Physical and Surface Properties of Food Packaging Paper Coated by Thyme Oil

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Paper coated with natural materials has advantages over paper coated with fossil resources, including easy recycling, renewable components, and cost-effective formulation. Coating the paper surface with thyme oil has antibacterial and antioxidant properties and is known to improve packaging product quality. In the current study, the water resistance of the materials was measured by the Cobb30 values. The base paper, the starch-coated paper, and the thyme oil and starch-coated paper had Cobb30 values of 20, 17.5, and 15.7 g/m^2, respectively. The tensile strength index of uncoating and coating paper samples was, respectively (machine direction M.D.) 64.3 and 64.7, and (cross direction C.D.) 32.2 and 37.2. The bursting strength index results were 72.7 and 84.0. Hence, according to the tensile strength results, the treated paper burst strength values were higher than the base paper samples. The starch and thyme oil coatings formed a film layer on the paper surface, which may have helped impart better burst-strength properties. Besides, compared to the untreated base papers, the surface of the coated papers was denser and smoother, with a less porous structure, according to SEM results. In addition, resistance features of papers that are desired in the end-use of paper are shown in this work based on paper strength property tests.

DOI: 10.15376/biores.18.4.7333-7340

Keywords: Antimicrobial surface treatment; Paper coating; Thyme oil coating

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INTRODUCTION

Various types of paper and paperboard materials are used in the packaging of food and beverages. As paper and paperboard are used in food packages, the demand for antioxidant and antibacterial products has gradually increased. Packaging materials that come into contact with food are subjected to special regulations throughout the world, so antibacterial food packaging products have gained importance. The goal of this research was to make packaging products suitable for contact with food by coating their surfaces with antioxidant substances to comply with stated regulations. The development of an antibacterial product will be a significant contribution. An additional goal of this study was to develop a method for determining the antimicrobial activities of food packaging paper.

The paper has a hygroscopic nature, as it absorbs water vapor, gases, and aromas. Synthetic polymers such as polyvinyl alcohol (PVA) are generally used to develop the barrier features of paper and paperboard. These particular chemicals serve the purpose of occupying empty spaces and enhancing the density of paper and paperboard materials. In recent times, there has been a notable shift toward the utilization of environmentally sustainable, renewable, and biodegradable materials in the development of surfaces, as opposed to the utilization of synthetic chemicals (Aloui *et al.* 2011).

Essential oils have been used in coating food contact papers (Paolucci and Volpe 2021). Qualitative analysis by solid-phase microextraction and determination of cinnamaldehyde in sliced bread was performed, and a strong correlation between the inhibition of the mold and the amount of cinnamaldehyde in the bread was found (Rodríguez *et al.* 2007).

The use of coated paper for wrapping peaches and plums with sodium permanganate, potassium sorbate, and potassium metabisulphite was found to retain the freshness of peaches and plums (Rudra *et al.* 2013). According to another study, the use of cinnamon essential oil with micro-perforated polypropylene increased the shelf-life of bakery products from 3 d to 10 d with maximum quality and safety (Gutiérrez *et al.* 2009).

According to research by Rhim *et al.* (2006), coating paper with biopolymer substances improved the water barrier features. It was reported that the physical features of paper and paperboard coated with noble proteins and alginate depended heavily on the coating material. This study investigated antimicrobial packaging materials made with low-density polyethylene (LDPE) coated with treated thyme (*Thymus vulgaris*) and oregano (*Origanum vulgare*). The objective was to demonstrate that films developed by extrusion and the incorporation of 4% (w/w) of essential oils had a higher inhibitory effect than films without the essential oil coating. Such active films may have been used as food packaging materials (Solano and Gante 2011).

The paper has hygroscopic properties, as it has the ability to adsorb water vapor, gases, and scents. Polyvinyl alcohol (PVA), a type of synthetic polymer, is commonly employed in the enhancement of the barrier properties of paper and paperboards. These particular chemicals serve to occupy empty spaces and enhance the compactness of paper and paperboard materials (Aloui *et al.* 2011).

The current study investigated paper qualities coated with thyme (*Thymus vulgaris*) oil mixed with cationic starch ether. The objective was to demonstrate the physical, and mechanical properties of paper coated with thyme oil were not affected by coating materials, and that the coated paper with essential oil has possible antimicrobial effects and could be recommended in food and other industrial applications.

The goal of this research was to make packaging products suitable for contact with food by coating their surface with antioxidant substances. The development of an anti-bacterial product will be a significant contribution. An additional goal of this study was to develop a method of determining the antimicrobial activities of food package papers.

