

ORIGINAL ARTICLE

Yasuyuki Matsushita · Toyoki Inomata · Yasuo Takagi
Tatsuya Hasegawa · Kazuhiko Fukushima

Conversion of sulfuric acid lignin generated during bioethanol production from lignocellulosic materials into polyesters with ϵ -caprolactone

Received: August 9, 2010 / Accepted: October 5, 2010 / Published online: February 21, 2011

Abstract In this study, polyesters were prepared from sulfuric acid lignin (SAL) that was generated as a by-product during the production of bioethanol from lignocellulosic materials using ϵ -caprolactone (CL). Carboxylic groups were introduced into SAL by a hydrothermal reaction under alkali conditions. The acid form (-COOH) of the obtained polymer (HSAL) was dissolved into ϵ -caprolactone and the mixture was heated at 150°C for 12 h with ZnCl₂ as a catalyst. The structure of the obtained polymer (PCL-HSAL) was proposed based on results of differential scanning calorimetric analysis, swelling tests, and dynamic mechanical thermal analysis. The hydroxyl group in HSAL participated in the ring-opening polymerization of CL. PCL-HSAL with a high HSAL content formed a three-dimensional network that did not dissolve in organic solvents and did not melt at high temperature. PCL-HSAL showed a high swelling property for a suitable ratio of CL to HSAL.

Key words Lignocellulosic materials · Bioethanol · Sulfuric acid lignin · ϵ -Caprolactone · Polyesters

Introduction

Recently, bioethanol production from lignocellulosic materials has attracted worldwide attention as a biofuel, since lignocellulosic materials are abundant and their use does not compete with the production of dietary food. Some pilot plants have used lignocellulosic materials to produce bioethanol through sulfuric acid hydrolysis. However, in this process, a large amount of residual lignin, termed sulfuric acid lignin (SAL), is generated as a by-product. In order to use this process in practice, it is necessary to develop methods for converting SAL into engineering polymers.

Lignin is one of the most abundant polymers on Earth. It is made of nonrepeating phenylpropane units, leading to a highly complicated structure. We have been studying SAL and found that its important negative characteristics are its very low reactivity and insolubility in water or commonly used organic solvents such as ethanol. To improve these disadvantageous characteristics, we previously conducted sulfuric acid-catalyzed phenolization of SAL, resulting in its depolymerization and the introduction of a reactive *p*-hydroxyphenyl group.¹ This phenolized SAL (P-SAL) can be dissolved in aqueous dioxane and changed into a functional, water-soluble polymer by a simple chemical reaction.^{2–8} Other direct conversions of acid hydrolysis lignin into functional materials have also been attempted. Tai et al.⁹ prepared an anion exchanger by chloromethylation and subsequent amination. Watanabe et al.¹⁰ showed that radical sulfonation of acid hydrolysis lignin with sodium sulfite and oxygen enabled the preparation of soluble lignosulfonate.

Recently, we attempted to develop a hydrothermal reaction system in order to convert SAL into engineering products.¹¹ SAL easily and completely dissolved in the reaction medium under alkaline conditions. The reaction products (HSAL) could be dissolved at neutral pH. IR spectrometric analysis of HSAL revealed that hydrophilic groups such as hydroxyl and carboxylic acid groups were formed during the reaction. This procedure is very effective in simplifying the conversion system for obtaining engineering products from SAL.

Y. Matsushita (✉) · T. Inomata · K. Fukushima
Graduate School of Bioagricultural Sciences, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan
Tel. +81-52-789-4160; Fax +81-52-789-4163
e-mail: ysmatsu@agr.nagoya-u.ac.jp

Y. Takagi
Nagoya Municipal Industrial Research Institute, Nagoya, Aichi
456-0058, Japan

T. Hasegawa
EcoTopia Science Institute, Nagoya University, Nagoya, Aichi
464-8601, Japan

Part of this report was presented at the 54th Lignin Symposium, Shizuoka, October 2009, and at the 77th Pulp and Paper Research Conference, Tokyo, June 2010

In recent studies, polyurethane, polyester, and polyether were produced using some industrial lignins, such as ligno-sulfonate, kraft lignin,^{12,13} alcoholysis lignin,¹⁴ and alkali-soluble, steam-exploded lignin.¹⁵ Teramoto et al.¹⁶ studied blend polymers with poly(ϵ -caprolactone) and organosolv lignin. Since it has hydroxyl and carboxylic acid groups, it is thought that HSAL could also be converted into engineering polymers by a simple chemical reaction. In this study, the preparation of polyester using HSAL and ϵ -caprolactone (CL) was investigated.

