Effect of Polyhydroxybutyrate and Ethyl Cellulose for Barrier Coating of Kraft Paper

Dong Gun Lim,[a] Yong Ju Lee,[b] Ji Min Lee,[b] Jae Hyeop Kim,[b] Tai Ju Lee,[c] and Hyoung Jin Kim [b,]*

Poly(3-hydroxybutyrate) (PHB), a biodegradable polymer, has been studied as a substitute for petroleum-based polymers used for barrier coating to improve the barrier and mechanical properties of paper. In this study, ethyl cellulose (EC), a cellulose derivative, was used to prepare a polymer blend for enhancing the barrier properties of PHB. The prepared PHB/EC blend was then applied as a paper coating material. Additionally, the barrier and mechanical properties of the PHB/EC blend-coated paper based on the PHB/EC mixing ratio and coating weight were analyzed. The results showed that the EC could act as a binder for the PHB/EC blend-coated paper. Consequently, the PHB/EC blend-coated paper exhibited significant improvements in mechanical and barrier properties, including a substantial increase of over 100% in internal bond strength, more than 20% in tensile strength, exceeding 60% enhancement in water resistance, and a remarkable increase of over 90% in air permeability.

DOI: 10.15376/biores.19.1.1618-1632

Keywords: Polyhydroxybutyrate; Ethyl cellulose; Biodegradable polymers; Barrier properties; Eco-friendly packaging materials; Kraft paper

*Contact information: a: Packaging Research Team, Pulmuone Institute of Technology, 29, Osongsaengmyeong 10-ro, Osong-eup, Heungdeok-gu, Cheongju-si, Chungcheongbuk-do, 28220, Republic of Korea; b: Department of Forest Products and Biotechnology, Kookmin University, 77 Jeongneung-ro, Seongbuk-gu, Seoul 02707 Republic of Korea; c: National Institute of Forest Science, Department of Forest Products and Industry, Division of Forest Industrial Materials, 02455, Seoul, Republic of Korea; * Corresponding author: hyjikim@kookmin.ac.kr*

INTRODUCTION

With the recent growth of e-commerce and delivery markets and the increasing number of single-person households, the packaging industry is continuously expanding. Consequently, the issue of packaging waste is at the forefront of environmental and sustainability discussions. To address this issue, eco-friendly packaging materials with excellent recyclability and biodegradability, such as paper, have gained remarkable attention compared with petroleum-based packaging materials. Paper, which comprises hydrophilic cellulose with a porous structure, has limited applications as a direct food packaging material due to its low water barrier properties. To achieve the desired level of barrier performance, additional surface treatment is required. Petroleum-based polymers, which are non-biodegradable, are commonly used as surface treatment materials to enhance the barrier properties of paper. Over the last few decades, the predominant approach in surface treating paper has involved the use of polyethylene (PE), ethylene vinyl alcohol (EVOH), and poly(ethylene terephthalate) (PET) as coating materials (Andersson 2008). However, this practice hinders the recyclability and biodegradability of paper, exacerbating environmental issues (Khwaldia *et al.* 2010).

Biodegradable polymers have garnered attention as alternative materials to conventional non-biodegradable polymers in various industries such as electronics, software, and fibers, *etc.* (Avérous and Pollet 2012). Biodegradable polymers can be broadly categorized into agro-polymers derived from biomass and biopolyesters derived from organic compounds, natural units, or synthetically derived monomers. Agro-polymers encompass polysaccharides such as cellulose, starch, chitosan, pectin, and proteins such as casein. On the other hand, biopolyesters include polyhydroxyalkanoates (PHAs) synthesized by microorganisms, and polymers such as polylactic acid (PLA) and poly(ε-caprolactone) (PCL), which are synthesized from starch or petroleum-based sources (Avérous and Pollet 2012; Lim *et al.* 2021). In the packaging field, extensive research has been conducted to explore the application of paper coating using biodegradable polymers (Rastogi and Samyn 2015, 2016).

Polyhydroxyalkanoates (PHAs), which are bio-based and biodegradable polymers synthesized by microorganisms, exhibit excellent biodegradability even in marine environments (Wang *et al.* 2018). Among PHA polymers, poly(3-hydroxybutyrate) (PHB), which possesses mechanical properties comparable to those of typical plastics, such as polypropylene, has been widely studied (Harding *et al.* 2007). PHB also has suitable packaging characteristics, such as high barrier properties (Khosravi-Darani 2015). Previous research on incorporating PHB as a coating material for paper has demonstrated improvements in the barrier properties of paper (Cyras *et al.* 2007, 2009; Safari and van de Ven 2015; Lim *et al.* 2021). However, challenges in commercialization persist because of the high production cost compared with those of conventional polymers. Thus, the application of alternative polymers and additives is required (Bugnicourt *et al.* 2014). Vaidya *et al.* (2019) investigated a reduction in the usage of PHB while securing its properties through the application of nanoparticles and polymer monomers. Additionally, Chen *et al.* (2016) conducted research aiming to enhance the physical properties by manufacturing blends through the mixture of other biodegradable polymers such as polybutylene succinate (PBS), PCL, and PLA.

Producing polymer blends, which involves the combination of two or more polymers, can be a cost-effective approach (Muthuraj *et al.* 2018). In this regard, attempts have been made to incorporate cellulose in the production of PHB-based biodegradable polymer blends to improve their mechanical and chemical properties (Zhang *et al.* 1997; Finelli *et al.* 1998; Chan *et al.* 2011; Costa *et al.* 2013; Chen *et al.* 2016).

