JOURNAL of THE TURKISH CHEMICAL SOCIETY SECTION: A CHEMISTRY

TURKISH CHEMICAL SOCIETY

Characterization of Active Food Packaging Films Based on Poly(vinyl alcohol)/Boric acid/Montmorillonite Nanocomposite Incorporated with Polyphenol

Serap MUTLU YANIC [1*], Esen Gul ATES [2]

[1] Istanbul Gedik University, Chemistry Technology Program, Istanbul, 34906, Turkey

[2] Turkish Energy, Nuclear and Mineral Research Agency, Ankara, Turkey

Abstract: Biopolymer-based nanocomposites are a new type of material that exhibits significantly improved properties, such as barrier, mechanical, and thermal characteristics. They are considered non-toxic and alternative food packaging materials. Therefore, the production of biopolymer-based active films has been initiated to reduce the environmental problems caused by non-biodegradable plastic waste and eliminate their negative effects on human health. In this study active food packaging films based on poly(vinyl alcohol)/boric acid/montmorillonite (PVA/BA/MMT) nanocomposite incorporated with ferulic acid (FA) were synthesized using solution casting method. The structural, thermal, transmittance, antimicrobial, and antifungal properties of nanocomposite films have been investigated. The fourier transforms infrared (FTIR) spectroscopy used to demonstrate the chemical structure of films and interaction between boric acid (BA) and PVA. X-Ray diffraction analysis (XRD) was performed to determine the dispersion and exfoliated of the montmorillonite in the PVA matrix. Thermal stability of PVA/BA/MMT films incorporated with FA were evaluated by using TG/DTA analyzer. Optical properties of films and PVA determined using by UV/VIS spectrophotometer in the range of 400-700 nm wavelength at scanning percent transmittance. The transmittance of PVA exhibited UV light 89.2% of T_{700} and 86.7% of T_{400}, indicating the high transparency of PVA. The antimicrobial activity of PVA membranes samples was carried out test method AATCC 100. According to the antimicrobial activity test, more than 300 colonies were detected for all microorganisms in the samples belonging to the PVA group. But the antimicrobial and antifungal activity of the films incorporated with FA could inhibit bacterial growth. It has been determined that the nanocomposite films have antibacterial properties against *Escherichia coli* (*E.coli*, ATCC 25922), *Staphylococcus aereus* (*S. aereus*, ATCC6538), and antifungal properties against *Candida albicans.*

Keywords: Polyvinyl alcohol, boric acid, montmorillonite, polyphenol, packaging film.

Submitted: April 30, 2023. **Accepted:** July 12, 2023.

Cite this: Mutlu Yanic S, Ates EG. Characterization of Active Food Packaging Films Based on Poly(vinyl alcohol)/Boric acid/Montmorillonite Nanocomposite Incorporated with Polyphenol. JOTCSA. 2023;10(4): 893-902.

DOI: https://doi.org/10.18596/jotcsa.1290365.

***Corresponding author. E-mail:** serap.mutlu@gedik.edu.tr.

1. INTRODUCTION

Plastic is one of the most widely used materials due to its excellent mechanical and barrier properties. However, many plastic materials are petroleum-based, biologically non-degradable, and cause significant environmental problems. Therefore, in recent years, research has increased on alternative biodegradable plastics that will reduce waste disposal problems, while also not posing a threat to consumer health (1-3). Biopolymer-based food packaging films, which exhibit significantly improved properties such as barrier, mechanical, thermal, and antimicrobial characteristics, are considered as alternative food packaging films.

As a type of synthetic linear polymer material, poly(vinyl alcohol) (PVA) have several advantages such as film-forming ability, high oxygen resistance, biodegradability, and water solubility (4). These advantageous properties have led to applications in a wide range of resins, and coatings in various fields such as papermaking, medicine, and food packaging. However, due to the hydroxyl groups present in the polyvinyl alcohol molecular chain, it is moisture-sensitive, which limits its applications in various fields. Therefore, improvement in their hydrophilic property of PVA is great of importance to investigate its applications (5-9).

Several studies have explored to advance the hydrophilic properties of synthetic PVA by many physical methods such as ultraviolet radiation, electron beam irridation and heat treatment. Many studies have used boric acid as a chemical crosslinking agent (10-12). Specifically, extensive research has been conducted on cross-linking polyvinyl alcohol (PVA) with boric acid (BA), resulting in enhanced water resistance, barrier properties, thermal stability, and mechanical properties. These advancements have led to the development of various water-soluble food packaging materials. (13-14).

On the other hand, using clay to improve the thermal and mechanical properties of PVA is a very interesting method. Montmorillonite (MMT) is a type of clay nanofiller that is commonly used due to its low cost and ability to good dispersed in a polymer matrix. Many studies have showed that incorporating an appropriate amount of MMT or modified MMT into PVA can result in the formation of intercalated or exfoliated composite materials (30-36). These composites exhibit improved mechanical strength, water resistance, gas barrier properties, and thermal stability when compared to pure PVA. (15-16).

