Effect of surface treatment with biodegradable materials on properties of linerboard made from old corrugated containers (OCC)

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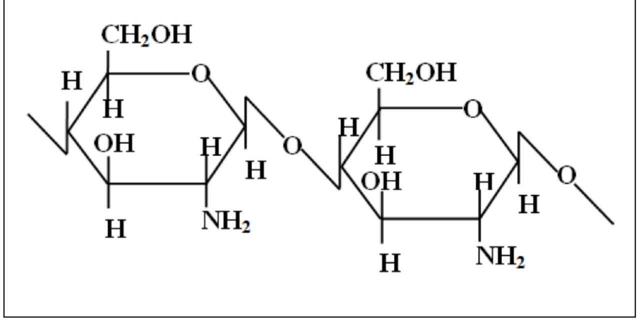
ABSTRACT: Linerboard produced from old corrugated containers (OCC) shows lower strength properties in comparison with linerboard produced from virgin fibers. This study determined the influence of surface treatment with polyvinyl alcohol (PVOH), ethylene vinyl alcohol (EVOH) (as synthesized biodegradable polymers), chitosan, and anionic starch (as biobased and biodegradable polymers) on properties of sheets produced from OCC. The polymers were applied from aqueous biodegradable dispersion, by using a laboratory-scale coater. This research investigated the burst index, tensile index, stiffness, water resistance, air resistance, and water absorption. The results showed that paper surfaces treated with water-soluble polymers increased the mechanical properties. In addition, PVOH increased the burst index value 136% and EVOH increased the tensile index, tear index, and stiffness values by 84.3%, 108.6%, and 22.43%, respectively. The anionic starch increased air resistance to 34.7% and chitosan decreased water absorption to 12.3%.

Application: Surface treatments with biopolymers can increase the strength properties of linerboard produced from old corrugated containers.

The use of secondary fiber for paper production is increasing all over the world. About 40% of the total paper production in the world was based on the secondary fiber in 2006 [1]. Paper recycling has many advantages. Every ton of recycled fiber saves an average of 17 trees plus related pulping energy, and for every ton of paper for recycling, the savings are at least 30000 L of water, 3000–4000 KW•h of electricity, and 95% of air pollution [2]. Therefore, recycled fibers have a very important role in the paper industry.

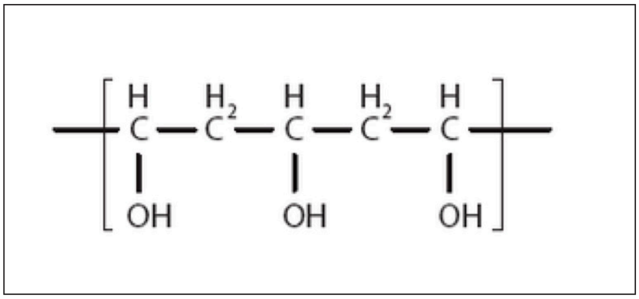
Linerboard is produced from virgin fiber, usually called kraft liner, whereas linerboard containing recycled fiber is called test liner. The major problem with recycling of old corrugated containers (OCC) is the loss of strength properties [3]. By increasing the number of cycles in the fiber recycling, the strength of papers is gradually reduced because of the decrease in interfiber bonding strength compared with virgin wood pulp fibers through the hornification phenomenon [4]. The strength of recycled fiber is not sufficient to meet the industry's demand; thus, the strength should be improved. Many polymers are used in paper manufacture to improve or enhance the strength and printability of paper. A number of these polymers are nonbiodegradable and might cause environmental problems, and some pose occupational health and safety risks to paper industry workers.

Chitosan, a natural polysaccharide, is a modified biopolymer (derived from the shells of certain crustaceans). It comprises an unbranched chain consisting of ß (1→4)-linked 2-Acetamido-2-deoxy-ß-D-glucopyranose [5]. The primary structure of chitosan is similar to cellulose except that the C-2-hydroxyl group of cellulose is replaced by an amino group (**Fig. 1**). Chitosan is insoluble in water under alkaline conditions, but it is soluble in acidified water because of its primary amino groups. It is a unique basic linear polysaccharide that has shown potential to improve both the strength and the printing properties of papers. Chitosan has been found to be effective as dry- and wet-strength agents [6], as well as in coatings [7] and sizing [8].



