Functions of Biopolyester – Lignophenol Composites

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The cresol-type lignophenols (lignocresols) were synthesized from beech (*Fagus crenata*), hinoki(*Chamaecyparis obtusa*) and rice straw (*Oryza stativa L.*) protolignins by the phase-separation process. The second functionality controls of lignocresols were carried out using the neighboring-group participation reactions. By the combination of Biopol with butylhydroxyanisol (BHA) and triacetin, the elongation ratios of the composite films got 2.6 and 2.3 times higher, respectively, compared with control films without additives, whereas that of the composite film with the beech lignocresol 2nd derivative was 20 times higher. This function by the combination with lignocresol 2nd derivatives was developed with its 5% addition, remained almost unchanged to 30%.

Key words: lignocresol, biopolyester, plasticizer, Biopol, resources circulation

1. INTRODUCTION

Recently, the attention has been given to renewable lignocellulosic resources, because of the shortages of petroleum in the near future. Chemicals comparable to those derived from the petroleum can theoretically be derived from wood, as one of the roots of fossil resources is the wood. However, the wood cell walls have the interpenetrating polymer network structures composed of cellulose, hemicellulose and lignin, and therefore, these polymers cannot be perfectly separated without the destruction of key structures through the simple processes such as extractions and evaporations. Several methods for the wood refining have been proposed recently [1-5], but most of them have been aimed to manufacture pulps or to utilize the carbohydrate moieties of lignocellulosic materials. In conventional processes, the lignin utilization has not been taken into account at all at the step of process design, and the lignin has been regarded as a barrier for the carbohydrates. Consequently, the lignin has been subjected to highly structural modifications during the conventional separation processes and the resulting lignins doesn't have any distinct characteristics.

A new separation process for separating lignocellulosics into carbohydrates and functional lignins has been developed (phase-separation system) [6,7]. This process consists of the two steps: the first step is the solvation of lignin with phenol derivatives, and the second the concentrated acid treatment. The acid has a strong affinity for carbohydrates, resulting in the release of the framework structure of cell walls, through the swelling and partial hydrolysis of carbohydrates. During this process, the lignin is always surrounded with phenol derivatives which are not mixed with acid. As a result, the lignin contacts with the acid for a short time only in the interface between organic and aqueous phases, and the resulting benzyl cations are quickly

stabilized with phenol derivatives, giving linear-type polymers (lignophenols) with 1,1-bis (aryl) propane type units.

Poly(hydroxybutyrate) (PHB) and its copolymers with hydroxyvalerate are bacterial polyesters which have been produced under the trade name "Biopol" by Monsanto [8]. These polymers are thermoplastics with environmental degradability, attracting the industrial attentions. However, their applications have been limited because of the brittleness by the presence of crystalline structures [8]. The block copolymerization of 3-hydroxybutyrate (HB) with other hydroxyalkanoates such as 3-hydroxyvalerate and 4-hydroxybutyrate is one method for improving the disadvantage [9]. The other method is blending of plasticizers such as butylhydroxyanisol (BHA) and triacetin.

In the present work, the plasticizing effect of lignophenols for Biopol film has been investigated. The lignophenols with the switching units for the functionality control were synthesized by the phase-separation process. Using the intramolecular switching units, the structure of lignophenols were modified to match with Biopol.

2. EXPERIMENTAL

2.1. Synthesis of lignocresols

Meals (20mesh) from hinoki (*Chamaecyparis obtusa*), beech (*Fagus crenata*) and rice straw (*Oryza stativa L.*) were extracted with acetone for 3 days. The lignocresols were synthesized from these extractives-free meals by the phase-separation process (two step process II). p-Cresol was dissolved in acetone and was added to the meals. After 24 hrs, the acetone was evaporated. Seventy-two percent sulfuric acid was added to the p-cresol-sorpted meals and the mixture was vigorously stirred at room temperature for 1 hr. The reaction mixture was added to excess deionized water

with stirring. The precipitates were collected by centrifugation, washed with water and dried. Acetone was added to the dried precipitates and stirred to extract the lignocresols. The acetone soluble fraction was collected by filtration and centrifugation. The acetone was evaporated completely from the filtrate to give crude lignocresols.