Cellulose, a renewable material, can be modified chemically to produce different cellulose derivatives with various properties (Liu *et al.* 2021). Rastogi and Samyn (2015, 2016) manufactured a superhydrophobic coating using nanofibrillated cellulose (NFC) as a binder for PHB nanoparticles. They also improved the properties of the coating by blending PHB with hydrophobically modified microfibrillated cellulose (MFC). Additionally, Seoane *et al.* (2018a,b) enhanced the interfacial bonding and properties between PHB and paper by utilizing cellulose nanocrystals (CNC). Among cellulose derivatives, research has predominantly focused on exploring the compatibility, crystallization behavior, and structural characteristics of polymer blends created by combining cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) with PHB (Suttiwijitpukdee *et al.* 2011, 2012; Yamaguchi and Arakawa 2007; Jain and Tiwari 2015). These studies have demonstrated the enhanced mechanical properties and improved biodegradation behavior of PHB resulting from its blending with CAB and CAP. Meanwhile, ethyl cellulose (EC) possesses hydrophobicity, excellent mechanical properties, film-forming ability, biodegradability, and nontoxicity, thereby making it suitable as a coating material (Li *et al.* 2015; Heinze *et al.* 2018; Ahmadi *et al.* 2022). Accordingly, studies have been conducted on the synthesis of coating mixtures by combining EC and PHB (Zhang *et al.* 1997; Finelli *et al.* 1998; Chan *et al.* 2011; Costa *et al.* 2013; Chen *et al.* 2016). The cited authors investigated the structure, crystallization behavior, mechanical properties, and biomedical applications of PHB/EC blends. However, there has been no research evaluating the potential application of PHB/EC blends as barrier coating materials for packaging, particularly in the context of paper coatings. In this study, a PHB/EC blend was applied as a barrier coating material to enhance the barrier properties of paper packaging materials.

EXPERIMENTAL

Materials

Kraft paper was used as a base for PHB/EC blend coating. The physical properties of the kraft paper are summarized in Table 1. The OptiTopo surface deviation (OSD) roughness was measured using OSD equipment (L&W, Sweden).

Table 1. Properties of Base Paper

Basis Weight (g/m^2)	Thickness (µm)	Apparent Density (g/cm^3)	Roughness (OSD, µm)
78.8 ± 0.9	121.8 ± 4.5	0.647 ± 0.011	2.39 ± 0.05

With a molecular weight of 550,000 g/mol and a nominal granule size of 5 mm, PHB pellets obtained from Goodfellow (Korea) were used for the PHB/EC blend coating preparation. Moreover, EC powder with an ethoxyl content range of 48.0% to 49.5% obtained from Sigma-Aldrich was used.

Coating

The coating materials were prepared by dissolving PHB pellets and EC powder in chloroform at 70 °C while stirring for 30 min. The mixing ratio of PHB and EC was adjusted based on the conditions shown in Table 2 to produce PHB/EC blends. The PHB/EC blend solutions in Table 2 were controlled to a concentration of 10% ± 1% and coated on the top side of the base paper.

Table 2. Blending Ratio of PHB/EC

Code	Blending Ratio (w/w)	
	PHB	EC
PHB	100	0
EC25	75	25
EC50	50	50
EC75	25	75
EC100	0	100

The coating was performed using a 4-sided applicator and an auto bar coater (Gist, Korea) at a 20-mm/s speed (Fig. 1). The gap size of the applicator was adjusted to 60 to 200 µm to control coating weights of 6, 12, and 18 g/m^2.

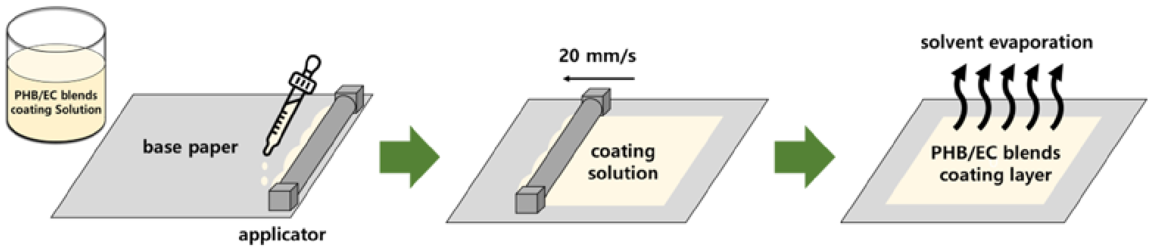

Fig. 1. Schematic of preparing PHB/EC-coated paper

Field-emission scanning electron microscopy (FE-SEM, JSM 7401F, JEOL, Japan) was employed to examine the continuity of the coating layer and the extent of fiber and pore exposure in the base paper. In addition, the thickness of the coated paper was measured using a thickness tester (L&W, Sweden), following ISO 534 (2011).

The internal bonding strength between the coating layer and base paper was evaluated using a Scott-type tester (IDM test, Spain) according to TAPPI method T 569 to assess the adhesion ability of the PHB/EC blend on the base paper.

Water Contact Angle (WCA)

WCA data was obtained using a drop shape analyzer (DSA 100, Krüss GmbH, Germany). The measurement duration was 30 sec with an interval of 1 sec. A droplet of each solution (5 μL) was carefully deposited on the coated paper surface; subsequently, the shape and contact angle of the droplet were determined. At least five measurements were conducted for each condition.

Barrier Properties

The air permeability, water absorption, water vapor transmission rate (WVTR), and oil resistance of the PHB/EC blend coating were analyzed. Air permeability was assessed using an air permeance tester (L&W, Sweden) following ISO 5636-3 (2013). Furthermore, water absorption was evaluated following ISO 535 (2014), with the absorption rate (Cobb size degree) measured at room temperature for 1,800 s.

For the analysis of water vapor transmission rate (WVTR), the calcium chloride method outlined in KS T 1305 was employed, and measurements were performed at 40 °C and 90% relative humidity for more than 24 h. Oil resistance was also evaluated using the Kit test as per TAPPI method T 559.

Mechanical Properties

Tensile strength and strain rate were analyzed using a tensile tester (L&W, Sweden) following ISO 1924-3 to evaluate the mechanical properties of the PHB/EC blend-coated papers.

RESULTS AND DISCUSSION

Coating Properties of Polyhydroxybutyrate/Ethyl Cellulose

Table 3 and Fig. 2 illustrate the surface analysis and thickness measurement results of the PHB-coated papers using FE-SEM at a 100× magnification. The coverage of the PHB at various coating weights was investigated. At first, the thickness gradually increased with coating weight and then increased rapidly when the coating weight reached 18 g/m². These findings agree with the results of Cyras *et al.* (2007, 2009), suggesting that during the coating process, the coating initially fills voids between fibers and then forms a continuous coating layer that completely covers the fibers.

