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Chitosan-titanium nanoparticle coated papers for active packaging

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ABSTRACT

In this study, it was aimed to increase the antimicrobial properties by combining chitosan and titanium nanoparticles. First, titanium nanoparticles were synthesized by sol-gel method and nanoparticles were modified with thiol groups. The chitosan has been modified with allyl glycidyl ether. Both obtained molecules were linked to each other by a thiol-ene click reaction. The chemical structure of the obtained chitosan modified titanium nanoparticles was elucidated by ATR-FTIR. Paper coating formulations were prepared by using the produced nanoparticles and hydroxy ethyl cellulose at different rates and applied on the base paper. Color, gloss, surface energy, contact angle, air permeability properties of the papers were determined by spectrophotometer, glossmeter, goniometer and L&W air permeability device, respectively. Screen prints were made on coated papers and their printability properties were examined. Antimicrobial properties of titanium nanoparticles, chitosan and chitosan modified titanium nanoparticles were determined against *E. coli* and *S. aureus* by disk diffusion method. As a result, it has been determined that both titanium and chitosan have antimicrobial properties against both bacterial species separately and the produced chitosan modified titanium nanoparticles increase this antimicrobial property more having a synergetic effect. It has been concluded that the produced antimicrobial papers have a high upside to be active packaging printing material.

1. Introduction

In recent years, the increase in mindshare and epidemic diseases has made the use of new systems in food packaging important. With the increase in environmental awareness, the functionality of the packaging will also increase, and this indicates an innovative packaging approach (Glaser et al., 2019). Unfortunately, hydrocarbons and their derivatives, which are frequently used in packaging production, remain as waste for many years, and even worse, the harmful wastes they leave in the environment enter the organism through water and soil over time (Taussarova et al., 2019). Nevertheless, research & developments activities in the food and packaging industry have been directed to studies on environmentally friendly, biodegradable, and shelf-life-enhancing packaging materials (Mangaraj et al., 2019; Grujić et al., 2017). In general, starting with the processing of food packaging, it is exposed to artificial or real daylight during packaging, storage, and transportation and even marketing processes, resulting in losses from shelf life and therefore product quality.

The concept of active packaging means to the state of interacting with the product, packaging, and environment to monitor the food product and better protect its quality. However, increasing environmental concerns about petroleum-derived materials, which are commonly used in the packaging industry, have increased the search for biocompatible materials (Kaewklin et al., 2018).

Today, the process of adding materials that will add antimicrobial and antioxidant activity to the packaging has become widespread to provide better protection against microbiological risks. However, the additional processes applied to the packaging should not disrupt the basic functions of the packaging material. This is where nanotechnology comes into play. Today, thanks to nanomaterials, it is possible to design multifunctional packages at the point of shelf life, product protection and monitoring (Enescu et al., 2019; Huang et al., 2018; Youssef and El-Sayed, 2018; Garcia et al., 2018; Bajpai et al., 2018; Ananda et al., 2017). Recently, some nanomaterials including carbon nanotubes (CNTs), TiO_2 NPs and silver NPs have extensive applications in various fields thanks to their antibacterial properties and many other properties (Moreno et al., 2019a; Hu et al., 2010). For example, TiO_2 NPs are bright and highly useful with a high refractive index of 2.4 for the pharmaceutical, toothpaste, coating, ink, plastic, paper, food products, textile, and cosmetics industries (Waghmode et al., 2019; Moreno et al., 2019b).

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The use of different type of NPs in paper production is becoming widespread to gain antimicrobial or antioxidant properties (Wu et al., 2018; Samyn et al., 2018). TiO_2, an inexpensive and non-toxic ingredient, is commonly used in medical industry as biocompatible and antibacterial coatings, to make safe gas sensors and to produce sunscreens against UV radiation (Goudarzi and Shahabi-Ghahfarrokhi, 2018). Environmental compatibility, non-toxicity and low cost are some of the advantages of TiO_2. Investigations are carried out to develop packaging materials with antibacterial properties and modified TiO_2 NPs (Krehula et al., 2017; Li et al., 2017). Most recently, safer foods emerging with biodegradable and recyclable packaging, as well as environmental problems caused by chemicals have been taken into consideration. Chitosan (Liu et al., 2020), alginate (Aristizabal-Gil et al., 2019), cellulose (Tirtashi et al., 2019), pectin (da Silva et al., 2018), starch (Engel et al., 2019), xanthine and gellan gum (Rukmanikrishnan et al., 2020), carrageenan (Huang et al., 2020), kefiran (Shahabi-Ghahfarrokhi and Babaei-Ghazvini, 2019) and agar (Sousa and Goncalves, 2015) are active used in the food packaging systems.