The second structural modifications of the lignocresols were carried out using the neighboring-group participation reaction [10]. The lignocresols were completely dissolved in 0.5N NaOH, and placed in the stainless steel autoclaves. The reaction mixtures were heated in an oil bath at 140℃ or 170℃ for 1 hr. After cooling, it was acidified with 1N HCl to pH2. The resulting precipitates were collected by centrifugation, washed with water and dried: the lignocresol 2nd derivative I (treatment at 140℃) and II (treatment at 170℃).

The lignocresols and lignocresol 2nd derivatives were acetylated with an acetic anhydride - pyridine mixture. The resulting solutions 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.

2.2. Preparation of films

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with 8% of hydroxyvalerate was provided by Monsanto. The composite films (0.1-0.15mm thickness) from Biopol and additives, BHA, triacetin and lignocresols, were prepared by casting the mixtures (chloroform solution) on the stainless steel plates and evaporating chloroform at room temperature.

2.3. Analysis of physical properties

The dumbbell-shaped Biopol films (measurement part: width 6mm, length 33mm) were used. The tensile strength and the elongation ratio of films were determined using EZ Test (Shimadzu) at room temperature.

2.4. Thermal analysis

Thermal analyses of the composites was performed using DSC-60 differential scanning calorimeter (Shimadzu) under nitroge n atmosphere. Measurements were carried out with first heating from room temperature to 200 ℃, then cooling down to -80℃ and re-heating to 200 ℃.

3. RESULTS AND DISCUSSION

3.1. Physical properties of Biopol films with additives

Load-elongation curves of Biopol films, were measured, from which the tensile strengths and elongation ratios of films were calculated (Fig.1). All composite films contain 20wt% of the additives. The control films, without any additives, had the tensile strength of 29 N/mm² and the elongation ratio of 18%. By the combinations with BHA and triacetin, the tensile strengths decreased to one-half of the control film, whereas the elongation ratios got higher (2.6 and 2.3 times higher, respectively). The composite film with beech lignocresol 2nd derivative II had 22 times-higher the elongation ratio with the highest tensile strength of additives used.
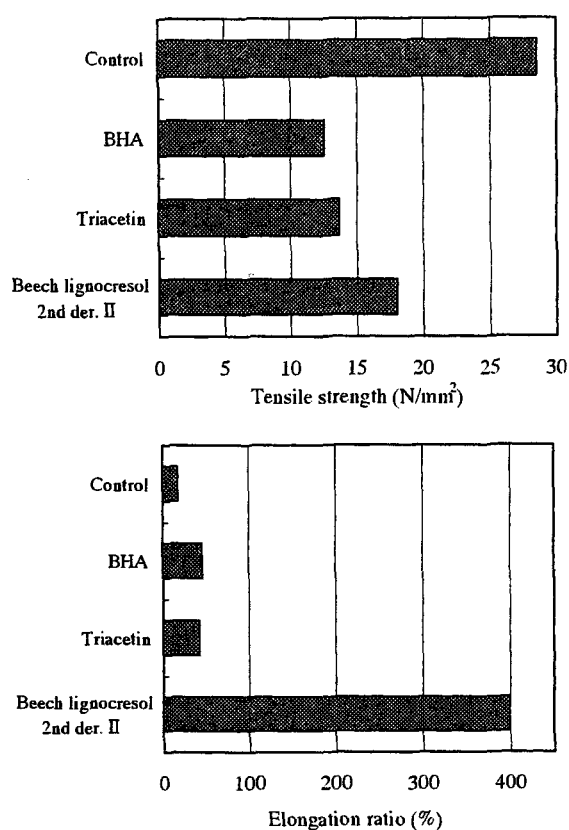

Fig.1   Tensile strength and elongation ratio of Biopol films.
Mixing ratio of BHA, triacetin and lignocresol: 20wt%.

3.2. Plasticizing effects of beech lignocresols

The tensile strengths and the elongation ratios of composite films with beech lignocresols are shown in Fig.2. All composite films contain 20wt% of lignocresols. The strength of the composite film with original lignocresol was comparable to that of the control film, while the elongation ratio got lower, indicating the poor plasticizing effect of original lignocresol.

The average molecular weights of lignocresols are shown in Table I .

The excellent plasticizing effects were observed for the composites with beech lignocresol 2nd derivatives. The molecular sizes of the beech lignocresol dropped to ca. 1/10 by the second functionality control, as shown in Table I . The lignocresol 2nd derivatives I and II were both miscible with Biopol and had similar molecular weights. However, the elongation ratios of the films with lignocresol 2nd derivative I and II got 9 and 22 times higher than the control film, respectively.