EXPERIMENTAL

Materials

In this study, thyme oil was used as an antimicrobial agent. Natural oregano oil was supplied ready-made from herbalists in Karaman, Turkey. For the coating process, butcher wrapping papers were preferred. The cationic starch ether sample was purchased from Emstald-Stärke GmbH (Emlichheim, Germany). The wrapping paper was obtained from a local company in Turkey.

Methods

Cationic starch preparation

The cationic starch samples were prepared to a 5% solid content. Viscosity was evaluated at 75 °C at a mixing speed of 100 rpm with a Brookfield DV-II + Viscometer (Middleboro, MA, USA), with a spindle #2. Distilled water was used throughout the process.

Surface treatment with thyme oil

For the preparation of the thyme oil-starch solutions, 10% of the thyme oil samples were added to the 70 °C starch samples. The surface treatment material was emulsified with vigorous mixing at 2000 rpm. The paper surface was coated with a #0 bar and applicator speed of 3 cm/s (K202; RK Print Coat Instruments, Litlington, UK) on a single side. After the surface sizing treatment, the paper samples were kept at a constant temperature of 23 °C and a relative humidity of 50% for 24 h. The water absorption of the paper samples was measured by the $Cobb_{30}$ value, in accordance with the ISO 535 standard (2014). The paper strength properties were performed at Istanbul University-Cerrahpaşa, Department of The Forest Product Chemistry and Technology. A Zwick universal testing machine was used to evaluate the tensile strength and the bursting strength, in accordance with the ISO 1924-2 (2008) and ISO 2758 (2014) standards.

The mechanical features of coated papers are controlled by the substrate or the base layer. Still, the tensile features of coated papers basically depend on the coating weight (Levlin 1999). In one study, the tensile resistance and the elastic modulus of coated papers increased as the coating weight increased from 5 to 16 g/m² (Khwaldia 2013). According to another study, the tensile strength of paper decreased after it was coated with crosslinked alginate and soy protein isolate (Rhim *et al.* 2006). Another study also confirmed this essential drawback during the manufacturing of active wrapping paper (Rudra *et al.* 2013). Similar results were obtained by Kjellgren *et al.* (2006) and Khwaldia (2013), where oil-proof papers were coated with chitosan and hydroxypropyl methylcellulose (HPMC). The most common aqueous absorption test is the Cobb test, outlined in the ISO 535 standard (2014). The Cobb test quantifies the water absorption of a sample in grams per square meter (g/m²) for a specified duration. The primary purpose of this test is to provide an indicator of the extent of size (Levlin 1999).

Surface morphology

The microstructures of the uncoated and thyme oil-coated papers were evaluated using a field-emission scanning electron microscope (SEM) (SU5000; Hitachi, Tokyo, Japan).

A visible layer was formed on the surface of the papers that were coated with the thyme oil solution. When viewed by the SEM, the coating solution densely closed the air gaps between the fibers.

RESULTS AND DISCUSSION

Coating Application

Compared to the base starch solution, the thyme oil starch formulation had a viscosity of 31 cP at 75 °C, evaluated at 100 rpm using the viscometer with a #2 spindle.

The solution was applied to the base paper at 65 to 75 °C, and the sizing weights of the paper sample were increased by 4.2 ± 1 g/m^2 compared to the base paper.

Paper Properties

The tensile strength results were increased slightly by the coating process, as shown in Fig. 1. The tensile strength may have been affected by the weakening of the inter-fiber bonding in both the machine direction (MD) and the cross direction (CD) of the paper samples.

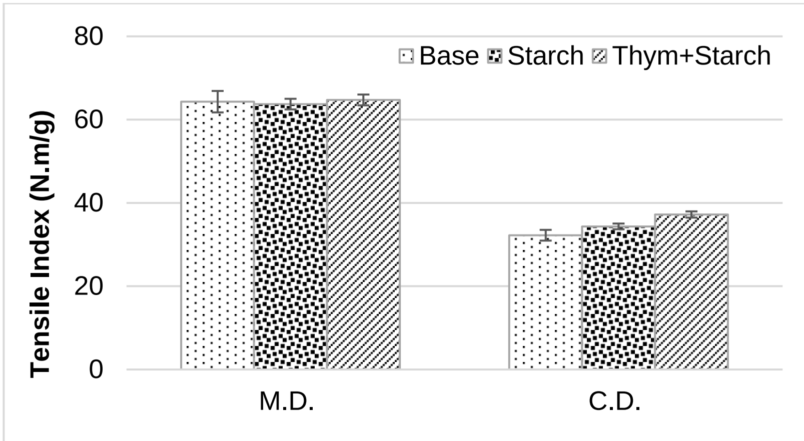

Fig. 1. Tensile strength index results for the paper samples

In contrast to the tensile strength index results, the coated paper burst strength values were higher than those of the base paper samples. The starch and thyme oil coatings formed a film layer on the paper surface, which may have helped impart better bust strength properties.