Figure 3 shows the FE-SEM images of the PHB/EC-coated papers (coating weight: 18 g/m^2) with different PHB/EC blend mixing ratios. As the EC proportion increases, even at the same coating weight, fiber contours on the base paper become more distinct. Owing to the enhanced base paper–EC interaction induced by hydrogen bonding, the coating polymer deeply penetrated the voids between fibers and formed a coating layer that enveloped individual fibers. This is attributed to the affinity of the base paper and PHB/EC blend coating layer.

Table 3. Thickness of the Base Paper and PHB-coated Paper with Different Coating Weights

Coating Weight	Thickness (μm)
Base paper	121.8 ± 4.5
6 g/m^2	121.3 ± 4.4
12 g/m^2	123.3 ± 4.9
18 g/m^2	128.6 ± 4.6

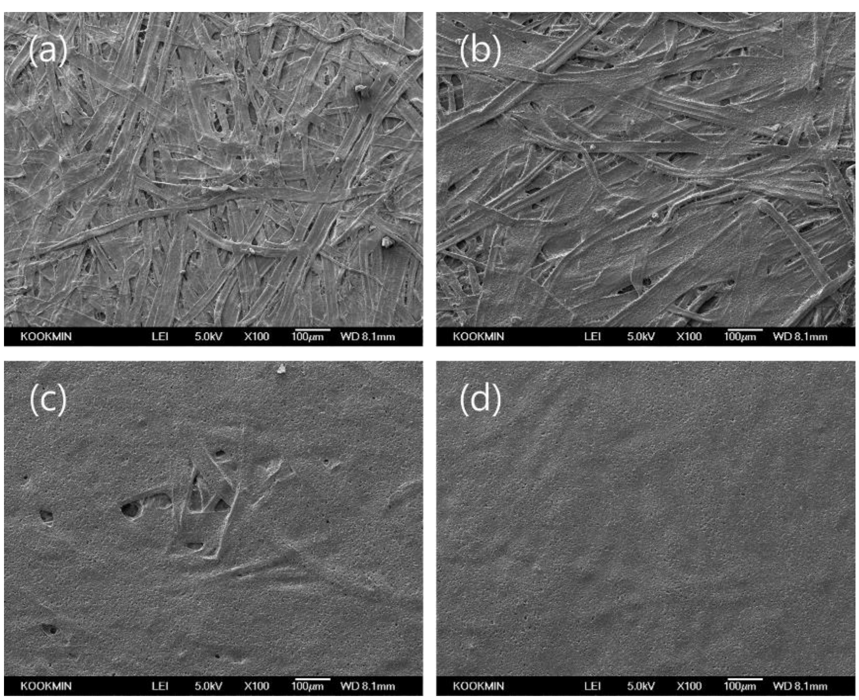

Fig. 2. SEM images (×100) of the PHB-coated kraft papers with different coat weights (a: base paper; b: 6 g/m^2; c: 12 g/m^2; and d: 18 g/m^2)

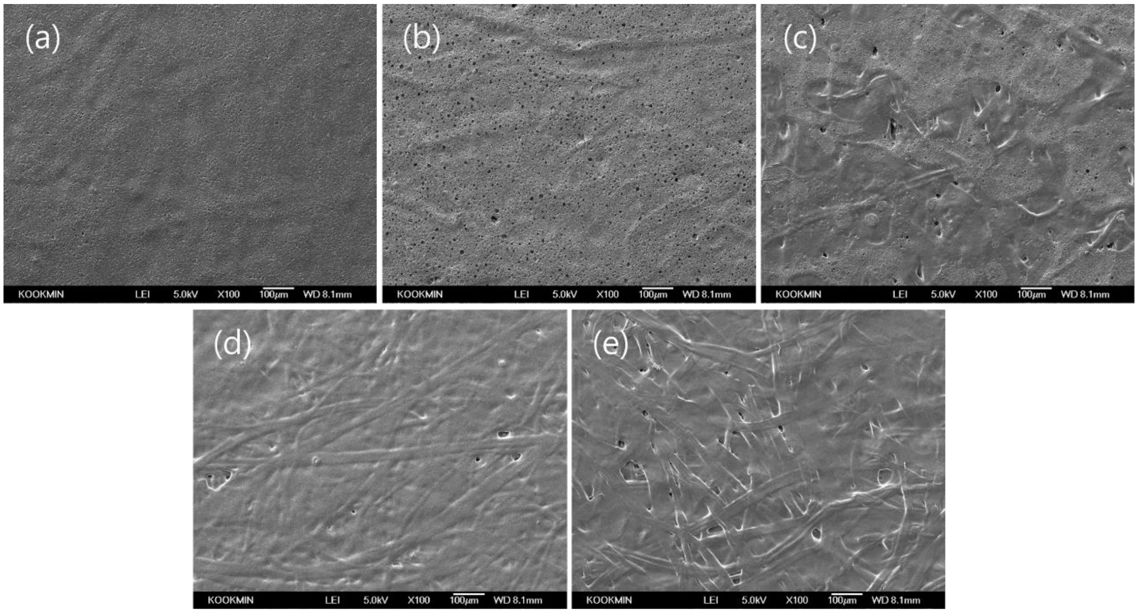

Fig. 3. FE-SEM images (×100) of 18 g/m^2 PHB/EC blend-coated kraft paper with different polymer blending ratios: (a) PHB, (b) EC25, (c) EC50, (d) EC75, and (e) EC100

The internal bond strength between the coating layer and base paper is a critical factor that influences the performance of coated paper (Seoane *et al.* 2018).

As shown in Fig. 4 and Fig. S1, when only PHB was applied to the coating material, the internal bond strength was considerably decreased by 41% compared with that of the base paper. This is attributable to the low compatibility between PHB and cellulose fibers, resulting in the easy delamination of the coating layer from the base paper. The internal bond strength increased when the EC was added. The addition of EC enhanced the PHB compatibility with the fibers, and the polymer blends strongly interacted with the base paper.

Furthermore, the separation with the base paper was not achieved when the EC mixing ratio was increased to more than 75%, which hindered measurement. The results demonstrated that EC can improve the physical properties of PHB-coated paper by acting as a binder for interaction with the base paper.

