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Screening of Agricultural and Food Processing Waste Materials as New Sources for Biodegradable Food Packaging Application

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Abstract Agar-based composite films were prepared with variety of food processing and agricultural processing waste materials in order to screen natural lingo-cellulosic resources for the value-added utilization of the under-utilized materials. The effect of these waste materials (10 wt% based on agar) on mechanical properties, moisture content (MC), water vapor permeability (WVP), water absorption behavior of biocomposite films were investigated. Biocomposite films prepared with various fibers resulted in significant increase or decrease in color and percent transmittance. The MC, WVP, and surface hydrophobicity of biocomposite films increased significantly by incorporation of fibers, while the water uptake ratio and solubility of the film decreased. SEM images of biocomposite film showed better adhesion between the fiber and agar polymer. Among the tested cellulosic waste materials, rice wine waste, onion and garlic fibers were promising for the value-added utilization as a reinforcing material for the preparation of biocomposite food packaging films.

Keywords Agricultural waste, Onion, Garlic, Agar, Biocomposite, Food packaging

Introduction

For the last few decades, petroleum based polymers and plastics have been widely used to replace metal, ceramics and glasses for packaging, automotive, adhesives, elastomers and other applications. However, increasing demand for the polymers caused to develop new polymers and polymer composites with improved properties and new functionality. The petrochemical-based conventional packaging materials are basically non-biodegradable resulting in general concerns on environmental problems as well as exhaust of natural resources. This aroused renewed interest to develop biodegradable packaging materials using biopolymers derived from renewable resources[1)]. More recently, biodegradable polymers such as poly(lactide) (PLA), poly(butylene succinate) (PBS), and other biodegradable polyesters have attracted attention in the packaging and other value added applications[2)]. Variety of naturally occurring biopolymers such as proteins, cellulose, starches, and other polysaccharides have been used for the development of biodegradable packaging film[3)].

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In addition, lingo-cellulosic materials derived from food processing and agricultural processing waste or by-products have emerged in the utilization as biofillers for the development of biocomposite films. Various agricultural waste residues such as rice husks, coconut fibers, maize cobs, bagasse fibers, peanut shells, stalks of cereal crops, sunflower, and corn, and sugar palm tree have been used for the preparation of biocomposites[4,5)]. The ligno-cellulosic resources derived from agricultural wastes are of particular interest due to their abundance, low cost, hollow cellular structure, biocompatibility, renewability, and biodegradability[6)]. Moreover, the cellulosic biofibers offers some other advantages such as light weight, reduced energy consumption, non-abrasiveness, high level of filler loading, safety in working environment, and CO_2 neutral[7)]. Annually, billions of tones of agricultural waste residues have been produced from various plants or crops worldwide. At present, most of the cellulosic wastes are used as house hold fuels, fertilizers, or animal feed. Only a few percentage of such wastes are utilized for the value-added utilization. Therefore, many research works have been focused on the utilization of such agricultural waste residues to make environment-friendly biocomposite films for the packaging application[6)]. For example, onion and garlic skins or stalks are potential lingo-cellulosic bioresources obtained from the food processing and agricultural processing industries. Tons of onion and garlic skin wastes are produced every year in the

Asian counties, for example, more than 144,000 tons of onion waste are produced annually in Japan[8]. Not only as new lingo-cellulosic natural resources, both onion and garlic skins are known to possess some functional compounds such as flavonoids, and free radical scavenging compounds[8,9]. Recently, research efforts have been made to utilize such lingo-cellulosic resources as reinforcing biofillers for the production of green biocomposites[10].

Another reliable resources for the production of biocomposites are by-products which are abundantly obtained in the food processing industry. Though some portions of such by-products are used as animal feed, a large portion of them are discarded as a waste. Zarrinbakhsh et al.[11] have recently used distiller's dried grain (by-product in the bioethanol industry) for making biodegradable composites with poly(butylene adipate-co-terephthalate) (PBAT). Oksman et al.[12] extracted nanocelulose from industrial by-products and found that the nanocellulose can be used as reinforcing filler for making biocomposites. Sugar cane bagasse obtained as a by-product in the sugar processing industry has been used for the production of nanocellulose and biocomposites[13].