1. Chemical structure of chitosan.

Polyvinyl alcohol (PVOH) is a water soluble and biodegradable synthetic polymer available in both fully hydrolyzed and



2. Chemical structure of polyvinyl alcohol (PVOH).

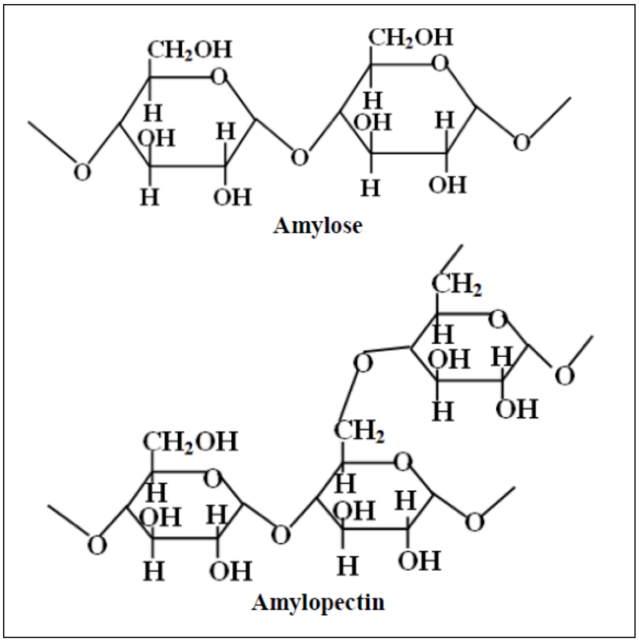
partially hydrolyzed grades (**Fig. 2**). It is an adhesive with superior bonding strength, film forming, and emulsifying properties. PVOH has been extensively used in the textile industry for warp sizing and resin finishing; in the paper industry for surface sizing and pigment coating; in the production of PVOH emulsion as a protective colloid; in the suspension polymerization of polyvinyl chloride as a dispersion agent; and as a binder for ceramics, magnet, foundry cores, and pigments [9].

Because of the presence of hydroxyl groups in every repeating unit of PVOH, it appears to be one of the best polymers to reinforce cellulose fibers [10]. In papermaking, PVOH is used for surface sizing to form films with very high tensile strength and a high degree of transparency, flexibility, and oil resistance [11]. PVOH can also be mixed with starch and applied at a size press [12].

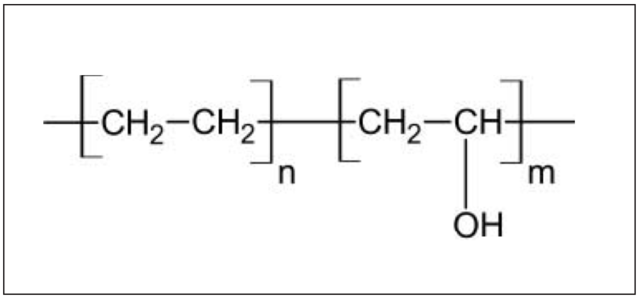
The other most abundant natural polymer is starch, regenerated from carbon dioxide and water by photosynthesis in plants [13]. Starch is a cheap, renewable, and completely biodegradable polymer [14] and thus is a promising candidate for developing sustainable materials. Starch is a semicrystalline polymer comprising two repeating units of 1, 4-α-D-glucopyranosyl: amylose and amylopectin (**Fig. 3**).

Ethyl-vinyl alcohol (EVOH) is used in conjunction with paper, foil, and other plastics for flexible and semirigid containers [15]. The properties of EVOH vary with the relative amounts of the two components, PVOH and polyethylene (PE) (**Fig. 4**). As the mol% of ethylene increases, the properties of EVOH become more like that of PE; conversely as mol% ethylene decreases, the material behaves more like PVOH. Similarly, materials with higher ethylene content resemble properties of PE. EVOH is a semicrystalline copolymer [16]. The repeating unit of EVOH has the following chemical structure. The copolymer composition (i.e., relative amounts of ethylene and vinyl alcohol) affects properties of EVOH copolymers (e.g., gas barrier, mechanical properties, and water vapor transmission) and hence influences EVOH processing and end use applications. EVOH resins are commercially available in a range of compositions, most commonly encompassing vinyl alcohol contents of about 52–76 mol% (Fig. 4)

One drawback of corrugated board is its hydrophilic character. Corrugated board usually absorbs water from the environment, especially when being stored under high humidity conditions or when coming into contact with high-moisture products such as fresh agricultural produce or frozen foods. Absorption of water reduces the physical and mechanical strength of corrugated board, causing corruption of the flute structures and failure of the corrugated package during storage and distribution. Surface treatments such as sizing, coating, and laminating are usually used on the kraft liner to improve the physical strength as well as water barrier properties [17,18].