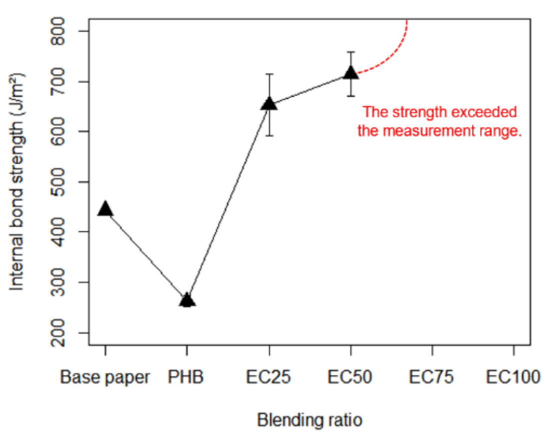

Fig. 4. Internal bond strength of PHB/EC-coated paper (coating weight: 18 g/m^2) depending on PHB/EC blending ratio

Water Contact Angle

Figures 5 and 6 show the droplet shapes and changes in water contact angles of PHB/EC blend-coated papers after 30 s. At 0 s, the contact angle of the bare PHB coating was highest (91.7°) (Fig. 6), and it decreased with an increase in the EC blending ratio. This is attributable to the changes in the surface contour of the coating materials, indicating that PHB exhibits stronger hydrophobicity than EC. As shown in Fig. 3 and Fig. S2, PHB/EC blends deeply penetrated paper structure, contributing to the formation of a rough surface. This roughness may play a role in enhancing wettability of a liquid on paper surface (Modaressi and Garnier 2002; Ko *et al.* 2020). However, the contact angle of the bare PHB coating decreased to 69.8° after 30 s. Figures 5(a) and 6 show a remarkable decrease in contact angle for the bare PHB as contact time elapses. Conversely, for the PHB/EC coating, the contact angle did not change. These results suggest that the addition of EC to PHB led to a decrease in hydrophobicity but exerted a positive effect on the formation of condensed coating surfaces without pores. This implies that incorporating EC into PHB coatings can effectively prevent the anomalous development of surface pores typically observed over time in PHB coatings.

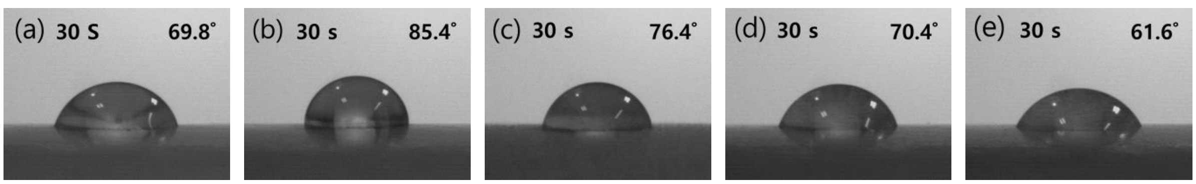

Fig. 5. Water droplets on PHB/EC blend-coated paper at 30 s (coating weight: 18 g/m^2) (a: PHB, b: EC25, c: EC50, d: EC75, e: EC100)

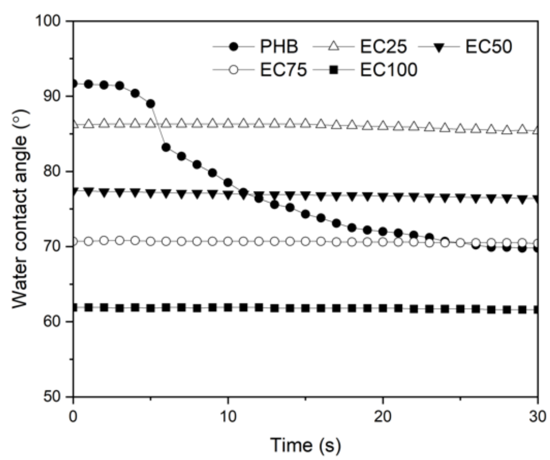

Fig. 6. Changes in water contact angles of PHB/EC-blend coated paper (coating weight: 18 g/m^2) between 0 and 30 s

Barrier Properties

Air permeability

Figure 7 shows changes in the air permeability of the coated papers according to the PHB/EC blend mixing ratio and coating weight. There was no considerable difference in porosity with different mixing ratios. However, a noticeable difference was observed at a coating weight of 18 g/m^2. These results suggest low coverage at 6- and 12-g/m^2 coating weights. To achieve a uniform coating layer for creating barrier properties, the coating weight should be controlled above 18 g/m^2.

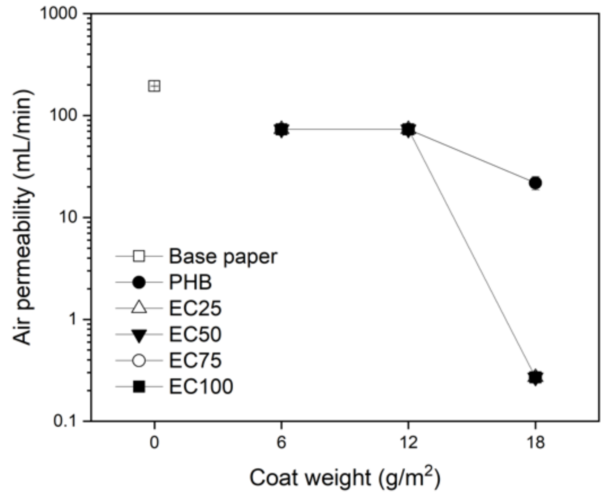

Fig. 7. Changes in the air permeability of PHB/EC blend-coated paper depending on polymer blending ratio and coating weight

Cobb size degree

Figure 8 shows changes in the Cobb size degree (water sorption) of PHB/EC blend-coated papers. The water absorbency decreased with an increase in coating weight and EC content. This is attributable to the coverage of exposed fibers and pores by the coating materials, thereby reducing the contact area with moisture. However, when PHB was coated with weights of 6 and 12 g/m^2, increased water absorbency was observed for all substrates compared with the base paper (Fig. 8(a)). This is attributable to the presence of residual moisture between the coating layer and base paper when removing surface moisture from the coating layer during water absorbency measurements caused by moisture penetration into the porous PHB coating layer (Fig. 2). To achieve a continuous coating in the paper structure, a coating weight of 18 g/m^2 is deemed suitable.