For the preparation of biocomposites reinforced with cellulose nanofillers, variety of biopolymers have been used as polymer matrices. As one of such biopolymers, agar is interesting since it has been used in the food packaging industry due to their renewability and biodegradability with good film-forming properties[14,15]. However, agar films are brittle and hydrophilic in nature with rather low mechanical strength and thermal stability. Usually, glycerol is used as a plasticizer to make flexible films by reducing brittleness of the films[16]. Agar has also been blended with other polymers or reinforced with nano-fillers to improve the mechanical and water vapor barrier properties[17,18].

The main objective of the present study was to screen new natural resources of lingo-cellulosic materials for their value-added utilization. Various agricultural processing wastes such as rice hull, rice straw, onion and garlic skin and stalk, and some of by-products obtained from food processing industry such as rice wine wastes, beer brewing wastes, raspberry wine wastes, and corn wastes were used for the preparation of composite films with agar. The effect of reinforcing filler on the performance of the biocomposite films was evaluated. The mechanical, water vapor permeability, and color properties of the biocomposite films were also evaluated.

Materials and Methods

1. Materials

Stalks of onion and garlic, which were discarded in the field after harvest of onion and garlic, were obtained from local farmers. Skins of onion and garlic, which were discarded as processing byproducts, were collected from a local food processing company. Rice wine wastes, beer brewing wastes, raspberry wine wastes, and corn wastes were collected from a local feed manufacturing company. Food grade agar was obtained from Fine Agar Co., Ltd. (Damyang, Jeonnam, Korea) and analytical grade glycerol was procured from Sigma-Aldrich Co. (St Louis, MO, USA).

2. Chemical analysis

All the selected agriculture waste materials washed twice with distilled water and dried in an air oven at 105 ^{o}C for 24 h, then ground using a Waring blender and passed through a 100-mesh standard sieve to get fine powder. Chemical composition (moisture, crude fat, crude protein, carbohydrate, and ash) of food processing by-products such rice wine waste, beer brewing waste, raspberry wine waste, and corn processing wastes was analyzed using the general method. The á-cellulose, hemicelluloses and lignin contents of agricultural processing wastes (garlic skin and stalk, onion skin and stalk) samples were determined by chemical analysis used for grass cellulose analysis.

3. Preparation of agar-based composites films

The agricultural waste powder (0.4 g) was dispersed in 150 mL of distilled water and stirred for 1 h using a magnetic stirrer. The fully wetted suspension was homogenized using a high speed shear mixer at 12,000 rpm for 10 min. Then, 4 g of agar and 1.2 g of glycerol as plasticizer were added into the suspension and stirred vigorously using a hot plate at 95^{o}C for 30 min. Fully solubilized mixture solution was cast evenly onto a leveled Teflon film coated glass plate (24×30 cm), and allowed to dry at room temperature for about 48 h. The dried films were peeled off from the plate and conditioned in a humidity chamber set at 25^{o}C and 50% RH for at least two days prior to further experimental analysis.

4. Color and transparency

The Hunter color values (L, a, and b) of the agar and biocomposite films were measured using a Chroma meter (Minolta, CR-200, Tokyo, Japan). A white color standard plate (L = 97.75, a = –0.49 and b = 1.96) was used as a background for color measurements. The total color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$

where ΔL, Δa, and Δb are difference between each color values of standard color plate and film specimen, respectively. Five measurements were taken for each film and the average values with standard deviation were reported.

The transparency of agar and biocomposite films was determined by measuring percent transmittance at 660 nm using a UV-vis spectrophotometer (Model 8451A, Hewlett-Packard

Co., Santa Alara, CA, USA).

5. Scanning electron microscopy (SEM)

The morphology of cross section of agar and biocomposite films with tensile fractured specimens was observed using a Field Emission Scanning Electron Microscope (FE-SEM, S-4800, Hitachi Co., Ltd., Matsuda, Japan).

