

Wetting Properties of Biopolyester Films Prepared by Thermo-Compression Method

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Abstract Water resistance of three biopolyester films, such as poly-L-lactate (PLA), poly-hydroxybutyrate-co-valerate (PHBV), and Ecoflex, and low density polyethylene (LDPE) film was investigated by measuring contact angle of various probe liquids on the films. The properties measured were initial contact angle of water, dynamic change of the water contact angle with time, and the critical surface energy of the films. Water contact angle of the biopolyester films (57.62-68.76°) was lower than that of LDPE film (85.19°) indicating biopolyester films are less hydrophobic. The result of dynamic change of water contact angle also showed that the biopolyester films are less water resistant than LDPE film, but much more water resistant than cellulose-based packaging materials. Apparent critical surface energy for the biopolyester films (35.15-38.55 mN/m) was higher than that of LDPE film (28.59 mN/m) indicating LDPE film is more hydrophobic.

Keywords: wetting property, contact angle, surface tension, biopolyester film, thermo-compression

Introduction

Recently, biopolyesters have been considered as an alternative of non-biodegradable petrochemical-based plastic materials due to their environmentally- or eco-friendly nature and their sustainability (1-6). Biopolyesters are polyesters produced by biological means, such as enzyme-catalyzed polymerization and microbial fermentation, from readily renewable resources (6). However, a chemical synthesis is sometimes involved in polymerization processing of some biopolyester such as poly(lactide) (PLA). Due to their biocompatibility as well as good performance and processability, these polymers have excellent potential for use in packaging applications.

For the use as packaging materials in specific areas, proper properties of packaging materials, depending on their application, should be determined. Wetting properties or water-related physical properties of packaging materials are one of the most important properties of packaging materials especially used in high moisture conditions. They include surface hydrophilicity/hydrophobicity, water resistance, and water absorption property (7, 8). Generally, packaging materials need a good water resistance to maintain their physical strength even after exposure in water. Therefore, wetting properties along with water vapor barrier properties are the basic material characteristics (8).

As an index of water resistance, contact angle of water or other liquid drops has been frequently used to test the wettability of packaging materials. Han and Krochta (8, 9) used contact angle measurement to test the wetting properties of whey-protein-coated paper, Rhim *et al.* (10, 11) also have tested contact angle of biopolymers (alginate, soy protein, and PLA) coated paperboards used for linerboard of corrugated fiberboard box, and Hong *et al.* (12) tested

the wetting property of whey protein isolate coated plastic films such as polypropylene (PP) and poly(vinyl chloride) (PVC). In addition, wetting properties determined by contact angle of various plastic films as well as some biopolymer films have been documented in the literature (13). However, such information on recently introduced biopolyester films has not been available yet.

The main objectives of the present study were to measure the wetting properties of biopolyester films prepared by a thermo-compression method, including initial contact angle, dynamic contact angle change, and critical surface tension of the films.

Materials and Methods

Materials PLA (poly-L-lactate, Biomer[®] L9000), PHBV (poly-hydroxybutyrate-co-valerate, 13% valerate content), Ecoflex, and low density polyethylene (LDPE), were obtained from Biomer Inc. (Krailling, Germany), Monsanto Co. (St. Louis, MO, USA), BASF Aktiengesellschaft (Ludwigshafen, Germany), and Sonoco Products Co. (Hartsville, SC, USA), respectively. All resins were dried in a vacuum oven at 60°C for 24 hr before use. As probe liquids, water (HPLC grade), formamide, and dimethylsulfoxide (DMSO) were purchased from Fischer Scientific (Fair Lawn, NJ, USA), and glycerol was obtained from Sigma Chemicals Co. (St. Louis, MO, USA).

Preparation of films Biopolyester films were prepared using a thermo-compression method described previously (14, 15). A Carver laboratory press (Hydraulic Unit, Model 3925; Carver Inc., Wabash, IN, USA) was used for thermo-compression of biopolymer resins. Two different compaction temperatures were used depending on polymer's melting point (i.e., 210°C for PLA and LDPE, and 150°C for Ecoflex and PHBV). About 2-3 g of the polymer resin was placed between 2 stainless steel plates (1 mm thick, 25.4 cm wide, and 25.4 cm long) lined with Teflon cloth and

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then inserted them between the platens of the press heated to the compaction temperature. After heating for 30 sec at the temperature, a pressure of about 68.9 MPa (10,000 psi) was applied for 2 min followed by the removal of the Teflon cloth liners. The compacted film was easily peeled out from the Teflon cloth layers after cooling to room temperature.