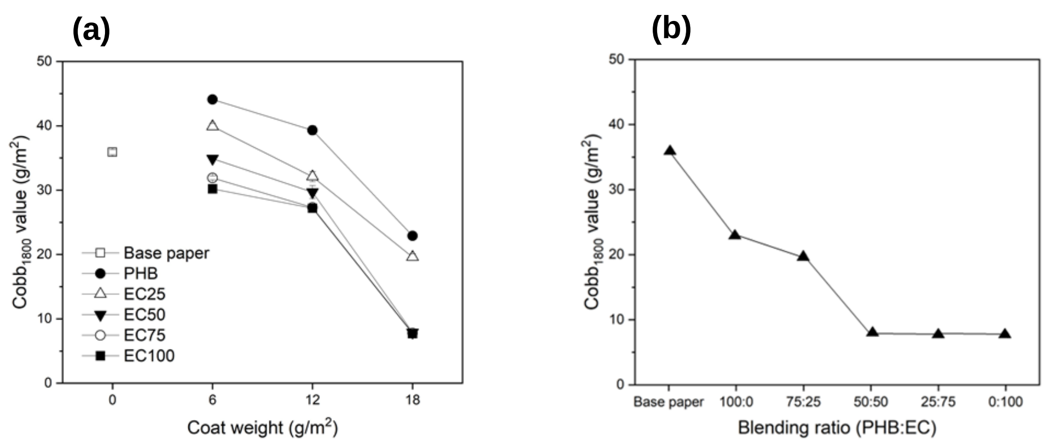

Fig. 8. Changes in the Cobb value of PHB/EC blend-coated paper depending on polymer blending ratio at (a) various coating weights and (b) 18-g/m^2 coating weight

As shown in Fig. 8(b), when the EC content of the PHB/EC blend exceeded 50%, the water absorbency decreased, indicating that an improvement in water resistance was proportional to the EC content. This is attributable to the interaction between EC and base paper, as shown in Fig. 3, resulting in the blockage of moisture penetration into fibers. In the amorphous EC polymer domain, moisture permeation primarily occurs. However, it is observed that when the crystalline PHB is mixed at an optimal ratio, a higher water resistance is achieved due to a synergistic effect (Cho *et al.* 2016). Therefore, a 50:50 PHB/EC blend mixing ratio was determined to achieve the highest water resistance.

Water vapor transmission rate

Figure 9 shows changes in the WVTR of coated papers according to the PHB/EC blend mixing ratio and coating weight. The WVTR also decreased with an increase in coating weight, and EC contributed to the improvement of barrier properties against moisture. Here, the results described the highest moisture barrier properties under the EC50 condition, with ~60% reductions in WVTR compared with that of the base paper. This is attributable to EC's ability to restrict PHB crystallization (Chen *et al.* 2016), leading to the formation of smaller crystalline domains and subsequently reducing the PHB coating layer's porosity (Safari and van de Ven 2015). Generally, in the domain of amorphous polymer EC, moisture permeation primarily occurs, indicating superior water resistance when PHB is judiciously mixed (Cho *et al.* 2016). However, considering the inherently low coating coverage of kraft paper, it is hypothesized that the observed results may be attributed to the distinctive characteristics of kraft paper itself. Upon consideration of contact angle data, the optimal condition is deemed to be a 50:50 blend of PHB and EC.

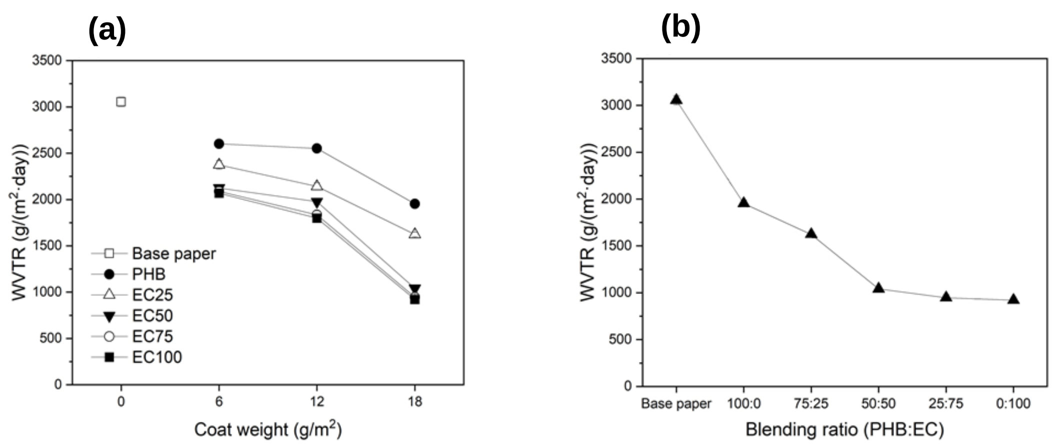

Fig. 9. Changes in water vapor transmission rate of the PHB/EC blend-coated paper depending on polymer blending ratio at (a) various coating weights and (b) 18-g/m^2 coating weight

Kit test

Figure 10 shows changes in the oil resistance of the coated papers based on the PHB/EC blend mixing ratio and coating weight, where a higher Kit number indicates greater oil resistance. The oil resistance improved with an increase in coating weight and EC content.

The changes in oil resistance based on the mixing ratio showed that higher EC content yielded better oil resistance. This agrees with the contact angle results presented in Fig. 5. The strong hydrophobicity of the PHB coating layer facilitates easy oil penetration. Conversely, because higher EC content made the coating layer denser, oil could not penetrate the coating layer with the increase in blending ratio of EC.