6. Mechanical properties

The mechanical properties of agar and biocomposite films were measured according to the standard test method ASTMD-882-88. Tensile strength (TS), elongation at break (E), and elastic modulus (EM) of the films were tested using Instron Universal Testing Machine (5565, Instron Engineering Corporation, Canton, MA, USA). The rectangular specimen of each film sample (2.54×15 cm) was stretched with an initial grip separation and crosshead speed of 50 mm and 50 mm/min, respectively. Ten replicates were tested for each film and the average values were reported.

7. Moisture content (MC) and water vapor permeability (WVP)

Moisture content of the agar and agar/fiber composite films was determined as the percentage of moisture removed before and after drying the films. The film samples were cut into 3×3 cm and dried in a hot air oven at 105°C for 24 h. Before and after drying, the weight loss was measured as water content and expressed as the percentages based on the initial weight of film.

Water vapor permeability of agar and biocomposite lms was determined gravimetrically using a modied ASTM method E96-95. WVP was calculated using the following equation:

$$\mathrm{WVP} = (\mathrm{WVTR} \times \mathrm{L})/\Delta p \quad (2)$$

where WVTR was the measured water vapor transmission rate (g/m^2s) through a lm, L was the mean lm thickness (m), and Δp was the partial water vapor pressure difference (Pa) across the two sides of the lm. The film specimens were mounted horizontally on poly (methylmethacrylate) cups lled with distilled water upto 1 cm underneath the lm. The cups were placed in an environmental chamber set at 25°C and 50% RH with air current movement of 198 m/min. The cups were weighed every 1 h interval for the period of 8 h. The slopes of the steady-state (linear) portion of weight loss versus time curves were used to calculate WVTR.

8. Water contact angle (CA), water solubility (WS), and swelling ratio (SR)

The surface hydrophobicity of the agar and agar/fiber composite films was measured using a water contact angle analyzer (model Phoenix 150, Surface Electro Optics Co., Ltd., Kunpo, Korea). The rectangular shape of films (3 cm × 10 cm) were placed on the horizontal movable stage (black Teflon coated steel, 7 cm × 11 cm) fitted with the water contact angle analyzer. 10 μL of water was dropped on the surface of film samples using a micro syringe[19]. The CA on both sides of the water drop was measured to assume symmetry and horizontal level. Triplicates were performed for each sample and the average values were reported.

Water solubility (WS) of agar and composite films was determined as the percentage of soluble matter from the initial dry matter of film samples. Three randomly selected specimens from each type of film were first dried at 105°C for 24 h to determine initial dry matter. The dried films were immersed in 30 mL of distilled water taken in a 50 mL beaker. The beaker was covered with Parafilm "M" wrap (American National. Can, Greenwich, CT, USA), and subsequently stored in an environmental chamber set at 25°C for 24 h with occasional stirring. The remaining pieces of undissolved films were removed from the beakers, gently rinsing them with distilled water, and then oven dried at 105°C, for 24 h to obtain final dry weight. The weight of solubilized matter was calculated by subtracting the weight of final dry matter with the weight of initial dry matter and expressed as a percentage of WS.

Swelling ratio (SR) of the films was determined gravimetrically. Pre-weighed square specimens (25 mm × 50 mm) were immersed in distilled water for 2 h, then the film samples were removed from water and weighed after removing the surface water with blotting paper. The percent SR of the films were calculated as follows:

$$\mathrm{SR}\ (\%) = (W_t - W_0)/W_0 \times 100 \quad (3)$$

where W_0 and W_t are the weight of the film samples before and after soaking into the water respectively.

9. Statistical analysis

The measurements of color, tensile properties, WVP, WCA, and WS were triplicated with individually prepared films as the replicated experimental units. One-way analysis of variance (ANOVA) was conducted. The significance of each mean property value was determined ($p<0.05$) with the Duncan's multiple range tests using a statistical software package (SPSS 12.0, SPSS Inc., Chicago, IL, USA).

