General paper

Mechanical and Thermal Properties of Biopolyester-Lignophenol Films

Eriko OHMAE*, Masamitsu FUNAOKA* and Syuzo FUJITA**

* Faculty of Bioresources, Mie University,
1515, Kamihama, Tsu, Mie 514-8507, Japan
CREST, JST

**Faculty of Health Sciences, Aomori University of Health and Welfare,
Mase 58-1, Hamadate, Aomori 030-8505, Japan

Abstract: Novel lignin-based polymers, lignophenols, have been derived from native lignins through the phase-separation system composed of phenol derivatives and concentrated acid. The molecular weight of lignophenol was controlled from ca.7400 to ca.520, using the intramolecular switching function under the alkaline condition. By the blending of the biopolyester [poly(3-hydroxybutyrate)] with butylhydroxyanisole (BHA), triacetin and lignophenol 2nd derivative, the elongation ratios of the resulting films became 5, 5 and 20 times higher, respectively, compared with the control film without additives. For the composite films with BHA and triacetin, the shrinkages and the weight losses were observed with increasing temperature, due to the evaporation of additives. On the other hand, for the composite film with lignophenol 2nd derivative, no shrinkage was observed, and the thermogravimetric profiles were almost compatible with that of the control film. The DSC analysis indicated that the crystallization enthalpies of biopolyester-lignophenols films decreased with increasing contents of lignophenols.

Key words: Lignophenol, Biopolyester, Plasticizer, Resources circulation, Composite film, Physical properties, Thermal analysis, Thermostability

1. INTRODUCTION

Poly-3-hydroxybutyrate (PHB) is an optically active biopolymer produced by bacterial fermentation [1]. PHB is a biodegradable thermoplastic [2, 3], and has drawn much industrial attention as raw materials for material productions. However, it is hard and brittle because of its high crystallinity. For improving these undesirable properties, some plasticizers have been mixed with PHB. Hammond *et al.* [4] indicated that butylhydroxyanisole (BHA), which is used as an antioxidant in foods, was effective as a plasticizer for PHB: the enthalpy of melting and Young's modulus of the resulting composite film were reduced, and the elongation ratio increased. Lignin, which is an aromatic polymer with alkyl side chains and methoxyl groups, may work as a plasticizer for PHB.

The native lignins have been converted into linear type-phenolic lignin based polymers (lignophenols) composed mainly of 1,1-bis(aryl)propane-type units (Fig.1) through the phase-separation process [5-8]. The molecular weight and phenolic properties of lignophenols can be controlled using the intramolecular switching function [9-12]: C1-phenols hybridized to lignophenol at ortho position to their hydroxyl group attack adjacent C2-carbons by mild alkaline treatment, followed by the cleavage of C2-aryl ether linkages.

In the present work, the lignophenols with different functionalities were synthesized through the phase-separation process, followed by the intramolecular switching treatment. The relationship between the structures of lignophenols and the effect as plasticizers for PHB was discussed.

Fig.1. Model of 1,1-bis(aryl)propane unit in lignophenols.

2. EXPERIMENTAL

2.1. Synthesis of Lignophenol Derivatives

The acetone solution of *p*-cresol (3mol/C₉) was added to the extractives-free beech (*Fagus crenata*) wood meals (14 mesh). After 24 hrs, the acetone was evaporated. Seventy-two percent sulfuric acid (4mL/g wood meals) was added to the *p*-cresol-sorpted wood meals and the mixture was vigorously stirred at room temperature for 1 hr. The reaction mixture was added to excess amount of deionized water with stirring. The precipitates were collected by centrifugation, washed with water and dried, from which lignophenol fractions were extracted with acetone.

The lignophenols dissolved in 0.5N NaOH were placed in the stainless steel autoclaves (100mL volume), and then heated in an oil bath at 140 °C or 170 °C for 1 hr. After cooling, the reaction mixtures were acidified with

1N HCl to pH2. The resulting precipitates were collected by centrifugation, washed with water, and dried: the lignophenol 2nd derivative I (treated at 140°C) and II (treated at 170°C).