Active food packaging can be categorized based on the specific additive it incorporates, with a primary focus on those that possess antioxidant properties and antimicrobial activity. Particularly, antimicrobial additives inhibit the growth and activity of microorganisms responsible for product contamination and deterioration (active 3-4-5). In recent years, polyphenols, which are compounds in which multiple phenol groups are present in a single molecule, have been utilized for their antimicrobial activity (1-3). Ferulic acid (FA) is a natural phenolic compound that belongs to the hydroxycinnamic acid family and is known for its various beneficial properties. Ferulic acid has been found to have antimicrobial properties, which means it can help to inhibit the growth of microorganisms such as bacteria and fungi. The incorporation of ferulic acid into active packaging films has demonstrated to improve their tensile strength, swelling performance, and antifungal activity which can make them more durable and effective in various applications (17-20).

In this study, polyvinyl alcohol based PVA/Boric Acid/Montmorillonite (PVA/BA/MMT) active food packaging film incorporated with FA were synthesized using solution casting method. Then, ferulic acid polyphenol compound at certain weight ratios (0,1,2,3) was added to PVA/BA/MMT nanocomposites to improve their antimicrobial and antifungal properties.

2. EXPERIMENTAL SECTION

2.1. Materials

PVA with a degree of hydrolysis: 99% was obtained from Sigma Aldrich. Montmorillonite clay was provided by Acros Organics, surface area = 240 m^2/g. Glycerol and BA were purchased Merck. Ferulic acid (FA, $C_{10}H_{10}O_4$) was purchased was purchased Wuhan ChemFaces Biochemical Co., Ltd.

2.2. Active Packaging Films Preparation

The PVA/BA/MMT active packaging films were prepared using the solution-casting method (1). PVA polymer (5 g), MMT (0.1 g) (2% w/w), and boric acid (0.25 g) were added to 100 mL of distilled water. The PVA mixture was heated to 90 °C and stirred continuously until the PVA/BA mixture was homogeneous. 1 g of glycerol was used as a plasticizer and added to the mixture, which was stirred continuously for 2 hours. Various amounts of FA (0%, 1%, 2%, 3%, w/w) were dissolved in 5 mL of distilled water at room temperature. The FA solutions were added to the PVA solution FA solutions were added to PVA solutions and then stirred for 2 hours at 40 °C on a magnetic stirrer. The prepared nanocomposite mixtures were then placed in a glass petri dish and dried at 45 °C for 1 day. The nanocomposite films containing 0%, 1%, 2%, and 3% FA were marked as PVA0, PVA1, PVA2, and PVA3 respectively.

2.3. Characterization

2.3.1 X-ray Diffraction (XRD) Analysis

The structural analysis of all samples was performed using a PANalytical/Empyrean X-ray diffractometer with a scanning rate of 0.4/minute, 40 kV, and 40 mA, using Cu K radiation at a wavelength of 0.1546 nm. The d-spacing value (d001) of the samples was made a calculated using the (20), Bragg's equation as following:

$$d = \frac{\lambda}{2 Sin\Theta}$$

Where d is the interplanar distance, λ is the wavelength of X-ray beam and θ is the diffraction angle.

2.3.2 Fourier transform infrared (FTIR) spectroscopic analysis

FTIR measurements were characterized the crosslinked PVA and the chemical structure of the PVA/BA/MMT films and by using a Varian/660-IR spectrometer in the range of 4000 cm^{-1} to 400 cm^{-1} (FTIR).

2.3.4 Transmittance

Optical property of the films, was determined by scanning the percent transmittance in whole visible light region (400-700 nm) using UV-VIS-NIR Spectrophotometer Shimadzu/UV 3600 Plusat at a scanning rate of 60 nm/min (32)..

2.3.5 Thermogravimetric Analysis (TGA)

The thermal stability of the pure PVA and nanocomposite films was determined using a Netzsch/STA 449 F3 Jupiter thermal analyzer. The mass of the active food packaging films used was in the range of 6-8 mg in aluminum oxide crucible. The film samples were cut and thermal analysis was performed by heating them up to 600 °C at a heating rate of 10 °C/minute under a nitrogen atmosphere with a purge flow of 20 mL/min (33).