Results and Discussion

1. Chemical composition

Results of proximate composition of food processing wastes and cellulose analysis of agricultural wastes are shown in Table 1 and 2, respectively. Major components of rice wine and beer brewing wastes are protein and carbohydrate, but raspberry wine and corn processing wastes contained high

Table 1. Proximate composition of food processing wastes[1)]

Sources	MC (%)	Fat (%)	Protein (%)	Carbohydrate (%)	Ash (%)
rice wine waste	3.6±0.0[b]	7.1±0.9[b]	27.1±0.2[c]	60.9±1.2[d]	1.4±0.0[a]
beer brewing waste	2.6±0.1[a]	8.9±0.3[c]	28.1±0.5[d]	55.4±1.0[c]	5.0±0.0[b]
raspberry wine waste	3.6±0.1[b]	4.3±0.4[a]	11.3±0.4[a]	50.2±1.1[b]	30.5±0.2[c]
corn waste	6.4±0.1[c]	20.9±0.8[d]	12.1±0.5[b]	27.4±1.8[a]	33.3±0.4[d]

[1)]Each value is the mean of five replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.

Table 2. Chemical composition of ligno-cellulosic fibers[1)]

Fibers	α-cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Garlic stalk	49.8±1.8[c]	17.53±0.9[d]	28.6±0.7[b]	2.48±0.09[a]
Garlic skin	41.7±2.1[a]	20.8±1.6[b]	34.62±2.4[c]	3.38±0.28[b]
Onion stalk	45.5±0.9[b]	25.5±0.3[c]	26.2±1.7[a]	2.78±0.36[a]
Onion skin	41.1±1.1[a]	16.2±0.6[a]	38.9±1.27[d]	3.8±0.012[b]

[1)]Each value is the mean of five replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.

amount of ash. The content of these waste materials mainly has decreased due to the filtering aid included during filtering process. On the contrary, the major component of the agricultural processing wastes was cellulose. In the case of garlic stalk, it composed of 50% of cellulose. This results suggests that the food processing by-products and agricultural processing wastes have high potential for being used as a reinforcement filler for the preparation of biocomposite films for the biodegradable packaging application.

2. Surface color and optical properties

Flexible and free-standing films were formed by blending powders of the food processing by-products and agricultural processing wastes with agar, in which agar has been used as a polymer matrix to test the function of the powders as biofiller to form composite films. The color and transmittance properties of the composite films were dependent on the type of fillers, their microstructure, the distribution and the size of particles, and the surface roughness. The surface color and optical properties of agar and agricultural and industrial waste incorporated agar films were shown in Table. 3. The lightness (L) values of all composite films were found to be lower than the control agar film. On the other hand, Hunter a-, b-, and ΔE values of biocomposite films were higher than those of agar film. However, the degree of change in L-, b-, and ΔE values was more signicant in case of onion skin, raspberry waste and rice straw reinforced composite films. The decrease in L-values and the increase in a-, b-, and ΔE values have been observed in the agar nanocomposite films[20)]. But a significant change occurred in color value for the composite films filled with onion skin and raspberry waste. This may be due to the natural pigments in the onion and raspberry wastes, i.e., quercetin and anthocyanin, respectively. The natural pigment in the onion skin influenced the change in L value of the composite film more than other fiber reinforced ones. Also the raspberry waste filled composite film showed higher b and ΔE values than the control agar film.

The percent transmittance of the agar and biocomposite films were shown in Table 3. Apparently, the transmittance values of the biocomposite films decreased significantly compared to the agar film. The decrease in transparency of the composite films is mainly due to the addition of opaque natural fiber materials into the agar biopolymer. Agar composite films with onion skin, stalk and garlic stalk raspberry waste showed significantly lower transmittance value compared with those of other biocomposite films. The transmittance value is affected by the particle size and the compatibility with the polymer matrix. The differences in refractive index of the agar and filler also led to decrease in transparency of the agar film. The similar result was observed by Venunadan et al.[21)] for cellulose/silk fiber composites, they reported that the variation of transparency between the control and composite films may be due to the difference in refractive index of the cellulose matrix and natural fibers.