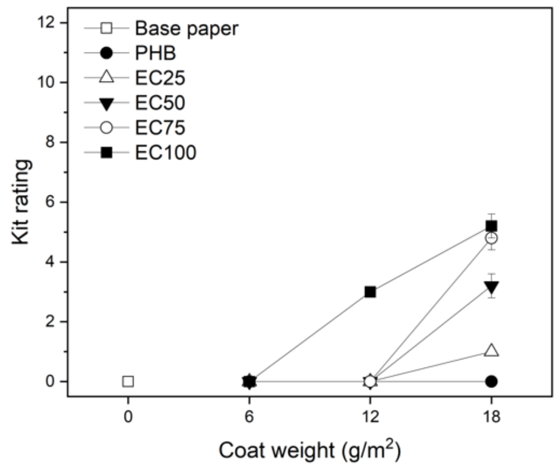

Fig. 10. Changes in Kit rating of PHB/EC-coated paper depending on polymer blending ratio and coating weight

Mechanical Properties

Figure 11 shows changes in the tensile strength and strain of the PHB/EC blend-coated paper depending on the PHB/EC mixing ratio and coating weight. As shown in Fig. 11(a), the tensile strength improvement due to PHB/EC coating is because of the hydrogen bonding between the hydroxyl groups of cellulose and the ester group of PHB that fills the fiber voids of kraft paper and the interaction between the hydrophobic molecules that make up PHB, EC, and cellulose (Seoane *et al.* 2018). Thus, the mechanical anchoring effect due to the coating layer formed by penetrating the voids might improve the strength of the coated paper (Cyras *et al.* 2007; 2009).

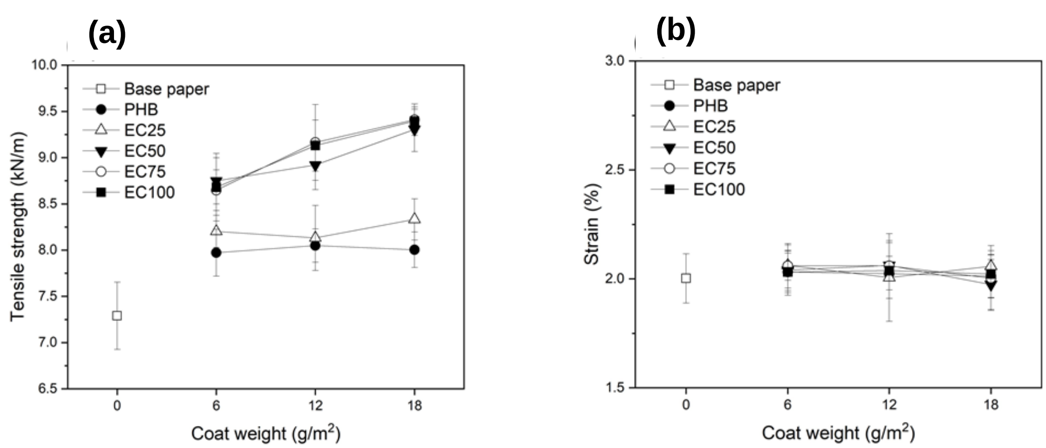

Fig. 11. Changes in (a) tensile strength and (b) strain of PHB/EC blend-coated paper depending on polymer blending ratio and coating weight

The greater improvement in tensile strength as coating weight increases is due to the formation of a thicker and more continuous coating layer, which is consistent with the previous thickness measurement results of coated paper. The change in tensile strength based on blend composition showed the smallest increase for the bare PHB coating and tended to increase with EC content. Chan *et al.* (2011) and Chen *et al.* (2016) also investigated the enhancement of the mechanical properties of PHB films through blending with EC for composite biomaterials. However, they observed the highest strength when the EC proportion was 50%.

As shown in Fig. 11(b), the mixing of PHB and EC did not affect the change in the strain of the coated paper. The mixing of PHB and EC did not contribute to the improvement of the elongation rate of the base paper because brittle PHB and EC could not be elongated. (Bugnicourt *et al.* 2014; Shi *et al.* 2020).

CONCLUSIONS

1. For the surface properties of poly(3-hydroxybutyrate)/ethyl cellulose (PHB/EC) blend-coated paper, EC was the critical component that influenced contour formation with distinct fibers. As EC content increased, the coating materials deeply penetrated the paper structure owing to the hydrogen bonding effect between the hydroxyl groups of cellulose. The internal bond strength results demonstrated that EC could act as a binder for PHB-coated paper.
2. In contact angle measurements, the initial contact angle was highest for the PHB-coated paper (91.7°). However, it rapidly absorbed water within several seconds because of surface contours. Conversely, although the initial contact angle of the PHB/EC blend-coated papers was lower than that of the PHB-coated paper, it remained unchanged over time because of the condensed surfaces without pores.
3. To achieve high barrier properties, the coating weight should be controlled above 18 g/m^2. Regarding the PHB/EC mixing ratio, 50:50 was determined to be optimal based on the Cobb test and water vapor transmission rate (WVTR). Moreover, the oil resistance test demonstrated enhanced resistance to oil penetration with an increase in the mixing ratio of EC.
4. Regarding the mechanical properties, the tensile strength of PHB/EC blend-coated papers with an EC proportion of 50% or more improved with an increase in coating weight. However, the PHB/EC mixing ratio and coating weight did not affect the change in strain rate because of the brittleness of PHB and EC.

ACKNOWLEDGMENTS

This study was conducted with the support of ´R&D Program for Forest Science Technology (Project No. 2023473B10-2325-EE02) provided by Korea Forest Service (Korea Forestry Promotion Institute). Also, this work was supported by the National Institute of Forest Science (Grant No. FP0400-2023-01).