2.3.6 Antimicrobial and antifungal activities

The antimicrobial activity of PVA membrane samples was carried out according to the test method (34) AATCC 100 with some modifications. For this purpose, samples sterilized by 25 kG γ irradiation were used and inoculum concentrations of $1x10^5$ cfu/mL of *Escherichia coli* (*E.coli,* ATCC 25922), *Staphylococcus aereus* (*S. aereus*, ATCC6538), and *Candida albicans* (*C. albicans*) were used. Samples with a surface area of 2 cm^2 were inoculated with 86.8 µL of *E. coli* or *C. albicans* inoculum of $1x10^5$ cfu/mL and incubated at 37 °C *for E. coli* and *S. aereus*, and 25 °C for *Candida albicans* for 24 hours. After incubation, the samples were washed by vortexing with 8.68 mL of phosphate buffer for 1 minute, which was 100 times the volume of the inoculum, and 100 µL of the solution obtained after washing was spread on agar petri dishes. Colonies were counted 24 hours after incubation. As experimental control groups, the inoculum concentration of each microorganism was diluted 100-fold and spread on agar petri dishes.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The X-ray diffraction analyses were carried out the morphology of the PVA/BA/MMT incorporated with FA in the region 2θ=5-50⁰, as shown in Figure 1. The pattern of pure PVA exhibits three characteristic diffraction peak at 2θ = 19,87⁰, 22,73⁰, and 40,99⁰, corresponding peaks of PVA (xrd pva). The peak intensity at 2θ = 19,87⁰ in the based on PVA films decreased and a new at peak 2θ =20,61⁰.

The XRD pattern of naturel MMT appeared a strong diffraction peak at around 2θ = 8.920⁰, corresponding to the d-spacing of 9.91 Å. No diffraction peaks of PVA0, PVA1, PVA2 nanocomposite films were found ranging 2θ=5-50⁰. This could be primarily attributed to the MMT silicate layers being in an exfoliated state, where the layers are considerably spaced apart (>5 nm), and the parallel stacking is disrupted (2). But PVA3 nanocomposite film showed that characteristic diffraction peak of clay MMT at 2θ =9,02⁰. These results demonstrate that MMT is exfoliated in the PVA0, PVA1, and PVA2 nanocomposite films, but not in the PVA3 nanocomposite film. The finding suggests that the MMT layers might be predominantly exfoliated or disordered intercalated arrangements in the PVA matrix (1,xrd)

3.2 FTIR Analysis

The FTIR spectra of interactions and crosslinking reactions between PVA and BA are showed in Figure 2. The greatest evidence of crosslinking interaction of boric acid with PVA is the covalent bonds established two slight indications O-B-O and B-O-C. The spectra of O-B-O linkage are observed at a frequency of 665 cm^{-1} in the PVA0 film. The PVA0 film exhibited a new broad peak at 1286 cm^{-1} corresponding to the B-O-C bond. Looking at the results, it can be seen in Figure 2 that crosslinking occurs between BA, which is used as a crosslinking agent to improve the hydrophobic property of PVA (37).

Figure 3 displays the FTIR spectra of PVA/BA/MMT active nanocomposite films with different weight ratios and FA contents. Pure PVA exhibited characteristic peaks at 3230 cm^{-1} was assigned -OH stretching, which includes the groups that participate in intramolecular and intermolecular hydrojen bonding. The bands at about 2923 cm^{-1}, 1423 cm^{-1}, and 1330 cm^{-1} were determined to $-CH_2$ asymmetric strecthing and symmetrical bonding the bands at about 1145 cm^{-1} and 1080 cm-1 were similar to C-O strectching of the crystalline and amorphous regions of PVA (10,17). The intensity of peaks at 1145 cm^{-1} and 1080 cm^{-1} decreased due to the interaction between boric acid and the crystalline regions of PVA. The peak at 1648 cm^{-1} was assigned C=O stretching of acetate groups remaining in partly hydrolized pure PVA. In addition, the characteristic peaks of PVA are given in Table 1. The peak at 1020 cm^{-1} in MMT added PVA/BA packaging films were assigned to Si-O stretching vibration (38). This peak is observed in all films, but with an increased amount of FA, it has shifted to 1035 cm^{-1} in the PVA2 film. The characteristic peaks at 3423 cm^{-1}, 1683 cm^{-1}, and 1280 cm^{-1} in the FTIR spectra of FA correspond to the stretching vibrations of carboxylic acid O-H, carboxylic acid C=O, and carboxylic acid C-O, at 1502 cm^{-1}, 1604 cm^{-1} for aromatic C=C bonds, respectively. (Figure 3) (39).