3. Morphology

The interfacial adhesion between the fiber and agar biopolymer was investigated using scanning electron microscopy (SEM). The SEM images of fractured surfaces of the composites of onion and garlic fiber composite films are shown in Fig. 1. It is clearly shown that the natural fiber materials are evenly distributed in the polymer matrix which indicates the fibers are well mixed with agar polymer matrix. Inter-space is observed between the fiber and the polymer matrix (Fig. 1(a)

Table 3. Apparent color and transmittance of various agricultural processing and food processing waste powder/agar composite films[1)]

Film	L	a	b	ÄE	T_{660nm}
agar control	92.39±0.09^{i}	-0.64±0.01^{a}	5.43±0.07^{b}	3.21±0.11^{a}	79.4±1.8^{e}
rice straw*	75.17±0.65^{c}	0.50±0.14^{c}	16.89±0.69^{g}	23.82±0.51^{g}	33.2±1.7^{b}
rice hull	83.67±1.18^{f}	0.28±0.02^{bc}	12.43±0.67^{e}	14.36±1.32^{d}	50.9±6.0^{c}
rice bran	88.63±0.95^{h}	-0.79±0.07^{a}	11.75±1.99^{de}	10.53±2.16^{c}	58.5±4.3^{d}
broken rice	92.16±0.46^{i}	-0.65±0.04^{a}	6.08±0.25^{b}	3.97±0.35^{a}	78.6±1.4^{e}
garlic skin	86.23±0.63^{g}	-0.40±0.04^{ab}	10.95±0.58^{d}	11.45±0.86^{c}	19.6±1.4^{a}
onion skin	69.43±1.41^{b}	2.11±0.50^{d}	25.54±0.22^{i}	33.80±1.14^{h}	17.4±0.7^{a}
garlic stalk	81.60±0.74^{e}	-0.70±0.08^{a}	17.13±0.46^{g}	18.95±0.99^{e}	19.7±0.8^{a}
onion stalk	80.17±0.56^{d}	-0.43±0.06^{ab}	18.16±0.35^{h}	20.85±0.61^{f}	16.4±1.2^{a}
rice wine waste	91.08±0.16^{i}	-0.85±0.08^{a}	8.71±0.33^{c}	6.65±0.32^{b}	52.1±3.3^{c}
beer brewing waste	80.24±1.90^{d}	0.83±0.44^{c}	15.16±1.64^{f}	18.77±2.51^{e}	22.1±4.9^{a}
raspberry waste	42.03±1.71^{a}	16.45±2.20^{e}	3.99±0.84^{a}	55.16±2.03^{i}	16.1±2.0^{a}
corn waste	82.47±1.78^{ef}	-1.07±0.09^{a}	9.48±0.29^{c}	13.70±1.63^{d}	19.7±2.6^{a}

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.
*10% waste powder based on agar.

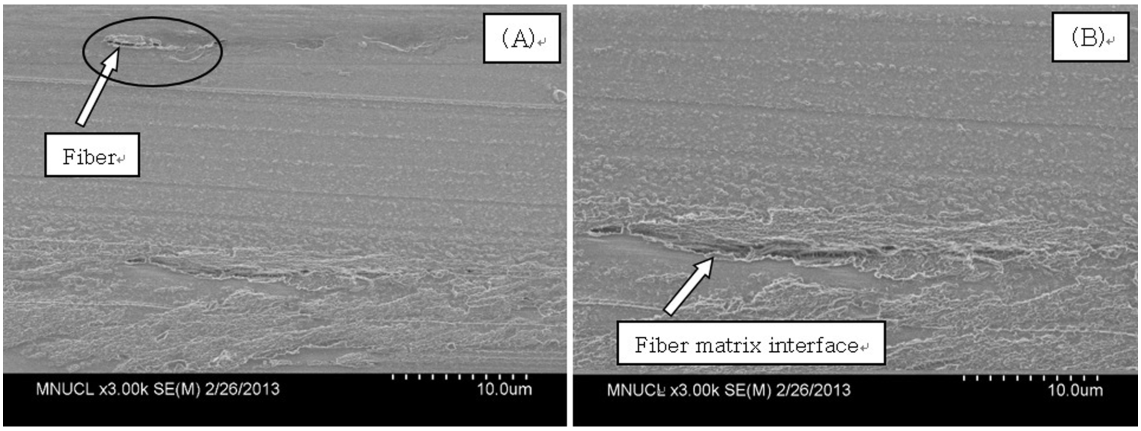

Fig. 1. SEM images of cross-section of (A) agar/onion skin and (B) agar/garlic skin biocomposite films.