REFERENCES CITED

Ahmadi, P., Jahanban-Esfahlan, A., Ahmadi, A., Tabibiazar, M., and Mohammadifar, M. (2022). "Development of ethyl cellulose-based formulations: A perspective on the novel technical methods," *Food Reviews International* 38(4), 685-732, DOI: 10.1080/87559129.2020.1741007

Andersson, C. (2008). “New ways to enhance the functionality of paperboard by surface treatment–a review,” *Packaging Technology and Science: An International Journal* 21(6), 339-373, DOI: 10.1002/pts.823

Avérous, L., and Pollet, E. (2012). “Biodegradable polymers,” in: *Environmental Silicate Nano-biocomposites*, Springer, London, pp. 13-39. DOI: 10.1007/978-1-4471-4108-2

Bugnicourt, E., Cinelli, P., Lazzeri, A., and Alvarez, V. (2014). “Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging,” *Express Polymer Letters* 8(11), 791-808. DOI: 10.3144/expresspolymlett.2014.82

Chan, R. T. H., Garvey, C. J., Marcal, H.,Russell, R. A., Holden, P. J., and Foster, L. J. R. (2011). “Manipulation of polyhydroxybutyrate properties through blending with ethyl-cellulose for a composite biomaterial,” *International Journal of Polymer Science* 2011, 1-8. DOI: 10.1155/2011/651549

Chen, J., Wu, D., and Pan, K. (2016). “Effects of ethyl cellulose on the crystallization and mechanical properties of poly(3-hydroxybutyrate),” *International Journal of Biological Macromolecules* 88, 120-129. DOI: 10.1016/j.ijbiomac.2016.03.048

Cho, S. K., Cho, T. Y., Ham, D. S., Lee, S. J., and Lee, J. H. (2016). “Gas permeation mechanism and technical trend for high shielding properties of plastic films,” *Journal of Adhesion and Interface* 17(4), 155-162.

Costa, M. M. E., Cabral-Albuquerque, E. C. M., Alves, T. L. M., Pinto, J. C., and Fialho, R. L. (2013). “Use of polyhydroxybutyrate and ethyl cellulose for coating of urea granules,” *Journal of Agricultural and Food Chemistry* 61(42), 9984-9991. DOI: 10.1021/jf401185y

Cyras, V. P., Commisso, M. S., Mauri, A. N., and Vazquez, A. (2007). “Biodegradable double-layer films based on biological resources: Polyhydroxybutyrate and cellulose,” *Journal of Applied Polymer Science* 106(2), 749-756. DOI: 10.1002/app.26663

Cyras, V. P., Commisso, M. S., and Analía, V. (2009). “Biocomposites based on renewable resource: Acetylated and non-acetylated cellulose cardboard coated with polyhydroxybutyrate,” *Polymer* 50(26), 6274-6280. DOI: 10.1016/j.polymer.2009.10.065

Finelli, L., Scandola, M., and Sadocco, P. (1998). “Biodegradation of blends of bacterial poly (3-hydroxybutyrate) with ethyl cellulose in activated sludge and in enzymatic solution,” *Macromolecular Chemistry and Physics* 199(4), 695-703. DOI: 10.1002/(SICI)1521-3935(19980401)199:4

Harding, K. G., Dennis, J. S., Von Blottnitz, H., and Harrison, S. T. L. (2007). “Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-β-hydroxybutyric acid using life cycle analysis,” *Journal of Biotechnology* 130(1), 57-66. DOI: 10.1016/j.jbiotec.2007.02.012

Heinze, T., El Seoud, O. A., and Koschella, A. (2018). “Etherification of cellulose,” in: *Cellulose Derivatives*, Springer, Berlin, pp. 429-477. DOI: 10.1007/978-3-319-73168-1_6

ISO 534 (2011). *Paper and Board — Determination of Thickness, Density and Specific Volume*, International Organization for Standardization, Geneva, Switzerland.

ISO 535 (2014). *Paper and Board — Determination of Water Absorptiveness — Cobb Method*, International Organization for Standardization, Geneva, Switzerland.

ISO 5636-3 (2013). *Paper and Board — Determination of Air Permeance (Medium Range) -Part 3: Bendtsen Method*, International Organization for Standardization, Geneva, Switzerland.

Jain, R., and Tiwari, A. (2015). "Biosynthesis of planet friendly bioplastics using renewable carbon source," *Journal of Environmental Health Science and Engineering* 13, 1-5. DOI: 10.1186/s40201-015-0165-3

Khosravi-Darani, K. (2015). "Application of poly(hydroxyalkanoate) in food packaging: Improvements by nanotechnology," *Chemical and Biochemical Engineering Quarterly* 29(2), 275-285. DOI: 10.15255/CABEQ.2014.2260

Khwaldia, K., Arab-Tehrany, E., and Desobry, S. (2010). "Biopolymer coatings on paper packaging materials," *Comprehensive Reviews in Food Science and Food Safety* 9(1), 82-91. DOI: 10.1111/j.1541-4337.2009.00095.x

Ko, Y. C., Melani, L., Park, N. Y., and Kim, H. J. (2020). "Surface characterization of paper and paperboard using a stylus contact method," *Nordic Pulp & Paper Research Journal* 35(1), 78-88. DOI: 10.1515/npprj-2019-0005

Li, X., Jiang, F., Ni, X., Yan, W., Fang, Y., Corke, H., and Xiao, M. (2015). "Preparation and characterization of konjac glucomannan and ethyl cellulose blend films," *Food Hydrocolloids* 44, 229-236. DOI: 10.1016/j.foodhyd.2014.09.027

Lim, D. G., Park, N. Y., Lee, Y. J., Yun, J. H., and Kim H. J. (2021). "Characterization of the paper coated with polyhydroxybutyrate/ethyl cellulose blends," *Journal of Korea TAPPI* 53(4), 41-52. DOI: 10.7584/JKTAPPI.2021.08.53.4.41

Liu, Y., Ahmed, S., Sameen, D. E., Wang, Y., Lu, R., Dai, J., Li, S., and Qin, W. (2021). "A review of cellulose and its derivatives in biopolymer-based for food packaging application," *Trends in Food Science and Technology* 112, 532-546. DOI: 10.1016/j.tifs.2021.04.016

Modaressi, H., and Garnier, G. (2002). "Mechanism of wetting and absorption of water droplets on sized paper: Effects of chemical and physical heterogeneity," *Langmuir* 18(3), 642-649. DOI: 10.1021/la0104931

Muthuraj, R., Misra, M., and Mohanty, A. K. (2018). "Biodegradable compatibilized polymer blends for packaging applications: A literature review," *Journal of Applied Polymer Science* 135(24), article 45726. DOI: 10.1002/app.45726

Rastogi, V. K., and Samyn, P. (2015). "Bio-based coatings for paper applications," *Coatings* 5(4), 887-930. DOI: 10.3390/coatings5040887