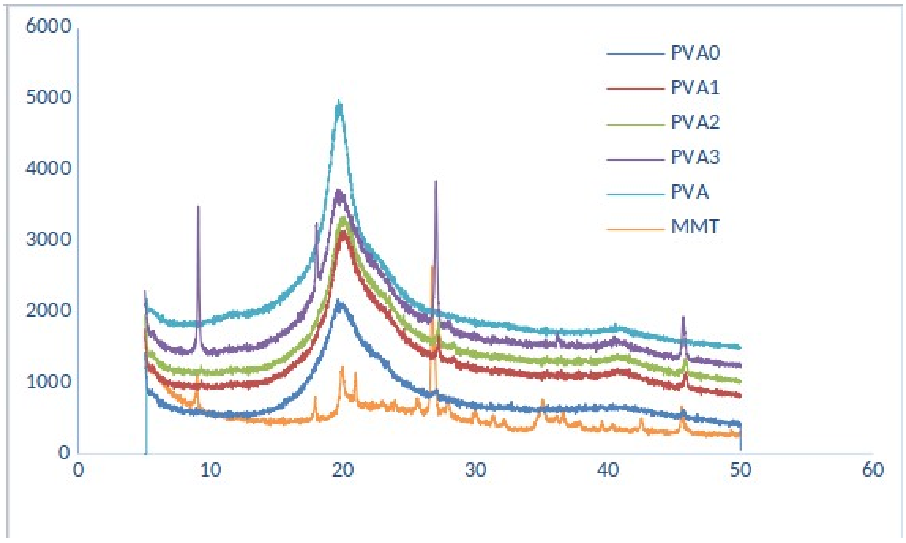

Figure 1: XRD patterns of the pure PVA and nanocomposite films incorporated with FA.

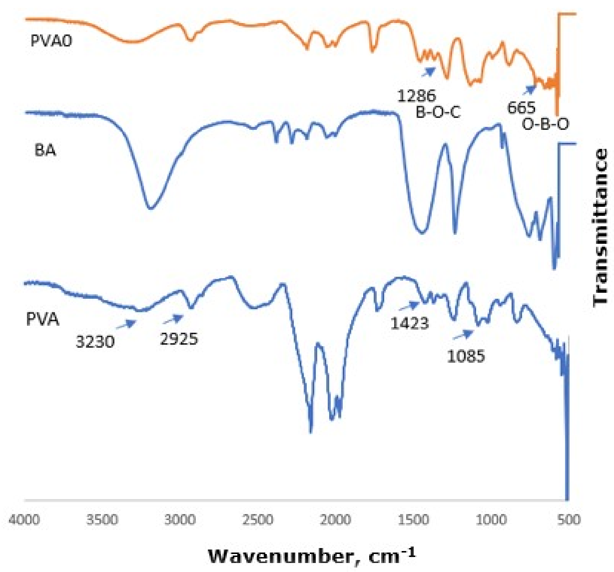

Figure 2: FTIR spectra of pure PVA, BA, and PVA0 nanocomposite films.

Table 1: The FTIR spectra of pure PVA and its band assignments.

Peaks, cm^{-1}	Assignments
3100-3500	-OH stretching band
2940-2906	$-CH_2$ asymmetric stretching and symmetric bending
1648	Symmetric stretching vibration of C-O-C band
1425	-CH wagging vibration band
1138-1085	C-O stretching of the crystalline

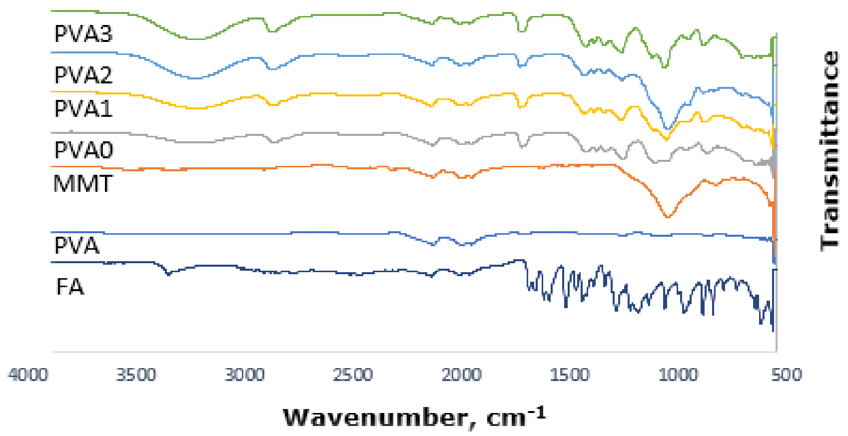

Figure 3: FTIR spectra of Pure PVA and nanocomposite films.

3.3 Effects of FA on Film Transmittance

Transparency is an important parameter for active packaging films. Films are generally desired to be transparent in order to observe changes such as mold, fungus, and discoloration that may occur in food materials (40,24). The transparent graph of the active packaging films measured with UV-Vis in the range of 400-700 nm wavelength is given in Figure 4. The transmittance of PVA exhibited UV light 89,2% of T700 and 86,7% of T400, indicating the high transparency of PVA. With an increasing amount of ferulic acid, the transmittance values are observed to decrease. In the case of PVA0 nanocomposite film, the T700 transmittance value is 74.2, whereas in the PVA3 film, this value decreased to 62.5. The results have shown that pure PVA has high transmittance properties but decreased transmittance due to the ferulic acid added to enhance and improve the properties of PVA.