and (b)), which is expected to affect the inferior tensile properties of the biocomposite films. Similar results were observed by Ashori and Nourbakhsh[4)] in PP/bagasse fiber composite films. The cell wall structures of the natural fibers are usually covered with lignin and waxy substance which made smooth film surface, but tended to reduce the affinity with the biopolymer.[22)]

4. Mechanical properties

Table 4 shows the tensile strength, elongation and elastic modulus of the agar and agar composite films. It is clearly shown that the tensile strength and modulus of agar composites films were lower than those of agar. In case of lignocellulosic resources (onion, garlic, rice hull, rice straw and beer brewing waste), the decrease in tensile strength could be due to not only the lack of compatibility of fiber powders with polymer matrix but also the random orientation of the short fiber in the composites. The tensile strength of the composites is mainly affected by the fiber orientation, fiber aspect ratio (length/width), nature of reinforcement, and the fiber-matrix interfacial adhesion[23)]. In addition, weaker bonding between the fibers and the agar polymer matrix leads to decrease their interfacial interactions, consequently decreased in the tensile strength. The interfacial bonding between the fiber and polymer matrix can be improved by using compatibilizer[24)]. In order to improve the mechanical property of biocomposite

Table 4. Tensile properties of various agricultural processing and food processing waste powder/agar composite films[1)]

Film	Thickness (μm)	TS (MPa)	E (%)	Modulus (MPa)
agar control	52.6±2.0^{a}	53.7±4.3^{i}	25.5±4.4^{de}	1647.1±88.5^{h}
rice straw*	136.8±17.2^{f}	12.2±2.8^{b}	12.0±3.0^{b}	401.2±148.3^{b}
rice hull	140.4±21.8^{fg}	11.8±2.0^{b}	16.8±2.4^{c}	363.9±94.7^{b}
rice bran	109.1±9.3^{e}	15.1±2.8^{c}	17.7±3.8^{c}	526.0±61.3^{c}
broken rice	82.9±10.7^{b}	28.9±2.4^{g}	17.5±2.1^{c}	1031.9±83.5^{ef}
garlic skin	147.4±16.7^{g}	15.9±2.9^{cd}	8.8±2.7^{a}	648.7±103.0^{d}
onion skin	104.6±4.4^{de}	24.8±1.2^{e}	11.7±2.9^{b}	974.2±163.1^{e}
garlic stalk	103.9±3.9^{de}	26.5±1.5^{f}	12.1±1.9^{b}	1044.5±84.0^{ef}
onion stalk	96.0±3.1^{cd}	28.9±1.7^{g}	12.4±2.2^{b}	1134.7±88.7^{g}
rice wine waste	72.5±6.2^{a}	31.2±3.1^{h}	20.2±4.5^{d}	1089.7±86.9^{fg}
beer brewing waste	135.3±13.4^{f}	11.9±1.7^{b}	18.2±3.6^{cd}	388.4±77.0^{b}
raspberry wine waste	188.4±22.9^{h}	7.6±1.2^{a}	13.0±3.9^{b}	276.0±57.5^{a}
corn waste	88.7±6.6^{bc}	17.0±2.5^{d}	27.2±6.0^{e}	408.2±116.0^{b}

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.
*10% waste powder based on agar.

films, surface modification of natural fibers by various types of physical or chemical treatments has been tried. The reinforcement of fibers decreased the flexibility of the film as indicated in the decrease of elongation at break, and it also decreased the stiffness of the composite films as indicated in the decrease of elastic modulus. Among the tested waste materials, the rice wine waste showed the least decrease in tensile strength indicating that it has high potential to be used as a filler for the preparation of biocomposite films.