Chitin is a type of polycarbohydrate found in abundance on earth, which is used to produce chitosan by deacetylation (Muzzarelli et al., 2012). Biodegradability, non-toxicity, antibacterial activity, ease of manipulation, biocompatibility as well as high mechanical strength are the features that make this material very important (Aider, 2010). Enzymatic and chemical methods are used to convert chitin to chitosan. Chemical method is the first choice as it provides cost advantage in mass production (Kou et al., 2021). Food additive in meat products, barrier material in different food products, purification of liquid beverages, biomedical applications, cosmetics industry and agricultural applications are some of the areas where chitosan is used (Muxika et al., 2017). The use of chitosan as a paper coating material and the advantages it offers are also available (Leceta et al., 2013). Again, in some industries, it is considered as an alternative polymer to synthetic materials (Mehdizadeh and Langroodi, 2019). As a film material, its selective permeability and mechanical properties are advantageous against gases, while its low resistance to moisture is its disadvantage (Huang et al., 2012). It has a wide variety of usage options in the food industry, both during product formation and related to the packaging structure (Giannakas et al., 2020).

Nowadays, polymeric, or metallic NPs are commonly used in food packaging industry because of their antibacterial activity. These can be organic or inorganic nanomaterials (Nakazato et al., 2017; Malhotra et al., 2015). By comparison, inorganic materials have high thermal resistance, while organic materials have lower resistance at high temperature rise (Metak and Ajaal, 2013). We can count the metallic inorganic materials used in food packaging as TiO_2, ZnO, CuO, CaO and MgO. These materials have strong biocidal effects against foodborne pathogens (Alsohaimi et al., 2020; Aalami et al., 2020). TiO_2 is one step ahead of others thanks to its biocompatibility, hydrophobic, UV light absorption, photocatalytic, non-toxic, and chemically stable properties, so it is widely used in smart packaging (Jbeli et al., 2018), cosmetics, environmental pollution prevention and health field (Ali and Ahmed, 2018; Zhang et al., 2017, 2019; Tsuang et al., 2008).

Electrochemical, sol-gel technique, solvothermal, precipitation, and hydrothermal method are some of the methods used in the synthesis of TiO_2 NPs. Each method has its own advantages and disadvantages. With its environmentally friendly and cost-effective microbial NPs synthesis, it is one step ahead of other methods. Sol-gel method was used to increase the interaction of these inorganic TiO_2 NPs and the organic particles in the coating and to ensure homogenization. Sol-gel is one of the most used methods; It is mainly used to produce thin film and powder catalysts. Many studies have revealed different predictions and modeling of processes to release pure thin films or powders with large homogeneous capacity and under stoichiometry control (Akpan and Hameed, 2010). Sol-gel processing has the advantage that sol-gel precursors can be applied to any solid substrate (Mülazim et al., 2011). Also, inorganic-organic hybrids can be prepared in the sol-gel method and have higher thermal and mechanical growth due to the synergy between organic and inorganic domains.

Combining chitosan, TiO_2, and some other NPs has begun to be tested in the packaging industry to exploit antimicrobial or antioxidant properties. By combining NPs with different properties, the positive aspects of each can be combined. These can be strong barrier, thermal stability, antimicrobial and antioxidant properties. TiO_2 destroys bacterial cells due to its photocatalytic properties and thus has a positive effect on prolonging the shelf life of the product. In addition, chitosan-TiO_2 films are both inexpensive and environmentally friendly and have high efficiency in the pharmaceutical and packaging industries (Mesgari et al., 2021).

In this study, it was aimed to increase the antimicrobial properties by combining chitosan and TiO_2 NPs. For this reason, TiO_2 NPs and chitosan were modified separately and then bonded to each other using a thiol-ene click reaction. Using the obtained NPs, coated papers with hydroxy ethyl cellulose binder were produced. The printability, strength and antibacterial properties of the obtained paper were investigated.

2. Material and methods

2.1. Materials

Uncoated paper was used as packaging substrate in coatings. The specifications of the used paper are given in Table 1.