Pyridine and acetic anhydride were added to lignophenols and lignophenol 2nd derivatives, and allowed to stand at room temperature for 48 hrs. The reaction mixtures were added dropwise to cold deionized water with vigorous stirring. The precipitates (acetylated products) were collected by centrifugation, washed with cold deionized water, and dried under reduced pressure.

2.2. Structural Analyses of Lignophenols

The average molecular weights were measured by gel permeation chromatography (GPC) on CLASS LC-10 system, LC-10AD, SPD-10A (Shimadzu) with four shodex columns (KF804, KF803, KF802 and KF801). THF was used as an eluent. The molecular weights of lignophenols were calibrated using polystyrene standards.

Thermomechanical analyses (TMA) were carried out by penetration mode using TMA/SS 6000 (SEIKO Instruments Inc.). Under the 5g loading, the solid-liquid transformation (T_m) of lignophenol was measured by heating from room temperature to 200°C with a heating rate of 2°C/min.

$^1\text{H-NMR}$ spectra of lignophenols were determined in $\text{C}_5\text{D}_5\text{N-CDCl}_3$ on a JEOL JMN-A500 fourier transform NMR. *p*-Nitrobenzaldehyde was used as the internal reference for the determination. The amounts of grafted phenols in lignophenol molecules were calculated based on the signal intensity of its methyl protons on $^1\text{H-NMR}$ spectra of lignophenols [12].

2.3. Preparation of Composite Films

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)[P(HB-*co*-HV)] with 8% of 3-hydroxyvalerate was provided by Monsanto Japan Limited. Butylhydroxyanisole (BHA), triacetin and lignophenol derivatives were used as additives. The lignophenols were acetylated before preparing the composite films.

P(HB-*co*-HV) and an additive were dissolved in chloroform at 50°C. Then the solution was cast on the stainless steel plates, and the solvent was evaporated at room temperature.

2.4. Physical and Thermal Properties of Composite Films

The test specimens (JIS K-6251, thickness of 0.10 - 0.15mm, length of 33mm and width of 6mm) were prepared from the composite films. The tensile strength and elongation ratio were measured at the rate of 5mm/min using EZ Test (Shimadzu) at room temperature.

Thermal properties of the composite films were investigated by thermomechanical analyses (TMA), thermogravimetry (TG) and differential scanning calorimetry (DSC).

Thermomechanical properties were investigated using TMA/SS 6000 (SEIKO Instruments Inc.). The both ends of the sample (initial length of 10mm and width of 4mm) were fixed on chucks under tensile load of 0.5g. TG was

carried out with about 5mg of sample using TG/DTA 6200 (SEIKO Instruments Inc.). TMA and TG were run at a heating rate of 2°C/min. DSC measurement of the film sample (about 3mg), which was sealed in an aluminum pan, was conducted on DSC-60 (Shimadzu). Thermograms were obtained by first heating at 20°C/min to 200°C, then cooling down to -80°C and re-heating at 20°C/min to 200°C.

3. RESULTS and DISCUSSION

3.1. Properties and Functionality Control of Lignophenols

The structural characteristics and TMA curves of lignophenol derivatives prepared from beech native lignin are given in Table 1 and Fig.2, respectively. The TMA curve for original lignophenol showed apparent phase-transition points at 118 and 144°C, supporting that lignophenols were linear-type polymers. After alkaline treatment at 140°C for 1hr, original lignophenol with the average molecular weight of ca.7400 was converted to lignophenol 2nd derivative I with that of ca.700, due to nucleophilic attack of C1-phenols in lignophenols to C2-carbons [12].

Table 1. Characteristics of beech lignophenol derivatives (acetates).