3. Chemical structure of starch.



4. Chemical structure of ethylene vinyl alcohol (EVOH).

This study was carried out to investigate strength properties, water, and air resistance of liner paper made from OCC surface treated with PVOH, EVOH, chitosan, and anionic starch.

MATERIALS AND METHODS

The materials used in this work were PVOH (98%–99% hydrolyzed, average mol. wt. 31000–50000), chitosan (medium mol. wt., 75%–85% deacetylated), EVOH, and anionic starch. The EVOH and anionic starch were purchased from Sigma Aldrich (St. Louis, MO, USA). Also, the samples used in this work were untreated linerboard made of OCC with a weight of 120±5 g/m² obtained from a local recycling paper mill.

Treatment	Biopolymer	Coated Weight, g/m²	Burst, Kpam²/g	Tensile, N.m/g	Tear, mN.m²/g	Stiffness, N/mm	Air Resistance, s/100 mL air	Water Absorption, g/m²
R	Reference	–	0.92±0.11	2.67±0.27	5.18±0.15	385.33±14	9.16±0.06	119±10.6
C	Chitosan	4.43±1.27	1.49±0.04	3.66±0.16	5.88±0.12	447.15±16.07	12.57±0.1	102±5.44
S	Anionic starch	5.56±0.84	1.31±0.08	3.35±0.34	5.74±0.06	435.07±35.4	20.77±0.17	144.26±10.65
P	Polyvinyl alcohol	5.27±1.38	2.17±0.02	4.55±0.38	5.63±0.23	477.5±33.8	10±0.67	152.46±7.65
E	Ethylene vinyl alcohol	4.43±1.45	1.92±0.05	4.92±0.27	6.02±0.08	490.73±35.55	10.7±0.06	217.21±4.51

I. Properties of sheets surface treated with different biodegradable polymers.

Solubilization of materials

The starch coating solution was prepared by gelatinizing 2% (w/w) of anionic starch at 90°C for 20 min. The chitosan solution was obtained by dispersing chitosan 1% (w/w) in aqueous acetic acid under continuous stirring for 2 h. The PVOH solution was prepared by dissolving it in distilled water and heating it on a hot plate with a magnetic stirrer at 90°C for 30 min. The EVOH solution was prepared by dissolving it in distilled water and heating it at 90°C for 20–30 min.

The untreated linerboard was used as substrate to apply the dispersion coating. The polymer coatings were applied from aqueous biopolymer dispersion using a laboratory coater (Auto BAR coater, BMIK Co.; Jeonmin-dong, Korea).