Titanium tetra-isopropoxide, ethanol, hydrochloric acid, ammonia, 3-mercaptopropyltrimethoxysilane, allyl glycidyl ether, chitosan, acetic acid, and acetone were purchased from Sigma-Aldrich (Germany). Magenta screen printing ink was provided by Toyo Ink Co (Turkey).

2.2. Methods

2.2.1. Preparation of chitosan modified TiO_2 NPs

TiO_2 NPs were produced with sol-gel technique. For this purpose, 9 mL of titanium tetra-isopropoxide was added dropwise into 50 mL of ethanol while stirring at 250 rpm for 20 min. At the end of this period, 0.1 N HCl was added until the pH reached 1.5 for the reaction to take place. The resulting mixture was stirred at 30 °C for 2 h, then temperature was increased to 125 °C and stirred for 1 h, and temperature was increased to 300 °C in the open atmosphere. After 2 h at this temperature, the resulting mixture was filtered and dried in a vacuum oven (Sharma et al., 2020). The obtained TiO_2 NPs were modified with –SH to be used in the thiol en click reaction. In this reaction, 50 mL of ethyl alcohol and 30 mL of water and 2 g of titanium NPs were mixed and homogenized by sonication for 15 min. Then, after adding 10 drops of 0.1 N ammonia and 3 mL of 3-mercaptopropyltrimethoxysilane, sonication was continued for more 2 h. The resulting dispersion was washed with ethyl alcohol, centrifuged and dried in a vacuum oven for 1 day at 45 °C (Tuna et al., 2022).

Allyl modified chitosan to be used in the thiol-en click reaction was synthesized in accordance with the literature (Illy et al., 2014). 5 g of chitosan were dispersed in water (containing 1% acetic acid). The pH of the mixture was regulated to a weak base, 7 g of allyl glycidyl ether was added to it, and it was mixed to 30 °C in a shaker for 3 days. The resulting mixture was precipitated in acetone, 3-times filtered and washed with acetone-ethanol mixture and dried in a vacuum oven.

Table 1
Technical properties of base paper used in the study.

Properties	Standard	Base paper
Grams per square meter (g/m^2)	ISO 536	80
Thickness (μm)	TAPPI T411	189
Whiteness (D65/10) (%)	ASTM E313	96
Gloss (75°)	ISO 8254-1 Part-1	5.9
Yellowness	ASTM E313	0.06

0.5 g of SH modified TiO_2 NPs were dispersed in 50 mL of water in an ultrasonic bath, 1.5 g of allyl modified chitosan was dissolved in water containing 1% acetic acid and added into it. By adding 5 drops of photoinitiator to the mixture, a click reaction was carried out in the photoreactor in 30 min. The resulting precipitate was decanted and cleaned with distilled water. Obtained product was dried in a vacuum oven at 60 °C (Geçer et al., 2010). The above reactions are schematized in Fig. 1.

2.2.2. *Preparation of antibacterial coating formulations*

The surface sizing formulation (sized paper), which is content hydroxy ethyl cellulose, was coated on paper. For this purpose, sizing formulation prepared by 0.25% hydroxy ethyl cellulose-water, the mixture was heated to 90 °C and stirred, for a while obtained hot surface sizing formulation was cooled to 60 °C after the mixture applied to paper with the Mayer rod #2 b y a laboratory-type paper coating machine. Produced all coated papers were conditioned at 50% relative humidity and 23 °C at 48 h. Paper coating formulations are listed at Table 2.

2.2.3. *Paper coating process*

In the coating process, TiO_2 NPs, chitosan and chitosan modified TiO_2 NPs were added to the sizing formulation, which was cooled to 60 °C (Ozcan, 2019). The paper coating formulations are given in Table 2. All formulations (containing hydroxy ethyl cellulose, water and TiO_2 NPs, chitosan and chitosan functionalized TiO_2 NPs) were prepared in a beaker with 2500 rpm with homogenizator about 10 min after the formulations kept under vacuum for 3 min for remove bubbles. At the end of this period formulations coated onto paper with Mayer rod 2.

2.2.4. *Spectrophotometric properties*

The color properties of the papers and prints were investigated with X-Rite eXact spectrophotometer according to ISO 13655:2017 standard. The color difference was calculated with CIE ΔE 2000 color-difference formula (1) ISO 11664–6:2014 (Luo et al., 2001).

