased, and printability increased. This result coincides with the result that the contact angle and surface energy increased with the coatings. There is a difference in the coatings that cannot be distinguished with the naked eye. Only in the coatings with TiO_2, the gloss was higher. In the coatings made with CS, properties such as contact angle and gloss were lower, which is due to the hydrophilic properties of CS. The chemical structures of the papers coated with biodegradable materials were analyzed by ATR-FTIR. When the FTIR analysis results were examined, no unusual difference was found in all experimental results. When the antimicrobial activity was examined, it was found to be effective against both gram-positive/negative bacteria in the test results performed according to TS EN ISO 20743 standards. Together with the antibacterial agents successfully synthesized into the coating made with PLA, it constitutes a good packaging material alternative. It is an alternative solution to petrochemical-based, nonbio-based products due to its water resistance, printability, and most important feature of being a biodegradable material.

Author Contributions

Serat Kotan: data curation (equal), formal analysis (equal), writing – original draft (lead). **Doğan Tutak:** data curation (equal), formal analysis (equal), methodology (lead), writing – review and editing (lead).

Ethics Statement

The authors have nothing to report.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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