5. Water vapor permeability

Water vapor permeability of the agar and composite films was presented in Table 5. Generally, the WVP of the agar/fiber composite films were significantly higher than that of the agar films. This is mainly attributed not only to the lack of interfacial affinity of the fibers with the agar biopolymer but also to the hydrophilic nature of the cellulosic materials. Onion and garlic fibers seemed to be less effective for reducing WVP of the agar film. The WVP of rice wine waste (1.51±0.10 g.m/m^2.s.Pa) and broken rice (1.56±0.2 g.m/m^2.s.Pa) included films were slightly higher than that of agar film. Various types of impermeable nanofillers with high compatibility with polymer matrix are usually used for the improvement of water vapor barrier property of biocomposite films. Rhim et al.[25)] reported that the WVP of the agar based nanocomposite films decreased by the addition of compatible nanofiller such as clay minerals. Rhim[26)] also reported that the addition of nanofiller with increasing aspect ratio or concentration of nanofiller could reduce the WVP of agar-based nanocomposite films. This could be due to the impermeable silicate layer of clay dispersed in the agar polymer matrix attributes to the increasing tortuous path length for water vapor diffusion.

Table 5. Water vapor permeability (WVP) and water contact angle (CA) of various agricultural food processing waste powder/agar composite films[1)]

Film	WVP ($\times10^{-9}$g.m/m^2.Pa.s)	CA (deg.)
agar control	1.41±0.08^{a}	63.5±0.8^{cd}
rice straw*	3.38±0.45^{e}	56.2±0.9^{c}
rice hull	4.38±0.34^{f}	51.5±2.3^{b}
rice bran	2.57±0.32^{d}	52.9±2.1^{b}
broken rice	1.56±0.27^{ab}	52.2±0.8^{b}
garlic skin	2.61±0.21^{d}	67.7±3.0^{d}
onion skin	2.03±0.26^{bc}	66.9±2.2^{d}
garlic stalk	2.02±0.16^{bc}	66.3±1.7^{d}
onion stalk	1.95±0.05^{bc}	66.8±2.6^{d}
rice wine waste	1.51±0.10^{ab}	53.8±0.4^{bc}
beer brewing waste	3.52±0.43^{e}	53.2±2.4^{b}
raspberry wine waste	4.56±0.11^{f}	54.0±2.3^{bc}
corn waste	2.31±0.25^{cd}	48.8±0.8^{a}

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.
*10% waste powder based on agar.

6. Water contact angle (CA)

The water contact angle (CA) is used as a measure of wettability or surface hydrophilicity/hydrophobicity of polymer films. Table 5 shows the CA of agar and agar composite films. The CA of composite films including corn waste, rice wine waste, raspberry waste was lower than that of the control agar film. It is probably due to the increased hydrophilicity of such food processing waste materials caused by the removal of hydrophobic materials such as natural wax during the food processing. However, the CA of agar composite films with lingo-cellulosic fibers increased indicating that the surface hydrophobicity of the composite films increased. Agar/garlic skin composite film showed a slightly higher CA value compared to that of other composite films. However, no significant differences were observed between the biocomposite films. On the contrary, the control agar film exhibited significantly lower value (63.5±0.8^{o}) than those of the composite films. Rhim[26] prepared agar/nanoclay composite films and reported that the incorporation of nanoclay decreased the water contact angle of agar-based nanocomposite films which could be due to the hydrophilic nature of the nanoclay.

7. Moisture content, water solubility, and swelling ratio

Table 6 shows the moisture content of the agar and agar/fiber composites films. The reinforcement of fiber materials with agar matrices increased the MC of the biocomposite films. However, agar composite with rice wine waste showed lower MC (14.8±0.1%) than the control agar film (15.9±0.3%). The moisture content depends on the reactive hydroxyl groups present in polymer that could react with cross-linking agent, which reduces the moisture content[27]. In the case of rice wine waste, a reduction in hydroxyl groups might occurred by the reaction with the hydroxyl groups present in agar.

Table 6 also shows the effect of fibers on water solubility of the agar and agar composite films. The composite films reinforced with garlic stalk (28.1±0.7%), rice hull (29.1±1.2%) rice wine waste (30.6±0.2%), and corn waste (29.9±1.2%) showed slightly higher water solubility than agar film (27.7±0.6%). Onion skin increased the water resistant property of the composite film (26.4±0.8%). However, no pronounced differences were observed between the control and biocomposite films. Similarly, Rhim[26] reported that the addition of nanoclay into the agar film decreased the water solubility of the nanocomposite films. This result could be attributed to the occurrence of strong interactions between the polymer matrix and nanoclay via hydrogen bond.