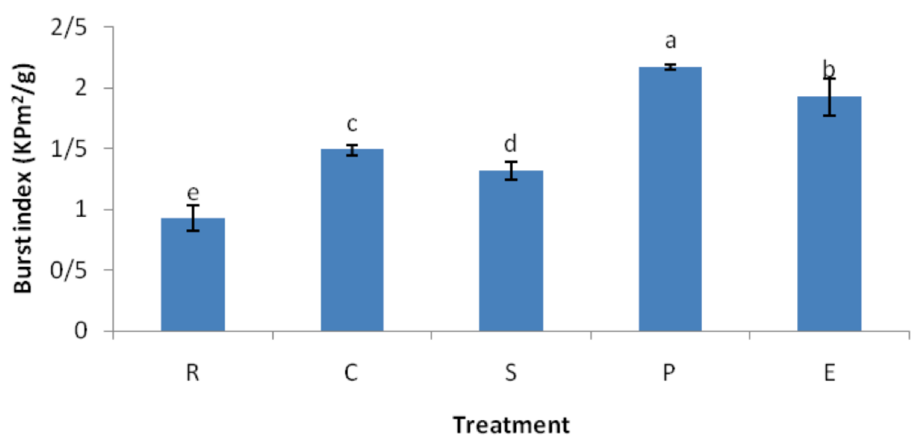
Determination of strength properties

For determination of strength properties, the samples were conditioned at 50±2% relative humidity (RH) and 23±1°C according to TAPPI Standard Test MethodT 402 sp-98 "Standard conditioning and testing atmospheres for paper, board, pulp handsheets, and related products" for at least 4 h. Dry-strength properties of sheets were tested according to the following TAPPI Standard Test Methods: tensile and stiffness (T 451 cm-84 "Flexural properties of paper [Clark stiffness]"), burst index (T 403 om-02 "Bursting strength of paper"), tear index (T 414 om-04 "Internal tearing resistance of paper [Elmendorf-type method]"), air resistance (T 460 om-98 "Air resistance of paper [Gurley method]"), and water absorption (T 441 om-09 "Water absorptiveness of sized [non-bibulous] paper, paperboard, and corrugated fiberboard [Cobb test]").

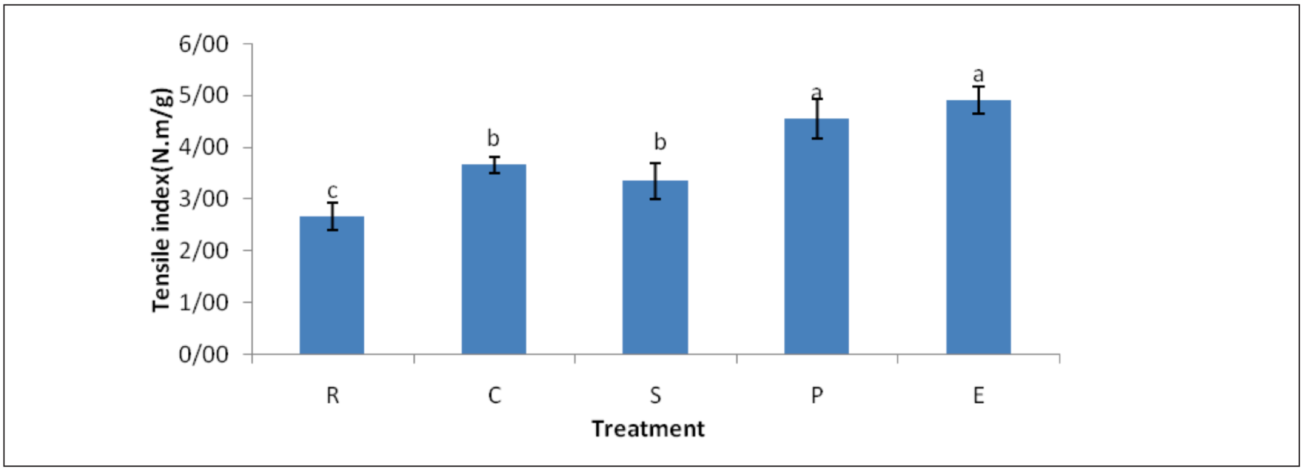
Analysis of variance was conducted using a randomized design. Mean values were compared using Duncan's test.

RESULTS AND DISCUSSION

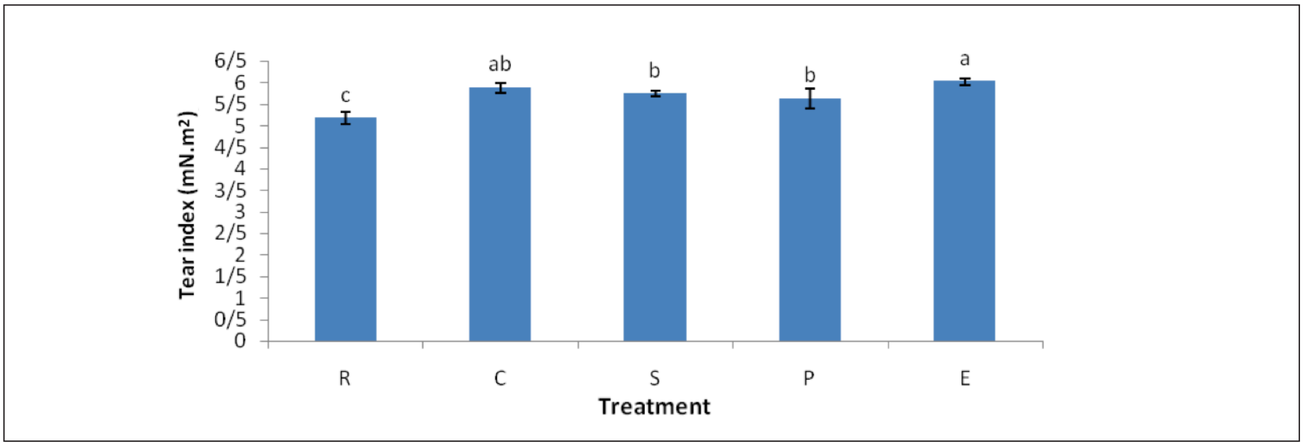
Data on burst index, tensile index, tear index, stiffness, air resistance, and water absorption of sheets surfaces treated by four biodegradable polymers are presented in **Table I**.