Contact angle of water A contact angle analyzer (model Phoenix 150; Surface Electro Optics Co. Ltd., Gunpo, Korea) was used to measure the contact angle (θ) of water in air on the surface of biopolyester films. A film sample (3×10 cm) was glued on a movable sample stage (black Teflon coated steel, 7×11 cm) and leveled horizontally, then a drop of about 10 μ L of water was placed on the surface of the film using a micro-syringe. The contact angles on both sides of the drop were measured to ensure symmetry and horizontal level. Dynamic contact angle change was measured by recording the contact angle change of a water drop with time within 200 sec at room temperature at 50±5% RH. Wetting energy (in mN/m) of the films was determined as follows:

$$\gamma \times \cos \theta$$

where, γ is a surface tension of a probe liquid (72.8 mN/m for water) and θ is a contact angle. The wetting energy is a liquid surface tension at which a liquid would spontaneously wet a particular solid film surface (13).

Critical surface energy To determine critical surface energy of the films, HPLC-grade water, glycerol, formamide, and DMSO were used as probe liquids. Apparent Zisman's critical surface energy ($\gamma_{c,app}$) of the films was determined by the Fox-Zisman plot (plotting $\cos \theta$ vs. surface energy of individual probe liquid). Surface energy for the probe liquids is 72.8, 63.4, 58.2, and 44.0 mN/m for water, glycerol, formamide, and DMSO, respectively (13). The critical surface energy of a film represents complete dispersion of any liquid with $\theta = 0$ (i.e., $\cos \theta = 1$). Then, $\gamma_{c,app}$ was estimated by extrapolating the straight line obtained from the Fox-Zisman plot to the $\cos \theta = 1$ (13).

Results and Discussion

Contact angle of water Results of the contact angle of water on biopolyester films are shown in Table 1. Contact angle of water is usually used as an index of water resistance of packaging materials. It is affected by hydrophilicity or hydrophobicity of the packaging materials. Therefore, contact angle of water on the biopolyester films is expected to depend on the chemical or structural properties of the film. PLA, a linear aliphatic polyester, is a highly versatile biopolymer derived from renewable resources like corn. It has high strength, high modulus, and good processability with properties of thermo-plasticity, biodegradability, and biocompatibility. PHBV is an aliphatic copolyester composed of 3-hydroxybutyrate and 3-hydroxyvalerate produced by microbial fermentation. PHBV is a highly crystalline polymer with melting points and glass transition temperatures similar to PP. Ecoflex is an aliphatic-aromatic copolyester based on butanediol, adipic acid, and terephthalic acid. Ecoflex is a thermoplastic material similar

Table 1. Contact angle of water and wetting energy of biopolyester and LDPE films¹⁾

Film	Contact angle (°)	Wetting energy (mN/m)
PLA	68.76±1.31 ^c	26.36±1.55 ^b
PHBV	60.38±1.71 ^b	35.83±1.98 ^c
Ecoflex	57.62±0.82 ^a	38.99±0.88 ^d
LDPE	85.19±0.62 ^d	6.10±0.78 ^a

¹⁾Means of three replicates±SD. Any two means in the same column followed by the same letter are not significantly different ($p>0.05$) by Duncan's multiple range test.

to LDPE with better mechanical properties such as excellent tear-resistance and flexibility (4-6).

In the present study, LDPE film was included for comparison. LDPE film showed the highest contact angle of water and followed by PLA, PHBV, and Ecoflex, respectively. Biresaw and Carriere (16) reported the contact angle of water on PLA film, prepared by a thermal compaction method using a Carver laboratory press, was 67.74°. Their result agrees well with the present study (68.76±1.31°). As mentioned previously, contact angle of water indicates hydrophilicity/hydrophobicity of a solid material (17). Many synthetic polymer films having hydrophobic surfaces usually give high contact angles with water, well above 90° (17). Generally, a film exhibiting a water contact angle greater than 65° is considered hydrophobic and a film whose water contact angle is greater than 150° is commonly called a superhydrophobic film represented by the surface of lotus or taro leaves (18). To obtain hydrophobic films, the combination of surface roughness and low surface energy is required (18).

The result of water contact angle of biopolyester films showed a similar trend as other water barrier properties such as water vapor permeability (WVP) and water solubility (WS). Rhim (15) reported that WVP of LDPE film (0.07-0.10×10⁻¹¹ g·m/m²·sec·Pa) (19) was the lowest among the films tested, and followed by PHBV (1.26×10⁻¹¹ g·m/m²·sec·Pa), PLA (2.54×10⁻¹¹ g·m/m²·sec·Pa), and Ecoflex (6.03×10⁻¹¹ g·m/m²·sec·Pa), respectively. Though the order of PHBV and PLA is reversed, generally, water vapor barrier property of the films determined by WVP coincided well with the hydrophilicity or hydrophobicity of the films determined by contact angle.

Wetting energy also indicates hydrophilicity or hydrophobicity of a film (17). The more hydrophilic a film is, the greater wetting energy it has. Generally, a film with a strong apolar surface (or hydrophobic, in the sense of low-energy surface) gives lower surface energy less than 40 mN/m (17). As shown in Table 1, wetting energy of LDPE film was very low compared with the biopolyester films, which indicates that LDPE is more water resistant than the other films.