	$\overline{M}_w$	T_m (°C)	Grafted phenols (mol/C ₉)
Original lignophenol	7400	118, 144	0.73
Lignophenol 2nd der. I	700	54, 71	0.71
Lignophenol 2nd der. II	520	45, 65	0.65

Fig.2. Thermomechanical profiles of lignophenol derivatives (acetates). Testing mode: penetration, load: 5g, heating rate: 2°C/min

Fig.3. (a) Tensile strength and (b) elongation ratio of PHB films with additives. Tensile rate: 5mm/min

With the treatment at 170°C, carbanions of C1 phenolic nuclei or C3 alkoxide ions attack to C2, resulting in the cleavage of cyclic C2 aryl ethers [6, 9]. In addition, the nucleophilic attack of the C1-carbanions to the C2 is followed by the aryl migration and the transformation into the corresponding stilbene (2nd derivative II) [13].

3.2. Mechanical Properties of Biopolyester Films with Additives

The control and composite films were translucent. The control films had the tensile strength of 29 MPa and the elongation ratio of 18% (Fig.3). The tensile strength of all composite films decreased as the additives content increased. By the blending with 20wt% of BHA and triacetin, the tensile strengths decreased to one-half of that for control film. For the composite films with 5wt% of BHA and with 30wt% of triacetin, the elongation ratios got about 5 times higher than that of the control film.

The tensile strength of the composite films with 5 and 10wt% of original lignophenol were comparable to that of the control film, while the elongation ratio got lower. On the macroscopic observation, the segregation of original lignophenols occurred at the surface area of film with increasing additive content, indicating the poor compatibility in the structure between original lignophenol and PHB. By the blending with 5wt% of lignophenol 2nd derivative I, the elongation ratio got 15 times higher than that of the control film. While by the blending with 5-30wt% of lignophenol 2nd derivative II, the elongation ratio got above 20 times higher, indicating that the molecular sizes and structures of lignophenol 2nd derivatives are effective as plasticizers for biopolyester. In the second modification at 140°C and 170°C of lignophenol, the five-membered cyclic structures and the stilbene type structures were formed, respectively [6, 9]. The lignophenol 2nd derivative I is bulky sterically because of the presence of the five-membered cyclic structures. On the other hand, the lignophenol 2nd derivative II has

Fig.4. Thermomechanical profiles of PHB films with additives. Mixing ratio: 5wt%, testing mode: tensile, load: 0.5g, heating rate: 2°C/min

plane-like structures because of the presence of stilbene type structures, which might facilitate the slide of biopolyester molecular chains.

3.3. Thermal Properties of Biopolyester Films with Additives

TMA curves (tensile mode) for the composite films with 5wt% of BHA, triacetin or lignophenol 2nd derivative II are shown in Fig.4. The thermal softening of the control film was observed at 151°C. Although the thermal softening temperature of the composite films with BHA and triacetin were equal to that of the control film, the shrinkages of films were observed before the thermal

Fig.5. Thermomechanical profiles of (a) PHB films with BHA and (b) PHB films with lignophenol 2nd derivative II. Testing mode: tensile, load: 0.5g, heating rate: 2°C/min

Fig.6. Softening temperature of PHB films with additives.

Fig.7. Thermogravimetry profiles of PHB films with additives. Mixing ratio: 5wt%, heating rate: 2°C/min

softening around 150°C. The composite films shrank extremely as the additives content increased (Fig.5(a)). On the other hand, in the films with lignophenol 2nd derivative II, no shrinkage was observed, and the thermal softening temperatures of the composite films shifted from 150°C (with 5wt%) to 140°C (with 30wt%) with increasing additive content (Fig.5(b) and Fig.6).

TG curves for the composite films with 5wt% of BHA, triacetin or lignophenol 2nd derivative II are shown in Fig.7. The weight loss of the control film was observed at 230°C, and the sample disappeared completely at 260°C, due to thermal degradation of PHB. For the composite films with BHA and triacetin, the weight losses were observed around 120°C and 230°C. These weight losses around 120°C increased with increasing

content of BHA and triacetin (Fig.8(a)). On the other hand, in the film with lignophenol 2nd derivative II, no weight loss was observed below the temperature at which biopolyester degraded. Further, the residue increased with increasing lignophenol 2nd derivative II above 260°C at which PHB decomposed (Fig.8(b)). TG curves for BHA, triacetin and lignophenol 2nd derivative II are shown in Fig.9. The weight losses of BHA and triacetin started around 100°C, followed by complete evaporation around 160°C. Lignophenol 2nd derivative II was stable up to 170°C. Therefore, the weight losses observed around 120°C for the composite films with BHA and triacetin were attributed to evaporation of BHA and triacetin from the composite films. The evaporation of