3.4 Thermogravimetric Analysis

Thermal stability is important in nanocomposite films because high temperature, mechanical stress, or other environmental factors can deteriorate the structural and functional properties of the film. Therefore, thermal stability is a significant factor in maintaining the durability and long-term performance of the film. Additionally, since high temperature conditions are frequently used in industrial applications, thermal stability is a critical feature for the food industrial production and use of composite films (41). The thermal stabilities of pure PVA and different nanocomposite films were investigated by TGA and the results are given in Figure 5.

According to TGA results, all the nanocomposite films exhibited one minor and two major thermal degradation from room temperature to 600 °C. The onset temperature for thermal degradation of PVA was 297 °C. The first slight weight loss located at around 100-180 °C was attributed to the evaporation of adsorbed moisture and/or water. The second significant weight loss observed at 200-295 °C and 388-395 °C for the PVA and PVA-based active packaging films. The maximum degradation temperature of PVA, T_{max}, is approximately 460 °C. The T_{max} value of PVA0 is 470 °C, and it can be observed from the thermogram that the thermal stability slightly increases with the addition of MMT and BA to pure PVA. However, the T_{max} values of PVA1, PVA2, PVA3 had no significant difference with pure PVA. In this study, it was observed that the addition of ferulic acid to PVA/BA/MMT nanocomposite films did not lead to a significant increase in thermal stability compared to pure PVA.

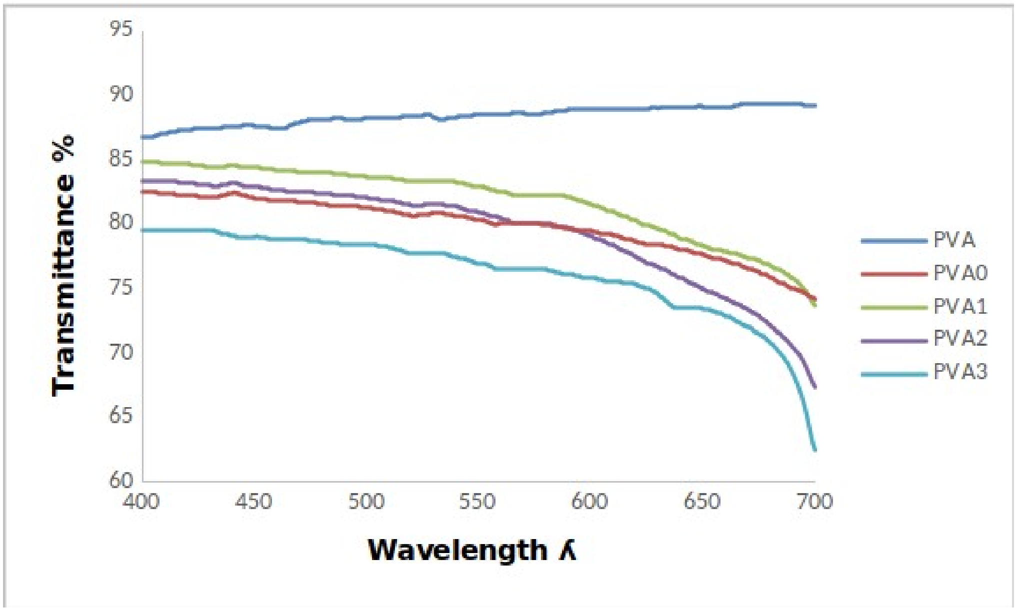

Figure 4: Transmittance spectra of pure PVA and nanocomposite films.

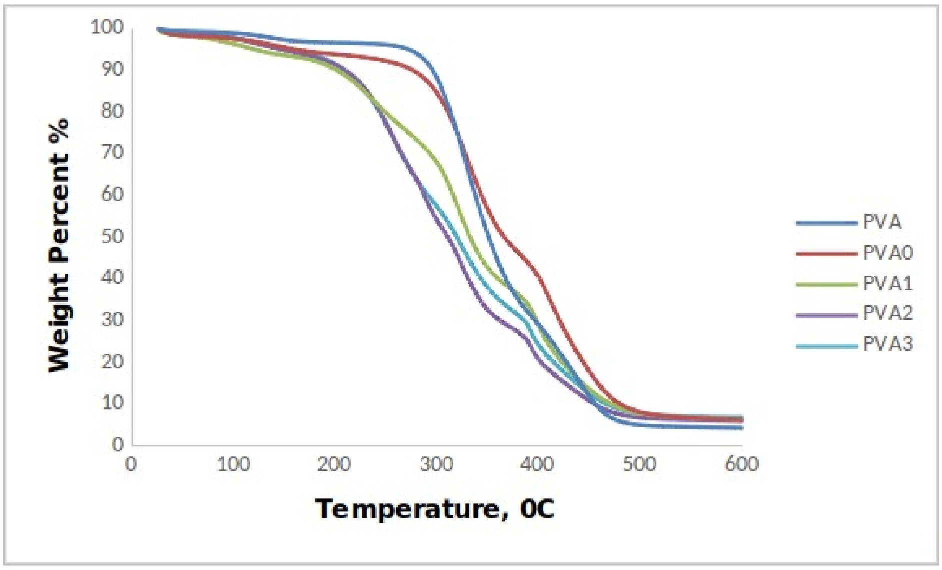

Figure 5: Thermogravimetric analysis (TGA) curve of pure PVA and nanocomposite films.