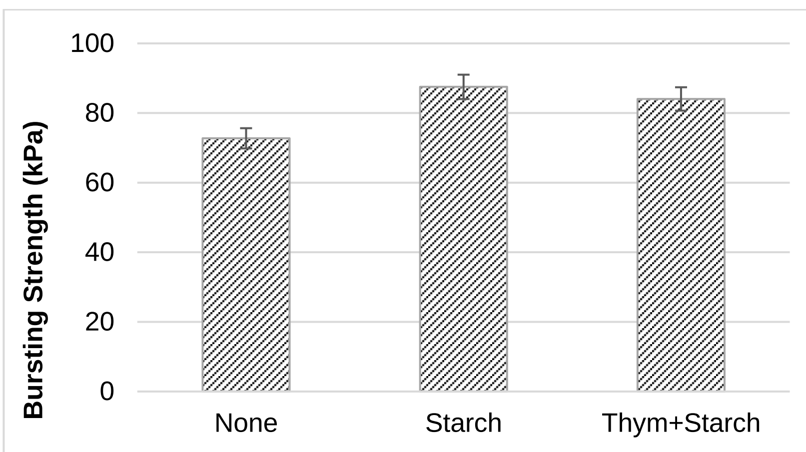

Fig. 2. Bursting strength results of the paper samples

The Cobb$_{30}$ values of the base paper, the starch-coated paper, and the thyme oil and starch-coated paper were 20, 17.5, and 15.7g/m^2, respectively. The Cobb$_{60}$ values are shown in Table 1.

The surface coating application with the starch and thyme oil solution had a lower Cobb$_{60}$ value compared to the paper with the starch coating alone (Table 1). The viscosity and structure of the thyme oil may have diminished the coating effect of the starch.

Table 1. $Cobb_{60}$ Values of the Uncoated and Thyme Oil-coated Papers

Coating	Standard Deviation	$Cobb_{30}$ (g/m^2)	$Cobb_{60}$ (g/m^2)
None	1.49	20.0	24.0
Starch	1.86	17.5	22.3
Thyme oil and starch	2.15	15.7	25.1

SEM Results

The uncoated and coated papers were examined by SEM to observe their structure, as shown in Fig. 3. The coated and uncoated papers had very different structures. Compared to the uncoated papers, the surface of the coated papers was denser and smoother with a less porous structure (Zhang *et al.* 2021).