Fig.8. Thermogravimetry profiles of (a) PHB films with BHA and (b) PHB films with lignophenol 2nd derivative II. Heating rate: 2°C/min

Fig.9. Thermogravimetry profiles of additives. Heating rate: 2°C/min

additives from the composites and the subsequent re-crystallization of PHB resulted in the shrinkages of films observed in TMA curves.

TMA curves for the composite films with 20wt% of lignophenol, lignophenol 2nd derivative I or II are shown in Fig.10. The TMA curves of all composite films were analogous to that of the control film, in which no shrinkage was observed. The thermal softening temperatures of

the films with original lignophenol shifted from 149°C to 147°C with increasing additive content. Those of the films with lignophenol 2nd derivatives, on the other hand, shifted from 150°C to 140°C. The crystal structure of PHB can be understood to disintegrate at the thermal softening point of the composite film. Thus it can be explained that the decrease of the thermal softening temperature means the decrease or loosening of the crystal structure, suggesting that lignophenol 2nd derivatives inhibit PHB from crystallizing by the penetration among PHB chains.

DSC thermograms of the composite films with lignophenols are shown in Fig.11. The exothermic peak

Fig.11. DSC thermograms of PHB films with lignophenol derivatives. Heating rate: 20°C/min

at 80°C and the endothermic peaks around 150°C, corresponding to the crystallization and the melting of PHB, respectively, were clearly observed for the control film. In the composite films, the peak-heights got lower as the lignophenol derivatives increased. By adding 20wt% of lignophenol 2nd derivatives or 30wt% of lignophenol, the exothermic and endothermic peaks disappeared completely.

The crystallization enthalpy of the control film was 9.0cal/g, calculated from the area of the exothermic peak. Avella *et al.* reported that the value of crystallization enthalpy is 10.5cal/g for P(HB-co-HV) with 5% of 3-hydroxyvalerate units [14]. The crystallization enthalpies were 8.6cal/g and 3.8cal/g for the composite films with 10wt% and 20wt% of lignophenol, respectively. On the other hand, for the films with 10wt% of lignophenol 2nd derivative I and II, it was 2.5cal/g. By the blending with lignophenol 2nd derivatives, the crystallization enthalpies of the PHB films got lower, compared with that of film with lignophenol. Therefore, the great drop of the thermal softening temperatures and the crystallization enthalpies indicated that lignophenol 2nd derivatives

blocked the crystallization of PHB more effectively than lignophenol.

4. CONCLUSIONS

The mechanical and thermal properties of the composite materials consisted of biodegradable biopolyester (PHB) and lignophenol derivatives were discussed. By the blending with lignophenol 2nd derivative from beech native lignin, the elongation ratio of the composite film got 20 times higher, compared with the control film without additives. Lignophenol 2nd derivative worked more effectively as the plasticizer for PHB than BHA and triacetin, the conventional plasticizers. The shrinkages of the composite films with BHA and triacetin were observed, due to the evaporation of additives, followed by the formation of the crystal structure between PHB chains. For the composite film with lignophenol 2nd derivative, no shrinkage and no weight loss were observed below the temperature at which PHB decomposed, because lignophenol 2nd derivative was stable until 170°C.

The lignophenols are recyclable materials, because their functionalities can be controlled using the intramolecular switching function. In the cascade utilization of lignophenols, lignophenol 2nd derivatives are placed in the final stage of material flow. If the PHB-lignophenol films were utilized such as agricultural materials and left on the soil, the PHB will be biodegraded by microorganisms. On the other hand, lignophenols may remain in the soil and act as carriers for nutrients and metals which plants need [6].

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