3.5 Antimicrobial and Antifungal Activities

Antimicrobial packaging is a new technology product that protects packaged food products from spoilage that can occur through the contamination of foodborne pathogens (bacteria, parasites, and viruses) and lead to foodborne illness (42). The antimicrobial and antifungal activities of pure PVA and PVA/BA/MMT nanocomposite films incorporated with different content FA were shown in the Tablo 2. After 24 hours of incubation, the average colony counts in the control group were found to be 252 for *E. coli,* 296 for *S. aureus*, and 240 for *C. albicans*. According to the antimicrobial activity test, more than 300 colonies were detected for all microorganisms in the samples belonging to the PVA group, which was the control group for the samples. This indicates that the PVA group did not have any antibacterial or antifungal effect. When the test results of the PVA0 group were examined, it was determined that it did not have an antibacterial effect against *E. coli* and *S. aureus* but had an antifungal effect against *C. albicans*. The PVA1, PVA2 and PVA5 groups, on the other hand, exhibited antibacterial and antifungal properties against all microorganisms tested. The results indicate that the addition of a polyphenol compound called ferulic acid to PVA-based nanocomposite films creates antimicrobial activity.

Table 2. The cfu (colony forming unit) averages (n=3) of the sample groups inoculated with *E. coli, S. aureus,* and *C. albicans*

	E. coli (cfu)	S. aureus (cfu)	C. albicans (cfu)
PVA	>300	>300	>300
PVA0	>300	76,67±11,59	0
PVA1	0	0	0
PVA2	0	0	0
PVA3	0	0	0

4. CONCLUSION

Polyvinyl alcohol-based and ferulic acid added active food packaging films were successfully prepared by solution casting method. The MMT was used as a nanofiller material to improve the mechanical and barrier properties of the nanocomposite films, and it was observed to be exfoliated in the XRD analysis of PVA0, PVA1, and PVA2 nanocomposites. It was demonstrated by FTIR analysis that boric acid added to the nanocomposites improved of PVA hydrophilic properties by forming a crosslink with PVA. The UV-VIS analysis revealed that the transmittance percentage of the nanocomposite films decreased with the increasing amount of FA. According to the TGA results of the nanocomposite films, thermal stability has not significantly changed. However, it was observed that the addition of montmorillonite and boric acid to pure PVA resulted in an increase in the degradation temperature. It was found that active packaging films showed antibacterial activity against *E. coli* and *S. aureus* microorganisms and antifungal activity against *C. albicans* microorganism.

In summary, the sensitivity of the hydroxyl groups in the molecular chain of PVA to water molecules has been eliminated by crosslinking with boric acid. Thus, by alleviating the moisture sensitivity of PVA, it has become suitable for utilization in active packaging films. The addition of ferulic acid to the nanocomposite films synthesized for active packaging films has resulted in gaining antibacterial and antifungal properties.

5. ACKNOWLEDGMENTS

The authors wish to thank Istanbul Gedik University, where nanocomposite film synthesis was carried out in this study, and Sema Akbaba for their useful cooperation.

6. REFERENCES

1. Chen C, Tang Z, Ma Y, Qui W, Yang F, Mei J. Physicochemical, microstructural, antioxidant and antimicrobial properties of active packaging films based on poly(vinyl alcohol)/clay nanocomposite incorporated with tea polyphenols. Progress in Organic Coatings. 2018;123:176-184.Available from: <DOI>.

2. Liu G, Song Y, Wang J, Zhuang H, Ma L, Li C, et al. Effects of nanoclay type on the physical and antimicrobial properties of PVOH-based nanocomposite films. LWT – Food Science and Technology. 2014;57:562-568. Available from: <DOI>.

3. Park K, Oh Y, Panda PK, Seo J. Effects of an acidic catalyst on the barrier and water resistance properties of crosslinked poly (vinyl alcohol) and boric acid films. Progress in Organic Coatings. 2022;173:107186. Available from: <DOI>.

4. Chen C, Chen Y, ie J, u Z, Tang Z, Yang F, Fu K. Effects of montmorillonite on the properties of cross-linked poly(vinyl alcohol)/boric acid films. Progress in Organic Coatings. 2017;112:66-74. Available from: <DOI>.

5. Lim M, Kwon H, Kim D, Seo J, Han H, Khan SB. Highly-enhanced water resistant and oygen barrier properties of cross-linked poly(vinyl alcohol) hybrid films for packaging applications. Progress in Organic Coatings. 2015;85:68-75. Available from: <DOI>.