Table 2
Paper coating formulations.

Ingredients	Hydroxy ethyl cellulose (%)	TiO_2 NPs (%)	Chitosan (%)	Chitosan functionalized TiO_2 NPs (%)
Base paper	0	0	0	0
Sized paper	100	0	0	0
F1	97.5	2.5	0	0
F2	95	5	0	0
F3	97.5	0	2.5	0
F4	95	0	5	0
F5	97.5	0	0	2.5
F6	95	0	0	5

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \quad (1)$$

2.2.5. *Gloss*

The gloss properties of the papers were performed by BYK Gardner GmbH micro gloss at 75° with ISO 8254–1:2009, and the gloss properties of printed papers performed by BYK Gardner GmbH micro-Tri-gloss 60° with ISO 2813:2014.

2.2.6. *Contact angle and surface energy*

Surface energy plays an important role in the interaction of paper with liquids. The content of the coatings is among the parameters that affect the morphological properties of a surface, angle of contact and surface energy.

The contact angle and total surface energy measurements of the base paper, sized paper and coated papers were performed by PocketGoniometer PGX+ in accordance with ASTM D5946 standard.

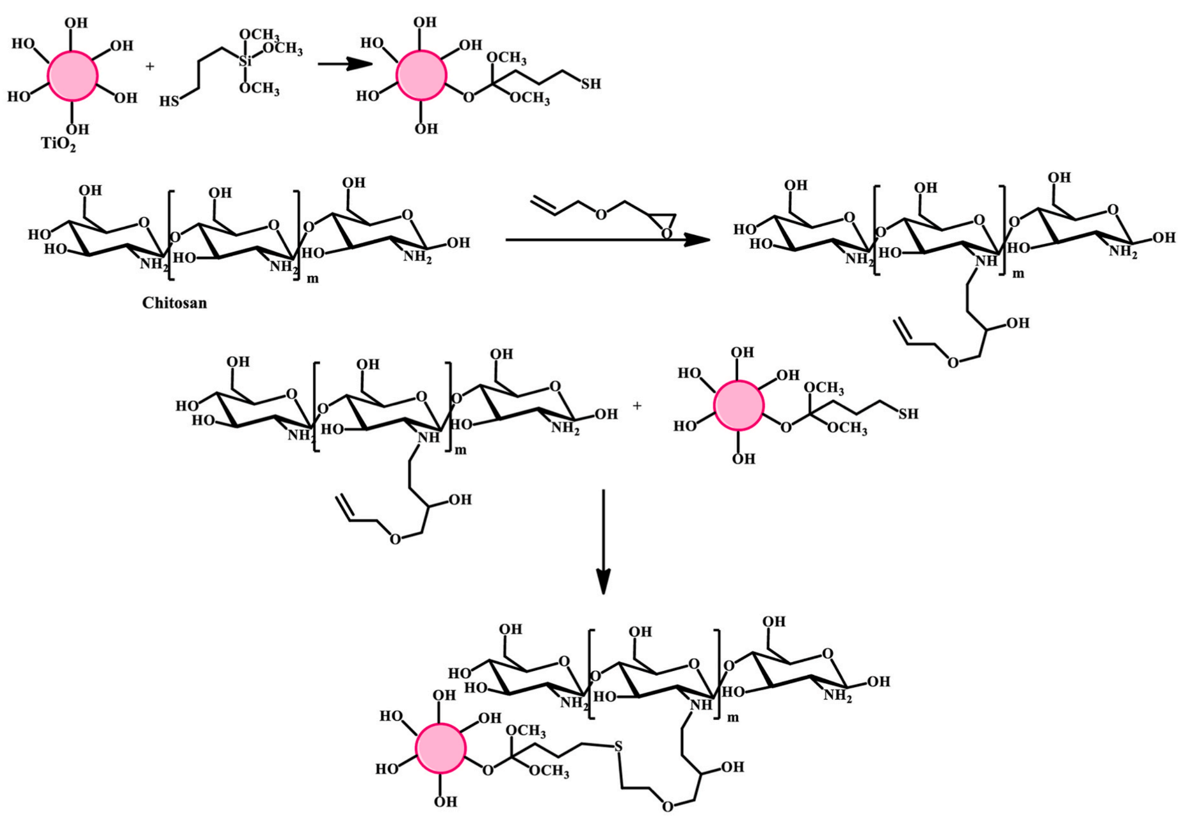


Fig. 1. The scheme of chitosan modified TiO_2 NPs synthesis.