5. Average burst index of different surface treatments with biodegradable polymers. (Letters indicate significant difference at α = 0.05.)



6. Average tensile index of different surface treatments with biodegradable polymers. (Letters indicate significant difference at α = 0.05.)



7. Average tear index of different surface treatments with biodegradable polymers. (Letters indicate significant difference at α=0.05.)

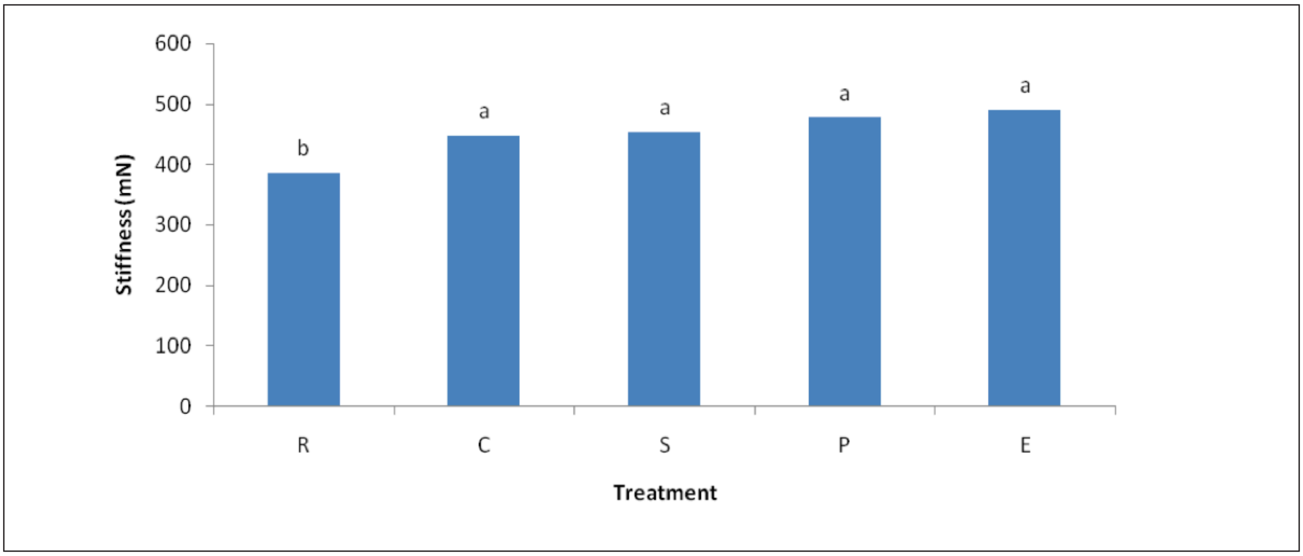
Strength properties

Figures 5, 6, and 7 show the effects of surface treatment with the biodegradable polymers on strength properties compared with controls. The results demonstrate that chitosan, anionic starch, PVOH, and EVOH increased burst, tensile, and tear indices. The surface treatment with PVOH and EVOH had a unique effect on the strength properties compared with surface treatment with anionic starch and chitosan. PVOH and EVOH enhanced tensile index of sheets 70.41% and 84.27%, respectively. PVOH is a biocompatible petroleum-based polymer. It is also one of the rare polymers with a carbon-carbon single-bond backbone that is fully biodegradable. Because of the hydroxyl (-OH) groups on the alternating carbon atoms, PVOH is strongly hydrophilic and soluble in water, which promotes its degradation and acetyl linkages with other materials such as cellulose and aldehydes [19]. This may be due to the formation of hydrogen bonding between the hydroxyl groups of cellulose and those of PVOH. There were interactions between cellulose and PVOH that involved the formation of interchange hydrogen bonds between hydroxyl groups of PVOH and ether oxygen in cellulose [20]. This polymer fills the paper pores and forms a dense layer at the paper surface. Hydrogen bonds that formed between the polar groups of EVOH mainly explain the high cohesive energy density of this film. However, these polar groups lead to the hydrophilic character of the polymer, and the different charges of the chitosan and cellulose can be expected to yield good adhesion between a chitosan and a cellulose-based substrate [21]. As the ionized amino groups of chitosan come into contact with fibers, they can form ionic and amino bonds in the presence of water.