Dynamic change of water contact angle Dynamic change of water contact angle on biopolyester and LDPE films is shown in Fig. 1. The contact angle of water on all the tested films decreased linearly over a short time period. However, there was a clear difference in initial water contact angle of the films tested. The initial contact angle values of water on the films obtained through linear regre-

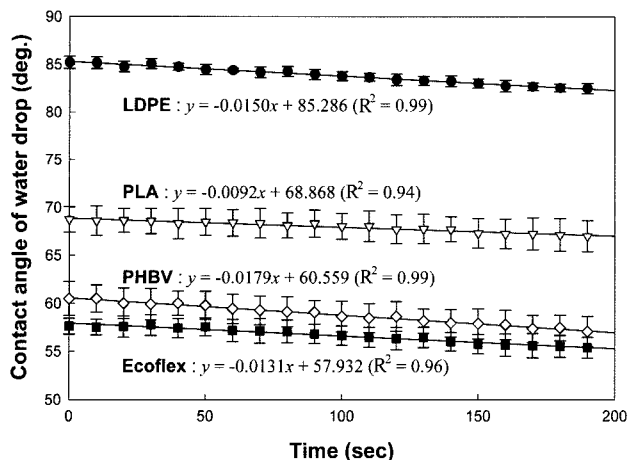


Fig. 1. Dynamic changes in contact angle of water drop on biopolyester and LDPE films.

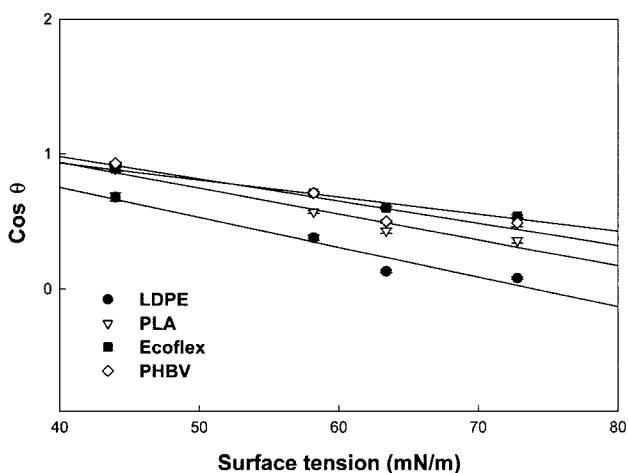


Fig. 2. Fox-Zisman plot of biopolyester and LDPE films. Data on each plot are for dimethylsulfoxide, formamide, glycerol, and water, lower to higher surface energy, respectively. θ is the contact angle of the respective probe liquid on the film.

ssion were agreed well with the static water contact angle measurement (Table 1). The rate of contact angle change (i.e., slope of contact angle changing line) was also varied depending on the films. The contact angle changing rate ranged from 0.0092 to 0.0179°/sec, which was much lower than that of paperboard (0.0650°/sec) (10). This indicates the biopolyester films are more hydrophobic or more water resistant than the paperboard.

Critical surface energy Wettability of the films was tested by measuring contact angles on the films using four different probe liquids. Cosine values of contact angle ($\cos \theta$) were plotted against surface tension values of the probe liquids using the Fox-Zisman plot as shown in Fig. 2. All wettability lines fit well to a linear model with high coefficient of determination (R^2) values. From the linear regression equation of the Fox-Zisman plot (Table 2), apparent critical surface energy ($\gamma_{c,app}$) was determined by calculating the surface tension (x) values corresponding to the zero values of the contact angle ($y=1$), and the results are also listed in Table 2. LDPE film showed lower critical surface energy

Table 2. Results of Fox-Zisman plot of biopolyester and LDPE films

Film	Linear regression eq.	R^2	$\gamma_{c,app}^1$ (mN/m)
PLA	$y = -0.0192x + 1.7081$	0.95	36.84± 9.78
PHBV	$y = -0.0163x + 1.6286$	0.90	38.55±14.47
Ecoflex	$y = -0.0129x + 1.4534$	0.97	35.15± 7.29
LDPE	$y = -0.0220x + 1.6282$	0.93	28.59±11.44

¹Calculated critical surface energy expressed as mean±95% confidence interval.

compared with biopolyester films indicating that LDPE is more hydrophobic than the others. Values of surface tension in polymers range from 20 mN/m for Teflon to 46 mN/m for nylon 6,6 (13). These critical surface energy values are comparable to the previously reported values of PLA (43.47 mN/m) (16) and other commodity plastic films (PP, 33.04 mN/m; PVC, 32.30 mN/m) (12). Surface tension is a free surface energy of liquids and solids, when their molecules at the surface are not completely surrounded by the same type of molecules, generating unbalanced forces. Surface tension is a major index of polymers for determining film's wettability which is very important properties in adhesion and printing as well as packaging industry (20).

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