2.2.7. Characterization of base paper, sized paper, and coated papers

Chemical structures of active TiO_2 NPs, chitosan and Chitosan functionalized TiO_2 NPs were illuminated with a Perkin–Elmer Spectrum 100 ATR-FTIR spectrophotometer (WA). The conditions of analysis were as follows; resolution 2 cm^{-1} and a frequency range of 400–4000 cm^{-1}.

Paper air permeance of all papers were carried out with Lorentzen & Wettre (L&W) in accordance with ISO 5636–3:2013 - Part 3 Bendtsen Method. It is applicable to papers and boards which have air permeances between 0,35 μm/(Pa·s) and 15 μm/(Pa·s) when tested with the Bendtsen apparatus.

2.2.8. Printing of base paper, sized paper, and coated papers

Magenta screen printing ink were used to make solid prints on base paper, sized paper and coated papers in the squeegee printing parameters which have 120 tpc weaving density, 75° squeegee angle and 75 shore hardness by ARUS semi-automatic silk screen printing machine.

2.2.9. Antibacterial test of base paper, sized paper, and coated papers

The inhibition properties of sized and coated papers against different bacteria, in which uncoated paper was used as a control group, were investigated. In this sense, the disk diffusion method was used as an antibacterial test. *Escherichia coli* (*E. coli)*, the most common Gram-negative bacteria, and *Staphylococcus aureus (S. aureus)*, the most common Gram-positive bacteria, were used as bacteria to determine antibacterial properties. Activated overnight in Tryptic Soy Broth (TSB) at 37 °C for both Gram-negative and Gram-positive bacterial cultures in the antibacterial test. The obtained inoculum was homogeneously distributed on the petri surface. 6 mm samples from all samples whose activation was to be measured (control group uncoated paper, sized paper, and coated papers) were cut and placed in the spreading inoculum. After the prepared petri dishes were incubated at 37° overnight, the inhibition radius around the test samples was measured.

3. Results and discussions

3.1. Characterization of base paper, sized paper, and coated papers

ATR-FTIR analysis results of TiO_2 NPs, chitosan and chitosan grafted TiO_2 NPs are given in Fig. 2. When the ATR-FTIR spectrum of TiO_2 NPs shows a characteristics absorption between 690 and 400 cm^{-1} this peak attributes to pure anatase phase of TiO_2 NPs (Katz et al., 2023). The peak observed 3000–3600 cm^{-1} shows to the OH stretching band (Praveen et al., 2014). It can also be attributed to the stress vibration of the peak *S*–H at 2570- 2590 cm^{-1}. When the spectrum of chitosan is examined, strong vibration peaks of hydroxide and amine groups can be seen at 3200-3500 cm^{-1}. In addition, the peak of the C–H bond was clearly revealed at 2910 cm^{-1}. However, the boardband vibrations of the C–*O*–C bonds in the polysaccharide molecular structure can be seen at 1028 cm^{-1}, and the vibrations of the glycosidic bond at 1153 and 895 cm^{-1}. At 1595 cm^{-1}, however, N–H vibration of the primary amine was exposed. The results are consistent with the literature (Tuna et al., 2022). When the ATR-FTIR spectrum of chitosan grafted TiO_2 NPs is examined, peaks belonging to both Titanium and chitosan are observed. The reduction of the hydroxide peak proves that the reaction was successful. The results are consistent with the literature (Mansur et al., 2008).

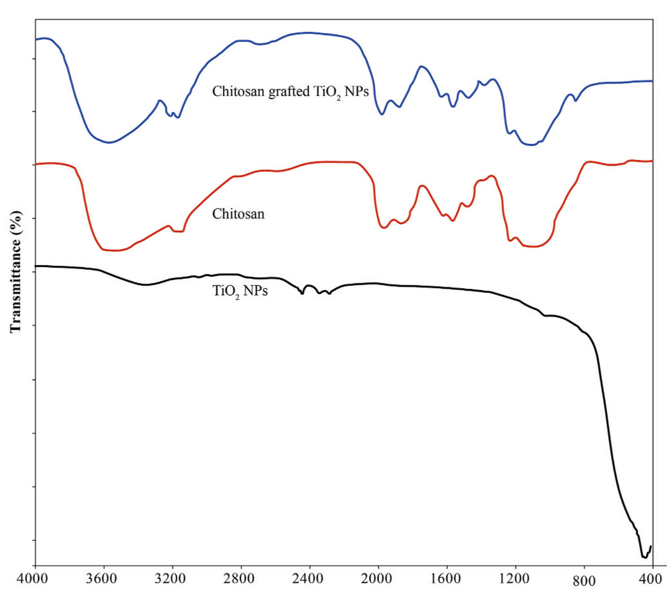


Fig. 2. The ATR-FTIR spectra of TiO_2 NPs, chitosan and chitosan grafted TiO_2 NPs.