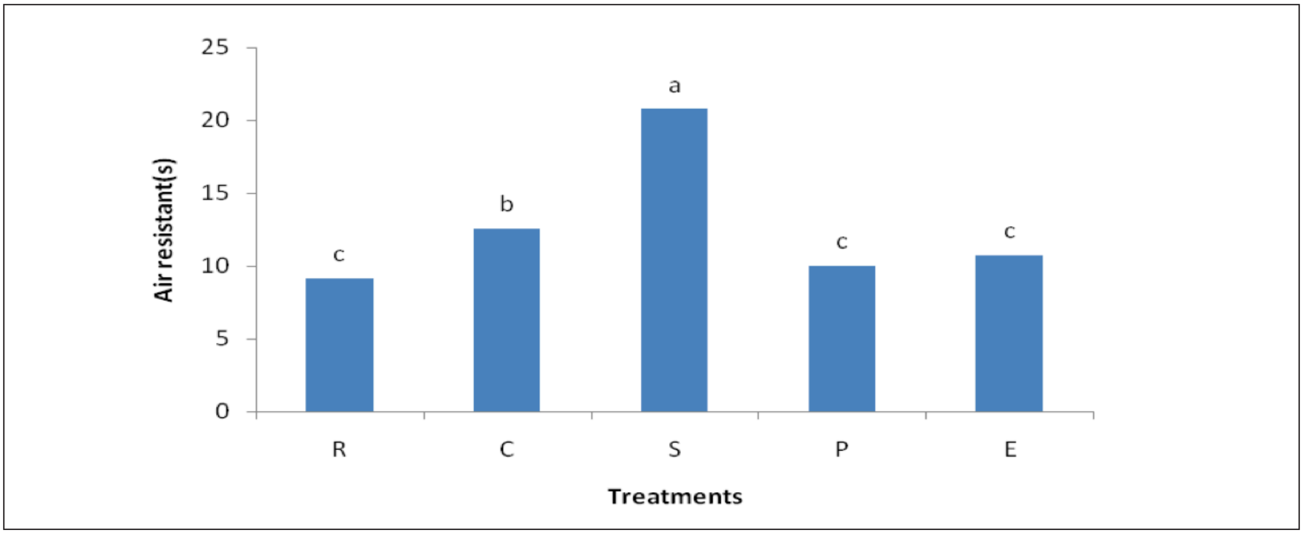
The results of stiffness are shown in **Fig. 8**. Stiffness is usually achieved through an increase in paper basis weight or densification of a sheet of some prescribed basis weight wet pressing. Both means involve high cost. Surface treatment with biodegradable polymers showed increased stiffness of sheets [22].

Air resistance

Effects of the surface treatment with biodegradable polymers on the air resistance of the sheets are shown in **Fig. 9**. The results indicated that anionic starch had a positive effect on air resistance of the sheets and the air resistance values were higher than for the other biopolymers. Starch seals the pores



8. Average stiffness index of different surface treatments with biodegradable polymers. (Letters indicate significant difference at α = 0.05.)