Rastogi, V. K. and Samyn, P. (2016). "Synthesis of polyhydroxybutyrate particles with micro-tonanosized structures and application as protective coating for packaging papers," *Nanomaterials* 7(1), 5. DOI: 10.3390/nano7010005

Safari, S., and van de Ven, T. G. M. (2015). "Effect of crystallization conditions on he physical properties of a two-layer glassine paper/polyhydroxybutyrate structure," *Journal of Materials Science* 50(10), 3686-3696. DOI: 10.1007/s10853-015-8929-9

Seoane, I. T., Luzi, F., Puglia, D., Cyras, V. P., and Manfredi, L. B. (2018). "Enhancement of paperboard performance as packaging material by layering with plasticized polyhydroxybutyrate/nanocellulose coatings," *Journal of Applied Polymer Science* 135(48), 1-11. DOI: 10.1002/app.46872

Seoane, I. T., Manfredi, L. B., and Cyras, V. P. (2018). "Bilayer biocomposites based on coated cellulose paperboard with films of polyhydroxybutyrate/cellulose nanocrystals," *Cellulose* 25, 2419-2434. DOI: 10.1007/s10570-018-1729-z

Shi, J., Liu, W., Jiang, X., and Liu, W. (2020). "Preparation of cellulose nanocrystal from tobacco-stem and its application in ethyl cellulose film as a reinforcing agent," *Cellulose* 27(3), 1393-1406. DOI: 10.1007/s10570-019-02904-0

Suttiwijitpukdee, N., Sato, H., Zhang, J., and Hashimoto, T. (2011). "Effects of intermolecular hydrogen bondings on isothermal crystallization behavior of polymer blends of cellulose acetate butyrate and poly (3-hydroxybutyrate)," *Macromolecules* 44(9), 3467-3477. DOI: 10.1021/ma200365e

Suttiwijitpukdee, N., Sato, H., Unger, M., and Ozaki, Y. (2012). "Effects of hydrogen bond intermolecular interactions on the crystal spherulite of poly (3-hydroxybutyrate) and cellulose acetate butyrate blends: Studied by FT-IR and FT-NIR imaging spectroscopy," *Macromolecules* 45(6), 2738-2748. DOI: 10.1021/ma201598s

Vaidya, A. A., Collet, C., Gaugler, M., and Lloyd-Jones, G. (2019). "Integrating softwood biorefinery lignin into polyhydroxybutyrate composites and application in 3D printing," *Materials Today Communications* 19, 286-296. DOI: 10.1016/j.mtcomm.2019.02.008

Wang, S., Lydon, K. A., White, E. M., Grubbs III, J. B., Lipp, E. K., Locklin, J., and Jambeck, J. R. (2018). "Biodegradation of poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) plastic under anaerobic sludge and aerobic seawater conditions: Gas evolution and microbial diversity," *Environmental Science and Technology* 52(10), 5700-5709. DOI: 10.1021/acs.est.7b06688

Yamaguchi, M., and Arakawa, K. (2007). "Control of structure and mechanical properties for binary blends of poly (3-hydroxybutyrate) and cellulose derivative," *Journal of Applied Polymer Science* 103(5), 3447-3452. DOI: 10.1002/app.25455

Zhang, L., Deng, X., and Huang, Z. (1997). "Miscibility, thermal behaviour and morphological structure of poly(3-hydroxybutyrate) and ethyl cellulose binary blends," *Polymer* 38(21), 5379-5387. DOI: 10.1016/S0032-3861(97)84642-3

Article submitted: November 6, 2023; Peer review completed: November 27, 2023; Revised version received: December 18, 2023; Accepted: December 19, 2023; Published: January 24, 2024.
DOI: 10.15376/biores.19.1.1618-1632

APPENDIX

Supplementary Materials

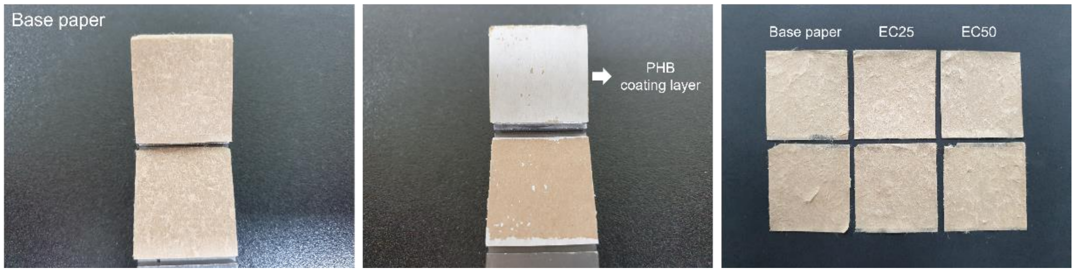

Fig. S1. Photograps of the fractured samples of the PHB/EC blend coated paper (coating weight: 18 g/m^2) after internal bond strength test

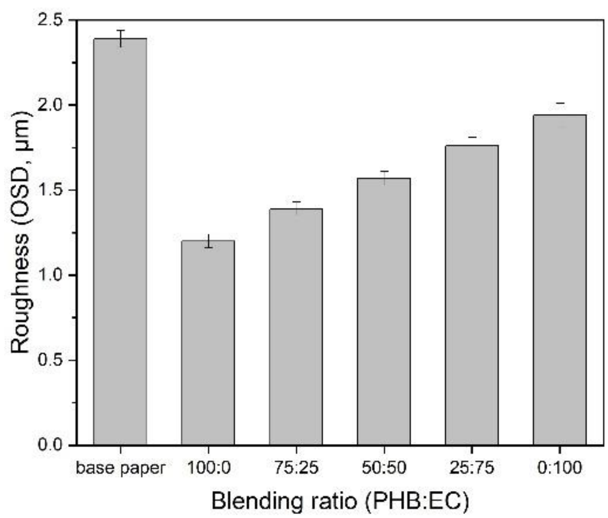

Fig. S2. Changes in surface roughness of the PHB/EC blend coated kraft paper (coating weight: 18 g/m^2) with different polymer blending ratio