3.2. Paper properties of base paper, sized paper, and coated papers

Coating formulations using produced chitosan modified TiO_2 NPs, TiO_2 NPs and chitosan were successfully prepared and coated on the paper surface. The color results of the coatings are given in Table 3. Table 3 shows the CIEL × a*b × color and color differences of the base paper, sized paper and coated papers. Base paper was used as reference. When the color differences were examined, it was determined that the surface treated paper with the most color change of the base paper was sized paper. Because the double bonds on hydroxyethyl cellulose showed chromophore property and caused the color to shift towards blue. However, due to the colors of the NPs, which are in the color differences of all coatings, they approached the base paper. The color difference has decreased. It has been determined that chitosan is one of the fillers used in coatings that minimizes the change in color, because the color of chitosan is naturally yellowish, giving this effect. It has been determined that the NP produced by modification is more than chitosan, although it causes less change than titanium. The color correction effect increased as the amount of all added fillers increased. It has been determined that the color differences of all coatings (except sized paper) are not perceived by the human eye. As a result, the color difference was reduced by adding NPs to the coatings. The results are similar to the literature (Rhim et al., 2006).

3.3. Contact angle and surface energy

The contact angle measurement results are listed in Table 4 and total surface energy values are listed in Table 5. When Table 4 was examined, it was determined that the contact angle of the base paper was reduced by coating the surface with hydroxy ethyl cellulose, and the wettability was increased. This enables printing with less water, improving the paper both financially and in terms of printability. The reason for this decrease in the contact angle is the formation of a percent more hydroxyl group and consequently the decrease in the number of hydrogen bonds. With the addition of NPs to the coating formulation, there was a slight

Table 3
Spectrophotometric color and color difference values of the papers used in the study.

Sample No	L*	a*	b*	ΔE_{00}
Base paper	92.22	2.19	−7.66	
Sized paper	90.74	3.41	−11.70	3.14
F1	91.82	2.73	−9.77	1.60
F2	92.50	1.65	−6.16	1.30
F3	92.48	1.64	−5.94	1.44
F4	92.03	2.11	−7.17	0.40
F5	92.01	3.27	−8.36	1.41
F6	92.23	1.48	−7.40	0.9

Table 4
Contact angle values according to ASTM D5946 method.

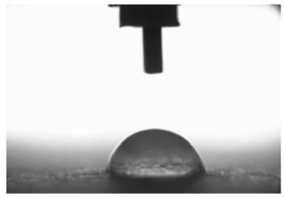
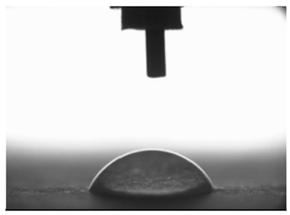
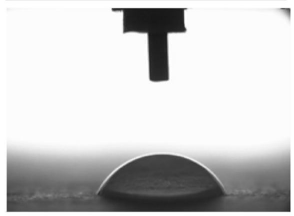
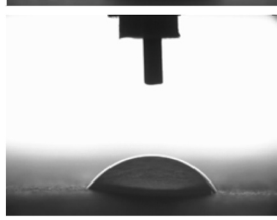
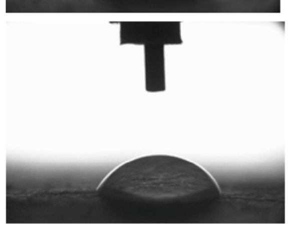
Paper samples	Contact Angle	Images
Base paper	70.3	
Sized paper	46.2	
F1	25.0	
F2	32.3	
F3	39.7	
F4	44.0	
F5	28.9	
F6	37.5	

Table 5
Total surface energy values according to ASTM D5946 method.