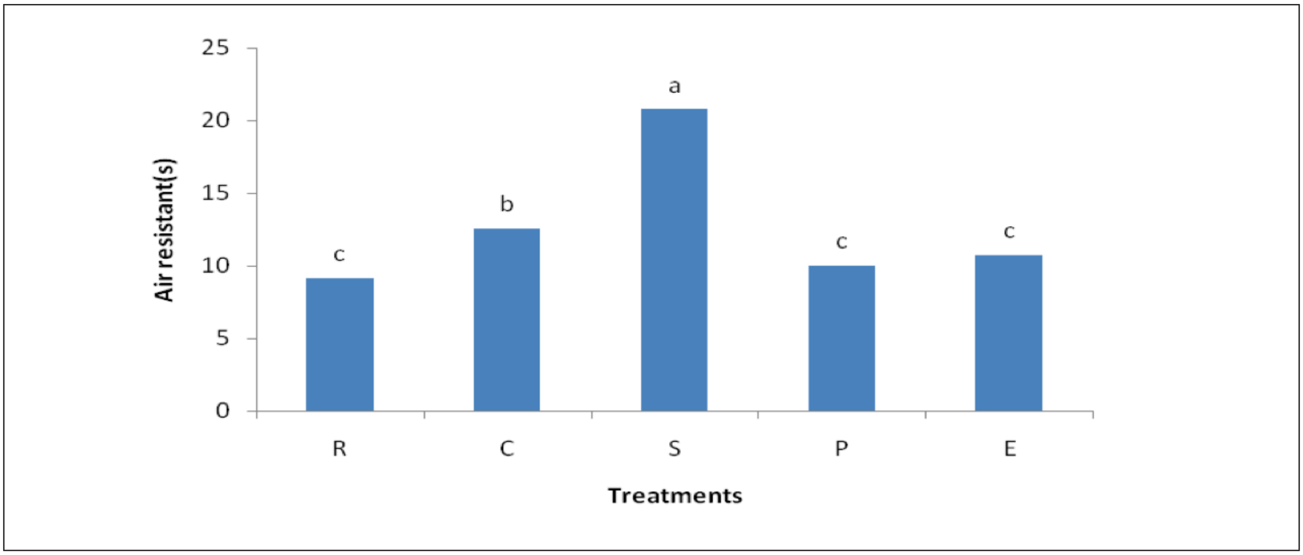


9. Average air resistant of different surface treatments with biodegradable polymers. (Letters indicate significant difference at α = 0.05.)

in the base papers. The air resistance is indicative of porosity, and this result suggests that either the numbers of pores in the paper surface treated with starch is reduced or their size is diminished. Chitosan coating showed change in the air resistance, but PVOH and EVOH showed no change in the air resistance compared with the uncoated control. A reason might be that PVOH and EVOH penetrated into the fibers and did not reduce the size of the pores.

Water absorption

Among the many properties of paper, one of the most important is its ability to control the penetration of various liquids, particularly those that are water based [23]. A water barrier can be formed by changing the wettability of the paper surface with sizing agents or through coating with hydrophobic materials [24]. **Figure 10** shows effects of the surface treatment with biodegradable polymers on the water absorption of the sheets. The lower the Cobb value, the less water penetrates into the sample. Starch, PVOH, and EVOH surface treatments did not provide any barrier against water, and their water sorption was found to be greater than the fiber sorption in the base paper. Hydrogen bonds formed between the polar groups of EVOH and PVOH. These polar groups are also the origin of the hydrophilic character of the polymers at high relative humidity [21]. The chitosan surface treatment reduced the Cobb60-values for the base paper. The results show that the chitosan surface treatment provided a barrier against water absorption. This might be due to the intrinsic chemical nature of chitosan [25]. A reduction in water absorption of chitosan may provide more appropriate absorbency characteristics in paper for improving printability. These properties make chitosan an attractive polymer for the barrier coating of cellulose-based materials for food packaging purposes [7].



10. Average water absorption of different surface treatments with biodegradable polymers. (Letters indicate significant difference at $\alpha = 0.05$.)

CONCLUSIONS

Surface treatment of linerboard with biodegradable polymers has the potential to provide quality paper packaging. PVOH and EVOH have more effect on strength, whereas chitosan showed less absorption of water. Surface treatment with chitosan provided the strongest barrier against water. **TJ**

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ABOUT THE AUTHORS

Linerboard produced from old corrugated containers (OCC) has lower strength properties than linerboard produced from virgin fibers. Previous research investigated dry additives for improved linerboard made from OCC. This research focused on coating with biopolymers to improve strength.

Our research showed that it is possible to increase the strength of recycled paper. Most surprising was the effect of polyvinyl alcohol (PVOH) and ethylene vinyl alcohol (EVOH) on burst strength. Mills producing linerboard with OCC can use biopolymers to increase mechanical properties. The next step is to investigate whether coating can improve printability as well as physical properties of linerboard.

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