The swelling ratio (SR) of the agar and biocompsoite films was also shown in Table 6. Generally, the SR of composite films reinforced with natural lingo-cellulosic materials decreased significantly (p<0.05). Among the tested waste materials, garlic stalk (576.4±29.6%) and corn waste (546.4±22.3%) exhibited lower level of SR compared with others. This may be due to the existence of less interfacial area and less swelling nature of the natural fibers. Similar result was observed by Sahari et al.[5] who reported that the incorporation of natural fibers into the sugar palm starch film decreased the water uptake of the composite films which could be due to the for-

Table 6. Moisture content (MC), water solubility (WS), and swelling ratio (SR) of various agricultural and food processing waste powder/agar composite films[1)]

Film	MC (%, w.b.)	WS (%)	SR (%)
agar control	15.9±0.3^{ab}	27.7±0.6^{bc}	1120.4±28.3^{f}
rice straw*	18.4±1.2^{d}	26.2±0.5^{ab}	709.4±31.2^{c}
rice hull	18.8±0.4^{d}	29.1±1.2^{cde}	1081.3±31.9^{f}
rice bran	18.1±1.5^{cd}	28.6±2.0^{cd}	1228.8±83.8^{g}
broken rice	16.6±0.3^{bc}	25.7±0.2^{a}	1199.5±42.0^{g}
garlic skin	16.3±0.3^{ab}	27.2±0.7^{abc}	893.9±63.1^{e}
onion skin	15.8±0.1^{ab}	26.4±0.8^{ab}	877.2±19.6^{de}
garlic stalk	16.4±0.2^{ab}	28.1±0.7^{bcd}	576.4±29.6^{ab}
onion stalk	16.2±0.5^{ab}	27.3±0.2^{abc}	810.0±45.7^{d}
rice wine waste	14.7±0.3^{a}	30.6±0.2^{e}	616.8±7.0^{b}
beer brewing waste	19.8±1.0^{de}	25.5±2.2^{a}	1102.8±17.0^{f}
raspberry wine waste	19.6±1.2^{de}	28.0±1.0^{bcd}	818.9±3.1^{d}
corn waste	21.1±1.8^{e}	29.9±1.2^{de}	546.4±22.3^{a}

[1)]Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly (p>0.05) different by Duncan's multiple range test.

*10% waste powder based on agar.

mation of good interfacial bonding between the fibers and polymer matrix. In addition, Demir et al.[28] reported that the formation of strong hydrogen or covalent bond between the free hydroxyl groups of fibers and water molecules can reduce water uptake ratio. Furthermore, lower interfacial adhesion could form cracks and voids between the polymer matrix and fiber, which make water molecules penetrate easily and hold water molecules in the voids.

Conclusion

For the value-added utilization of under-utilized natural resources, thirteen different type of wastes or by-products obtained from food processing industries and agricultural processing field were tested for their reinforcing effect in the biocomposite films. To achieve this goal, the selected waste powders were used as reinforcing filler in agar-based film and their effect on the film properties were evaluated. Mechanical properties of the composite films decreased with the addition of natural fibers and industrial wastes, due to the lack of compatibility with the agar biopolymer. The water vapor permeability of the biocomposite films was found to be higher than the agar film. In addition, composite films with natural fibers resulted in significant decrease of swelling ratio. The percentage transmittance of the agar film decreased by blending with onion, garlic fibers, and other industrial by-products, due to the difference in refractive index values of the agar and the fillers. Among the tested materials, agricultural processing wastes such as stalks of onion and garlic, onion skin, and food processing waste, rice wine waste showed high potential for the value-added utilization as new bio-resources for the preparation of biocomposite films. For the better utilization of these bio-resource materials, further process such as chemical treatment for the modification of surface to improve the interfacial interaction between the fiber and polymer matrix which can be enhanced the performance of the biopolymers. In addition, the utilization of such under-utilized ligno-cellulosic materials can be further improved by extracting cellulose nanocrystals from those lingo-cellulose sources to make bio-nanocomposite materials.

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