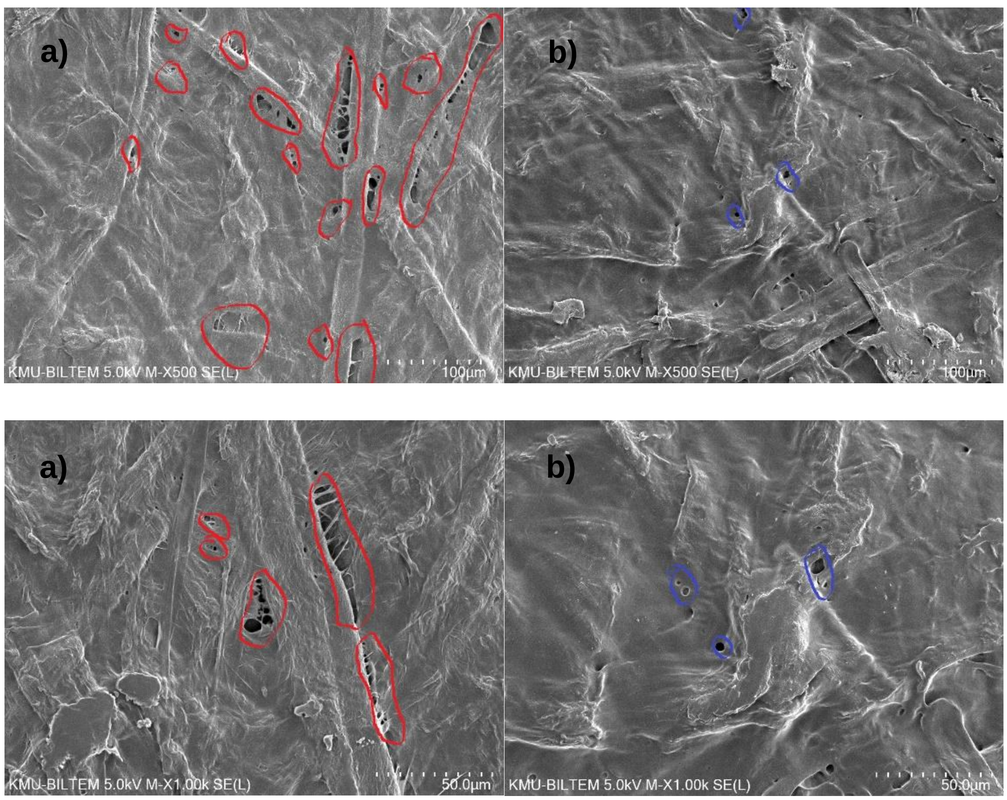

Fig. 3. SEM images of the a) uncoated and b) thyme oil-coated papers

FTIR Results

In Figure 4, it was clearly apparent that there were strong stretching vibrations at 3600 to 2800 cm^{-1} and 1800 to 750 cm^{-1} wavenumbers of thyme-coated paper, as compared to the normal paper without coating. There was strong chemical bonding of the reactive groups of thyme molecules with –OH, –CH, $-CH_2$, and $–CH_3$ groups of paper at the wavenumbers of 3600 to 2800 cm^{-1}, and moreover the region of 1800 to 750 cm^{-1} wavelength is mainly associated with –C=0, -CHO, -OH, and -CH groups bonding with paper. These strong vibrations are actually added to the paper by the coating of thyme molecules, which showed strong interaction with the paper.

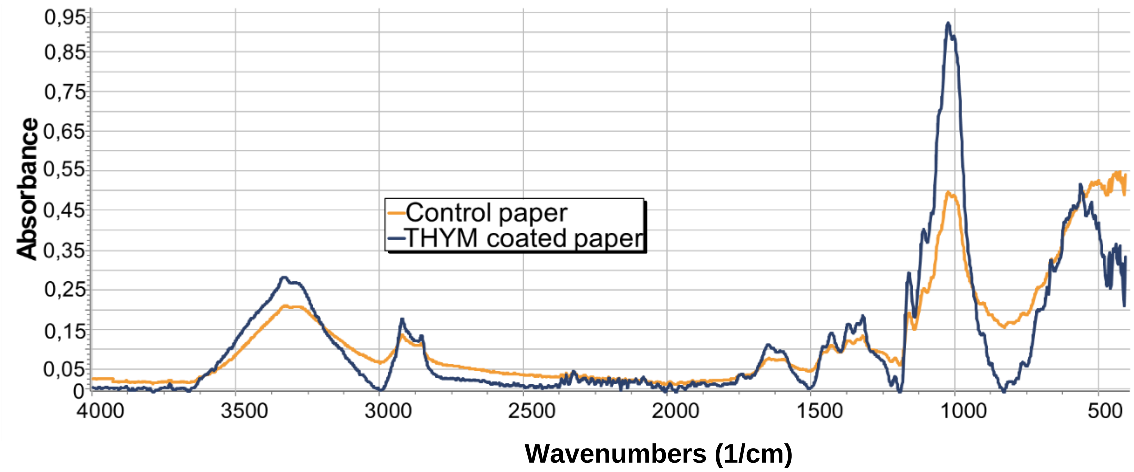

Fig. 4. FTIR results of the uncoated and thyme oil-coated papers

The coated and uncoated papers had very different structures. As expected, compared with uncoated papers, the surface, coated with thyme oil was much more continuous and homogeneous (Zhu *et al.* 2023). Compared to the uncoated papers, the surface of the coated papers was denser and smoother with a less porous structure (Zhang *et al.* 2021). In the literature, there have been several results showing that plant essential oils thyme or cinnamon have antibacterial effects (Gutiérrez *et al.* 2009; Solano and Gante 2011). SEM results indicated that the paper coated had good surface incorporation with thyme essential oil which can give an antibacterial effect in food and other applications.