In the mild alkaline conditions, the p-cresol nuclei on the lignocresol dissociates, and the resulting phenolate anions attack the β -carbons. This leads to the cleavage of β -aryl ether linkages and the formation of the five-membered cyclic structures (2nd derivative I) (Fig.3(a)) [11]. Under more drastic condition, the necleophilic attack to the β -carbon atoms of the

C_1-carbanions is followed by the transformation into the corresponding stilbene (2nd derivatives II) (Fig.3(b)). The lignocresol 2nd derivative I is bulky sterically because of the presence of the five-membered cyclic structures. On the other hand, the lignocresol 2nd derivative II has plane-like structures because of the presence of stilbene type structures. Such differences in the structures would cause the difference in the plasticizing effect.

The similar results were obtained for the composite films with hinoki and rice straw lignocresols.
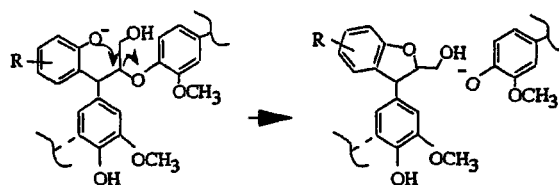

Fig.3(a)   Cleavage of C_β-aryl ether linkages by the participation of phenolic OH.
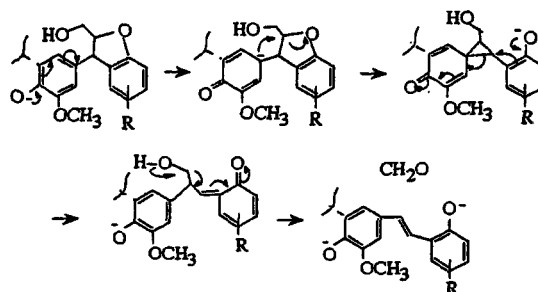

Fig.3(b)   Cleavage of phenolic C_β-aryl ether linkages followed by aryl migration.

Fig.4 shows the relationship between the mixing ratio and plasticizing effect. With 3% of lignocresol 2nd derivative II , the elongation ratio was only 3 times higher than that of the control film, while with 5% addition, the elongation ratio got 20 times higher. The elongation ratios remained almost unchanged with 5%-30%. The composite film with 3% and 5% additives had the tensile strengths of 96% and 87% of the control film, respectively.
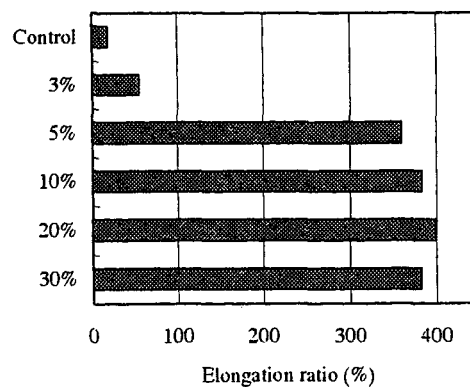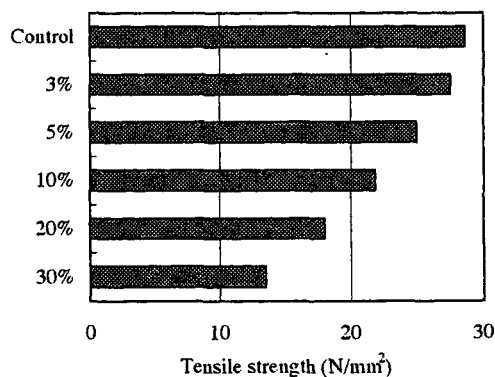

Fig.2   Tensile strength and elongation ratio of Biopol films with beech lignocresols.
Mixing ratio of lignocresols: 20wt%.

Table I   Average molecular weights (Mw) of lignocresols.

	Original lignocresol	Lignocresol 2nd der. I	Lignocresol 2nd der. II
Hinoki	25000	1430	1040
Beech	7400	700	520
Rice straw	3600	930	830

Fig.4   Tensile strength and elongation ratio of Biopol films with beech lignocresols 2nd derivativeII .