6. Miyazaki T, Takeda Y, Akane S, Itou T, Hoshiko A, En K. Role of boric acid for a poly (vinyl alcohol) film as a cross-linking agent: Melting behaviors of the films with boric acid. Polymer. 2010;51:5539-5549. Available from: <DOI>.

7. Balasubramaniam MP, Murugan P, Chenthamara D, et al. Synthesis of chitosan-ferulic acid conjugated poly(vinyl alcohol) polymer film for an improved wound healing. Materials Today Communications. 2020;25:101510. Available from: <DOI>.

8. Kokabi M, Sirousazar M, Hassan ZM. PVA–clay nanocomposite hydrogels for wound dressing. Macromolecular Nanotechnology. 2007;43:773-781. Available from: <DOI>.

9. Ochiai H, Fukushima S, Fujikawa M, Yamamura H. Mechanical and Thermal Properties of Poly(vinyl alcohol) Crosslinked by Borax. Polymer Jpurnal. 1976;1(8):131-133. Available from: <DOI>.

10. Das Mi Ghatak S. Synthesis of boron nitride from boron containing poly(viynl alcohol) as ceramic precursor. Bulletin of Materials Science. 2012 Feb;35:99-102. Available from: <DOI>.

11. Ochiai H, Fujino Y, Tadokoro Y, Murakami I. Polyelectrolyte behavior of poly(vinyl alcohol) in aqueous borax solution. Polymer Journal. 1982;14:423-426. Available from: <DOI>.

12. Lin, HL, Liu WH, Shen KS, Yu TL, Cheng CH. Weak Gel Behaviour of Poly(vinyl alcohol)-Borax Aqueous Solutions. Journal of Polymerr Research. 2003;10:171-179. Available from: <DOI>.

13. Lim M,Kwon H, Kim D, Seo J, Han H, Khan SB. Highly-enhanced water resistant and oxygen barrier properties of cross-linked poly(viynl alcohol) hybrid films for packaging applications. Progress in Organic Coatings. 2015:85;68-75. Available from: <DOI>.

14. Woo JH, Kim NH, Kim S, Park OK, Lee JH. Effects of the addition of boric acid on the physical properties of Mene/polyvinyl alcohol (PVA) nanocomposites. Composites Part B: Engineering. 2020 Oct;199:108205. Available from: <DOI>.

15. Strawhecker KE, Manias E. Structure and properties of poly(vinyl alcohol)/ Na+ montmorillonite nanocomposites. Chem. Mater. 2000;12 (no. 10):2943–2949. Available from: <DOI>.

16. Li C, Hou T, Vongsvivut J, Li Y, She X, She F, Gao W, Kong L. Simultaneous crystallization and decomposition of PVA/MMT composites during non-isothermal process. Thermochim. 2015;618:26–35. Available from: <DOI>.

17. Li C, Li Y, She X, Vongsvivut J, Li J, She F, Gao W, Kong L. Reinforcement and deformation behaviors of polyvinyl alcohol/graphene/montmorillonite clay composites. Compos. Sci. Technol. 2015;118:1–8. Available from: <DOI>.

18. Yang Y, Liu C, Wu H. Preparation and properties of poly(vinyl alcohol)/exfoliated α-zirconium phosphate nanocomposite films, Polym. Test. 2009;28: 371–377. Available from: <DOI>.

19. Johansson C, Clegg F. Effect of clay type on dispersion and barrier properties of hydrophobically modified poly(vinyl alcohol)–bentonite nanocomposites. Journal of Applied Polymer Science. 2015;132(28). Available from: <DOI>.

20. Andrade J. Martinez CG, Chiralt A. Physical and active properties of poly (vinyl alcohol) films with phenolic acids as affected by the processing method. Food Packaging and Shelf Life. 2022;33:100855. Available from: <DOI>.

21. Rodriguez-Felix F, Corte-Tarazon JA, Rochin-Wong S, et. al. Physicochemical, structural, mechanical and antioxidant properties of zein films incorporated with no-ultrafiltered and ultrafiltered betalains extract from the beetroot (Beta vulgaris) bagasse with potential application as active food packaging. Journal of Food Engineering. 2022;334:111153. Available from: <DOI>.

22. Bhowmik S, Agyei D, Ali A. Bioactive chitosan and essential oils in sustainable active food packaging: Recent trends, mechanisms, and applications. Food Packaging and Shelf Life. 2022;34:100962. Available from: <DOI>.

23. Ahmed W, Haque A, Mohibbullah Md, et. al. A review on active packaging for quality and safety of foods: Current trends, applications, prospects and challenges. 2022;33:100913. Available from: <DOI>.

24. Abbas M, Saeed F, Anjun FM, Afzaal M, Tufail T, Bashir MS. Natural polyphenols: An overview. International Journal of Food Properties. 2017;20(8):332-338. Available from: <DOI>.