CONCLUSIONS

1. The described research resulted in an antimicrobial paper packaging material that can be used as food packaging. Simultaneously, an examination was conducted on the alterations in the physical characteristics of the paper.
2. The $Cobb_{30}$ values of the base paper, the starch-coated paper, and the thyme oil and starch-coated paper were recorded as 20, 17.5, and 15.7 g/m^2, respectively. The tensile strength index of uncoated and coated paper samples in the machine direction (M.D.) were 64.3 and 64.7, respectively. In the cross direction (C.D.), the tensile strength index for uncoated and coated paper samples was 32.2 and 37.2, respectively. The results obtained for the bursting strength index were 72.7 and 84.0.
3. A typical phenomenon observed in coated sheets is the fall in Cobb value. Nevertheless, the findings of this study indicate that the impact on the physical properties of the paper was minimal, as evidenced by the observed rise in shrinkage and burst values.
4. Based on the findings of this study, it is advisable to explore the synergistic characteristics of different binders to optimize the utilization of coating materials.

ACKNOWLEDGEMENTS

Acknowledgments: The author would like to thank Professor Sulhattin Yaşar at Karamanoglu Mehmetbey University for his help in FTIR analysis.

REFERENCES CITED

Aloui, H., Khwaldia, K., Slama, M. B., and Hamdi, M. (2011). "Effect of glycerol and coating weight on functional properties of biopolymer-coated paper," *Carbohydrate Polymers* 86(2), 1063-1072. DOI: 10.1016/j.carbpol.2011.06.026

Gutiérrez, L., Sánchez, C., Batlle, R., and Nerín, C. (2009). "New antimicrobial active package for bakery products," *Trends in Food Science & Technology* 20(2), 92-99. DOI: 10.1016/j.tifs.2008.11.003

ISO 535 (2014). "Paper and board – Determination of water absorptiveness – Cobb method," International Organization for Standardization, Geneva, Switzerland.

ISO 1924-2 (2008). "Paper and board – Determination of tensile properties – Part 2: Constant rate of elongation method (20 mm/min)," International Organization for Standardization, Geneva, Switzerland.

ISO 2758 (2014). "Paper – Determination of bursting strength," International Organization for Standardization, Geneva, Switzerland.

Khwaldia, K. (2013). "Physical and mechanical properties of hydroxypropyl methylcellulose–Coated paper as affected by coating weight and coating composition," *BioResources* 8(3), 3438-3452. DOI: 10.15376/biores.8.3.3438-3452

Kjellgren, H., Gällstedt, M., Engström, G., and Järström, L. (2006). "Barrier and surface properties of chitosan-coated greaseproof paper," *Carbohydrate Polymers* 65(14), 453-460. DOI: 10.1016/j.carbpol.2006.02.005

Levlin, J.-E. (1999). "General physical properties of paper and board," in: *Pulp and Paper Testing*, J.-E. Levlin, and L. Söderhjelm (eds.), Finnish Paper Engineers' Association, Espoo, Finland, pp. 137-162.

Paolucci, M., and Volpe, M. G. (2021). "The effect of novel packaging technology on food safety and quality," *Foods* 10(2), 269-271. DOI: 10.3390/foods10020269

Rhim, J.-W., Lee, J.-H., and Hong, S.-I. (2006). "Water resistance and mechanical properties of biopolimer (alginate and soy protein) coated paperboards," *LWT - Food Science and Technology* 39(7), 806-813. DOI: 10.1016/j.lwt.2005.05.008

Rodríguez, A., Batlle, R., and Nerín, C. (2007). "The use of natural essential oils as antimicrobial solutions in paper packaging. Part II," *Progress in Organic Coatings* 60 (1), 33-38. DOI: 10.1016/j.porgcoat.2007.06.006

Rudra, S. G., Singh, V., Jyoti, S. D., and Shivhare, U. S. (2013). "Mechanical properties and antimicrobial efficiency of active paper for primary packaging of fruits," *Food Bioscience* 3, 49-58. DOI: 10.1016/j.fbio.2013.07.002

Solano, A. C. V., and Gante, C. R. (2011). "Two different processes to obtain antimicrobial packaging containing natural oils," *Food Bioprocess Technology* 5, 2522-2528. DOI: 10.1007/s11947-011-0626-3

Zhang, J., Guo, Z., Chen, S., Dong, H., Zhang, X., Qin, Y., Yao, C., and Xu, F. (2021). "High-barrier, strong, and antibacterial paper fabricated by coating acetylated cellulose and cinnamaldehyde for food packaging," *Cellulose* 28, 4371-4384. DOI: 10.1007/s10570-021-03778-x

Article submitted: November 8, 2021; Peer review completed: February 5, 2022; First revision received: August 9, 2022; Second revision received and accepted: August 11, 2023; Published: September 7, 2023.
DOI: 10.15376/biores.18.4.7333-7340