Paper samples	Total surface energy (mJ/m^2)
Base paper	39.6
Sized paper	48.3
F1	56.0
F2	53.4
F3	50.7
F4	49.1
F5	54.6
F6	51.5

decrease in contact angle compared to sized paper. Because both TiO_2 NPs and chitosan have a highly hydrophilic structure. This reduces the contact angle. In addition, when each filler material is examined separately, small increases are seen in the contact angles as the amount of filler increases. This is thought to be because the excess molecules reduce the number of hydrogen bonds. Even so, the contact angles of all coatings are lower than sized paper, meaning that the paper appears to be wetted with less water. When the surface energies (Table 5) are examined, it is seen that they are inversely proportional to the contact angles as expected. The results obtained are compatible with the literature (Nau et al., 2019).

3.4. Gloss of paper

Gloss is an attractive feature for paper and other substrates. The gloss values of the coated papers were measured and given in Fig. 3. When Fig. 3 was examined, it was determined that the gaps between the fibers of the paper were filled with the sizing process and the gloss value increased compared to the base paper. However, TiO_2 NPs added to the coating formulations created roughness on the surface, scattering the light and reducing the gloss. As the percentage of TiO_2 NPs in the coating formulation increased, the gloss decreased. The addition of chitosan reduced the gloss less than TiO_2 NPs. It can be thought that this is because chitosan restores some of the gloss, which it reduces with roughness, with its own molecular shine, or that it enters the cavities on the surface more easily thanks to its fiber structure and size. In summary, the highest gloss is in sized paper (due to filling the surface voids). It is followed by the gloss of the coated papers containing chitosan, and then the coated papers containing Chitosan functionalized TiO_2 NPs. The lowest gloss was obtained only on papers in which TiO_2 NPs nanoparticles were used the most. The results are consistent with the literature (Kandirmaz et al., 2021).

3.5. Surface properties of base paper, sized paper, and coated papers

In addition, depending on the surface treatments on the papers, the air permeability of the papers was measured and given in Fig. 4. When the figure was examined, it was determined that the air permeability of

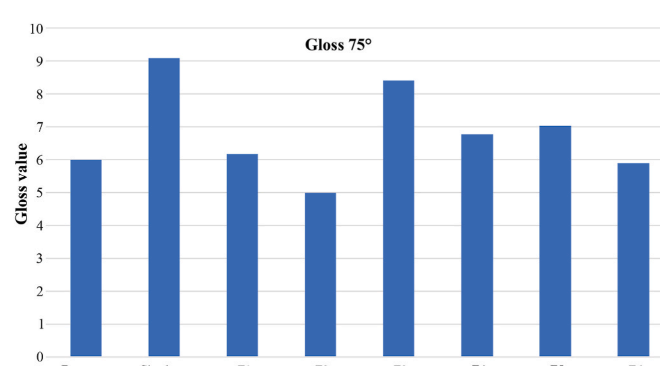


Fig. 3. Gloss measurements of all papers used in the study.

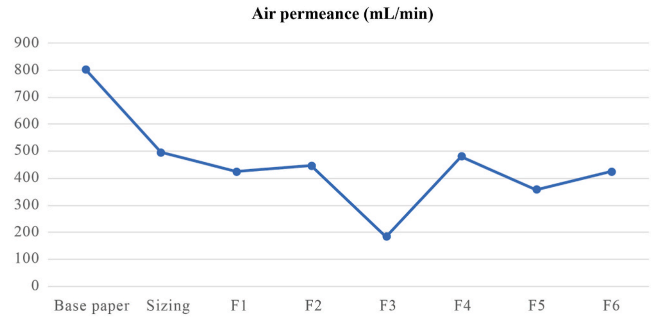


Fig. 4. Air permeance measurements of papers used in the study.

the base paper was reduced by all surface treatments. Because the binder used in sizing and coating formulations has formed a thin polymeric film layer on the surface, which has emerged as a reduction in air permeability of the processes. Slight increases in air permeability were observed due to slight deformation on the film of coating formulations containing a high percentage of filler. The results are consistent with the literature (He et al., 2021).

3.6. Printing properties of base paper, sized paper, and coated papers

Screen printing has been successfully carried out on base paper, hydroxy ethyl cellulose sized paper and coated papers with different contents. The color and gloss values of the prints are given in Table 6. When the table was examined, it was determined that the change in colors was at the b value the most. This change appeared in the form of a blue shift. However, the variation in colors is quite low and is within the acceptable range specified in ISO 12647–2. When the printing glosses were examined, it was determined that the printed papers were glossier than the unprinted papers because the thicker film layer formed by the ink binder on all papers increased the gloss. The results agree with the literature. (Santos and Velho, 2002).