25. Scalbert A, Johnson IJ, Saltmarsh M. Polyphenols: antioxidants and beyond. The American Journal of Clinical Nutrition. 2005;81(1):215-217. Available from: <DOI>.

26. Othman L, Slemien A. Antimicrobial Activity of Polyphenols and Alkaloids in Middle Eastern Plants. Frontiers. 2019; 10:293-298. Available from: <DOI>.

27. Mallakpour S, Madani M. Transparent and thermally stable improved poly (vinyl alcohol)/Cloisite Na /ZnO hybrid nanocomposite films: Fabrication, morphology and surface properties. Progress in Organic Coatings. 2012;74(3):520-525. Available from: <DOI>.

28. Cepeda MV.P, Nastasiienko NS, Kulik TV, Palianytsia BB , Alonso E, Aspromonte SG. Adsorption and thermal transformation of lignin model compound (ferulic acid) over HY zeolite surface studied by temperature programmed desorption mass-spectrometry, FTIR and UV–Vis spectroscopy. Microporous and Mesoporous Materials. 2023 Jan; 348:112394. Available from: <DOI>.

29. Qian K, Shen Z Zhang L, iang , Feng T, Zhang L. Preparation of MgF –CaF nanocomposite ceramics with high infrared transmittance. Journal of the European Ceramic Society. 2022 Dec; 42(15):7203-7208. Available from: <DOI>.

30. Feng Z, Xu D, Shao Z, Zhu P, Qiu J, Zhu L. Rice straw cellulose microfiber reinforcing PVA composite film of ultraviolet blocking through pre-cross-linking. Carbonhydrate Polymers. 2022 Nov;296:119886. Available from: <DOI>.

31. Karimi A, Daud WM. Comparison the properties of PVA/Na^+-MMT nanocomposites hydrogels prepared by physical and physicochemical crossling. Polymer Composites. 2014;37(3):897-906. Available from: <DOI>.

32. Gaume J, Gueho CT, Cros S, et.al. Optimization of PVA clay nanocomposites for ultra-barrier multilayer encapsulation of organic solar cells. Solar Energy Materials and Solar Cells. 2012;99:240-249. Available from: <DOI>.

33. Krumova M, Lopez P, Benavente R, Mijangos C, Perena M. Effect of crosslinking on the mechanical and thermal properties of poly(vinyl alcohol). Polymer. 2000;41(26):9265-9272. Available from: <DOI>.

34. Fei Y, Wang H, Gao W, Wan Y, Fu J, Yang R. Antimicrobial activity and mechanism of PLA/TP composite nanofibrous films. 2014;105:196-202. Available from: <DOI>.

35. El-Gama S, El sayed AM, Abdel-Hady EE. Effect of cobalt oxide nanoparticles on the nano-scale free volume and optical properties of biodegradable CMC/PVA films. Journal of Polymer and the Environment. 2017;26:2536-2545. Available from: <DOI>.

36. Strawhecker KE,, Manias E. Structure and Properties of Poly(vinyl alcohol)/Na+ Montmorillonite Nanocomposites. Chem. Matter. 2000;12:2943-2949. Available from: <DOI>.

37. Gao X, Li R, Hu L, Lin J, Wang Z, Yu C, Fang Y, Liu Z, Tang C, Huang Y. Preparation of boron nitride nanofibers/PVA composite foam for environmental remediation. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2020 Nov;604:125287. Available from: <DOI>.

38. Mohamed MB, Heiba ZK, Imam NG. Optical and thermogravimetric analysis of $Zn_{1-x}Cu_xS$/PVA nanocomposite films. Journal of Molecular Structure. 2018 July; 1163:442-448. Available from: <DOI>.

39. Mroz P, Bialas S, Mucha M, Kaczmarek H. Thermogravimetric and DSC testing of poly(lactic acid) nanocomposites. Thermochimica Acta. 2013 Dec;573:186-192. Available from: <DOI>.

40. Zhao W, Xu H, Yanxia L, Xu J, Luan R, Feng. Temperature-dependent transmittance nanocomposite hydrogel with high mechanical strength and controllable swelling memory behavior. European Polymer Journal. 2019 March;112:328-333. Available from: <DOI>.

41. Chen X, Wang M, Cheng J, Zhao C, Tang Z. High thermal conductivity, good electrical insulation, and excellent flexibility of FGN/PVA films based on a large sheet and narrow diameter distribution of fluorographene. Materials Today Chemistry. 2023 Ap; 29:101422. Available from: <DOI>.

42. Gou J, Lu Y, Xie M, Tang X, Chen L, Zhao J, Li G, Wang H. Antimicrobial activity in Asterceae: The selected genera characterization and against multidrug resistance bacteria. Heliyon. 2023 Ap;9(4):e14985. Available from: <DOI>.