Fig.5 shows DSC curves of Biopol films. The exothermic peak around 70°C on the crystallization and the endothermic peak around 160°C on the melting were evidently observed in the control film. In the composite films with 5% and 10% additives, the exothermic and endothermic peaks were still slightly observed, but their energies were lower than the control film. With 20 and 30% additions, the DSC of the composite films didn't have any peaks, indicating that lignocresol derivatives perfectly inhibited the crystallization of Biopol.
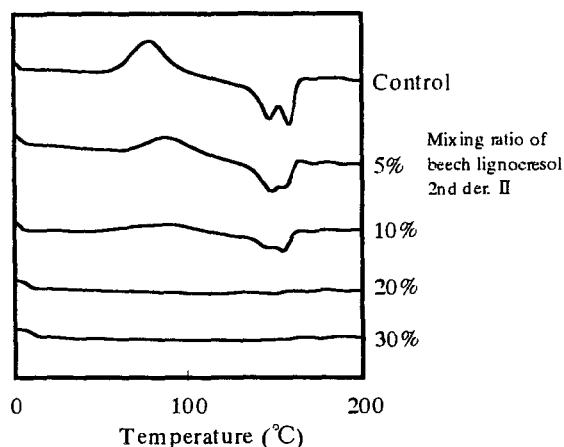

Fig.5 DSC Curves of biopol films with beech lignocresol 2nd der. Ⅱ.

3.3. Effect of the species

The difference in plasticizing effects of the lignocresol 2nd derivative Ⅱ from different protolignins was investigated (Fig.6). All composite films contain 20wt% of lignocresols. The film with hinoki lignocresol 2nd derivative Ⅱ had the highest strength of three composites, while its elongation ratio was only 6 times higher. The composite film with beech lignocresol Ⅱ had the second strength, and the elongation ratio was the highest. The elongation ratio of the film with rice straw lignocresol Ⅱ was also 17 times higher.

The difference in the plasticizing effect would be attributed to the difference in structural units of protolignins. Hinoki native lignins consist of only guaiacyl units having extended network type structures. Beech native lignins consist of guaiacyl and syringyl units, which is of more linear types than softwood lignins.

Rice straw native lignins have the core composed of guaiacyl and syringyl units, which is linked *p*-hydroxyphenyl units through ester bonds. During the phase-separation process, *p*-hydroxyphenyl units are eliminated from the core, and furthermore, more amounts of soluble low molecular weight fractions are formed because of the presence of more ether bonds. As a result, grass lignophenol would be rich in condensed type units. Actually, the molecular weights of rice straw lignocresol 2nd derivatives are larger than those of beech lignocresols and therefore the difference in these molecular size and flexibility would cause the difference in plasticizing effects.
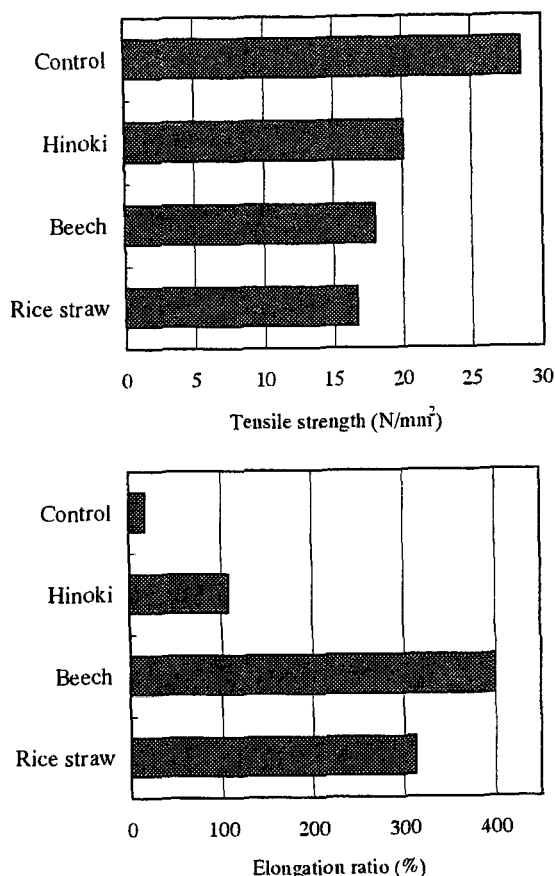

Fig.6 Tensile strength and elongation ratio of Biopol films with lignocresols 2nd derivativeⅡ. Mixing ratio of lignocresols: 20wt%.

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