3.7. Antimicrobial activity of base paper, sized paper, and coated papers

Antimicrobial activity of the paper coatings prepared were tested against Gram positive (*S. aureus*) and Gram negative (*E. coli*) bacteria. Diameter of the inhibition zones of the samples are shown on Table 7. Base paper and hydroxyethyl cellulose sized papers have no inhibition effect, so *E. coli* and *S. aureus* grew homogenously in all regions of the petri plates. When table aa is examined, it is seen that TiO_2 NPs and chitosan have antibacterial properties against Gram-negative and Gram-positive bacteria separately. These activities can be explained as follows. Production of reactive oxygen species (ROS) is among the main reasons why TiO_2 NPs increase antibacterial properties. It is thought that this increases phospholipid prooxidation and decreases the viability of bacteria. The amino group ($-NH_2$) attached to the second carbon of the glucosamine component on chitosan in weak acidic environment binds proton and turns into a positively charged ($-NH_3^+$) form. Accordingly, polycationic charged chitosan interact with the negatively charged surface of bacteria. It is thought that this provides antimicrobial activity of chitosan molecules. It was determined that the activities of the papers coated with F5 and F6 formulations increased against both bacterial species. In other words, it was determined that the produced modified new NPs had a synergetic effect. In addition, as the amount of filler increased in all coatings, the antibacterial properties increased. The results are in line with the literature (Ma et al., 2010; Albukhaty et al., 2020).

Table 7. Antimicrobial activity of base paper, sized paper and coated papers against *E. coli* and *S. aureus* (inhibition zone diameter in millimeter).

Table 6
Magenta color spectrophotometric measurements of printed papers.

Sample	Density	L*	a*	b*	Gloss
Base paper	2.13	47.17	67.77	31.77	9.00
Sized paper	2.11	47.80	71.12	31.95	12.80
F1	1.95	50.54	66.41	23.08	11.40
F2	1.96	47.56	70.46	32.92	10.90
F3	2.09	50.54	67.81	27.43	12.30
F4	1.83	51.11	69.22	21.97	11.90
F5	1.71	49.72	70.13	25.80	11.10
F6	1.77	49.70	68.04	23.99	10.80

Table 7
Antimicrobial activity of base paper, sized paper and coated papers against *E. coli* and *S. aureus* (inhibition zone diameter in millimeter).

Sample	*E. coli* (mm)	*S. aureus* (mm)
Base paper	0	0
Sized paper	0	0
F1	6.3	7.2
F2	11.3	11.4
F3	7.8	6.2
F4	9.1	7.5
F5	7.2	8.2
F6	10.3	12.0

4. Conclusions

In this study, TiO_2 NPs were synthesized and modified with –SH. Chitosan has also been modified with allyl. Titanium and chitosan molecules were linked to each other via a thiol-ene click reaction using both molecules. ATR-FTIR results prove that the synthesis has been carried out successfully, depending on the literature. Using the obtained NPs, paper coatings with hydroxy ethyl cellulose binder were made and it was determined that the color change of the obtained coated papers could not be perceived by the human eye and the gloss increased with all the processes. The contact angle, surface energy and air permeability of the coated paper were determined, and it was concluded that printing can be done with less water and the polymeric hydroxyethyl cellulose film formed on the surface reduces the air permeability of the paper. Prints were made on the produced papers, and it was observed that the color change in the prints was in accordance with the range specified in the ISO 12647 standard compared to the base paper. Antimicrobial test was applied to the obtained papers against *E. coli* and *S. aureus*, and it was determined that the antibacterial properties of chitosan and TiO_2 NPs against both bacterial species separately increased with the synergistic effect of the produced chitosan modified TiO_2 NPs. These results show that the produced NPs have the potential to be used in antimicrobial packaging.

Credit author Statement

The authors, Arif Ozcan, Emine Arman Kandirmaz, and Gulhan Acar Buyukpehlivan, collaborated on all phases (Conceptualization, Methodology, Data curation, Writing- Original draft preparation, Investigation, Validation, Writing- Reviewing and Editing) of the study.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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