Experimental

Sulfuric acid lignin

SAL was prepared from gymnosperm wood powder (*Cryptomeria japonica*:*Chamaecyparis obtusa* = 1:1) by hydrolysis using sulfuric acid as follows. To 12.5 g of the wood powder (30–80 mesh), 30.5 ml of 75 wt% sulfuric acid was added and stirred at room temperature for 30 min with stirring. Then 70 ml of water was added and the system was allowed to react at 90°C for 90 min. The reaction products were filtrated using a glass filter and the filtrate washed with water until the cleaning fluid was neutral. The residue was dried at 105°C to obtain SAL (33.6% yield based on wood powder).

Hydrothermal reaction

The hydrothermal reaction was conducted as follows: a mixture containing 2 g of SAL, 2 g of NaOH, and 30 ml of water was sealed in a stainless steel tube with an inner volume of 57 cm³ and heated at 200°C for 3 h. After the reaction, the stainless steel tube was immediately cooled in a water bath (room temperature). The reaction mixture was dialyzed in a cellulose tube with a molecular weight cutoff of 3500 (BioDesign, BioDesignDialysis Tubing 3500 MWCO) to remove NaOH and then dried at 105°C to obtain the salt form of HSAL (85.0% yield based on SAL).

Preparation of the acid form of HSAL

The salt form of HSAL (100 mg) was dissolved in a solvent mixture (5 ml chloroform, 4.8 ml methanol, and 0.2 ml sulfuric acid). The mixture was poured into 500 ml of water with stirring. The HSAL contained in the chloroform was obtained as a precipitate. The precipitate was washed with water until the cleaning fluid was neutral and then dried at 105°C to obtain the acid form of HSAL (85.8% yield based on salt form of HSAL).

Solubility tests

Dimethyl sulfoxide, acetone, tetrahydrofuran, chloroform, polyethylene glycol, diethylene glycol, CL, 50% aqueous acetone, and a mixture of chloroform and methanol (1:1 v/v) were used as organic solvents. To 1 ml of solvent, 5 mg of

HSAL was added. The solubility was classified visually into three groups, namely soluble, partially soluble, and insoluble.

Reaction of the acid form of HSAL with ϵ -caprolactone

The acid form of HSAL was dissolved in CL and a very small amount of ZnCl₂ was added to the solution. The reaction mixture was heated at 150°C for 12 h and then cooled to room temperature.

Fourier transform infrared spectrometry

Fourier transform infrared (FT-IR) spectra were recorded on a Horiba FT-720 spectrophotometer.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a DSC3100 (MAC Science) at a heating rate of 20°C/min under a nitrogen atmosphere. The sample mass was 5–10 mg. Scans were conducted in the temperature range –100° to 250°C.

Swelling study

The swellability of the prepared polymer was determined according to the previously reported method.^{17,18} The polymers were weighed and placed in vials to which the appropriate solvent was added in excess. The solvents used for the swelling studies were water, methanol, chloroform, and toluene. The vials were sealed and the samples were kept and allowed to swell for 3 days at room temperature with frequent swirling. Excess solvent was removed by filtration, the residual solvent on the surface was rapidly dried with filter paper, and the swollen polymers were weighed. The swellability was calculated as

$$S \text{ (ml/g)} = (W_s - W_d) / (d \times W_d)$$

where W_s is the weight of the swollen polymer, W_d is the weight of the dry polymer, and d is the density of the solvent used.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMA) was carried out with the TA instrument DMA Q800 in single cantilever mode. The temperature range was from –50° to 100°C at a heating rate of 3°C/min. The oscillation frequency was 1 Hz and the amplitude was 15 μ m. Changes in the dynamic storage modulus and the dynamic loss modulus were obtained.

Results and discussion

Solubility test of HSAL

In our previous study, it was found that HSAL has a carboxylic group. Since the chemical reactivity was expected to

Table 1. Solubility of HSAL in organic solvents

Solvents	HSAL	
	Salt	Acid
Dimethyl sulfoxide	○	○
Acetone	△	△
Tetrahydrofuran	△	○
Chloroform	×	×
Polyethylene glycol ($M_w = 600$)	○	○
Diethylene glycol	○	○
ϵ -Caprolactone	×	○
Acetone + water	×	○
Chloroform + methanol	×	○

HSAL, the polymer obtained when sulfuric acid lignin undergoes hydrothermal reaction under alkali conditions

Circles, soluble; triangles, partially soluble; crosses, insoluble

be different between the salt (-COONa) and acid form (-COOH) of HSAL, the acid form was prepared by acidification of the HSAL salt. To confirm this conversion, FT-IR spectra were measured. From the results, a new peak at 1600 cm^{-1} appeared in the acid form of HSAL.

To obtain a homogeneous copolymer, HSAL has to be soluble in organic solvents. The solubility of HSAL in various organic solvents was investigated and the results are shown in Table 1. The results are different between the salt and acid forms of HSAL. The salt form of HSAL cannot be dissolved in chloroform, CL, aqueous acetone, or a chloroform–methanol mixture. On the other hand, the acid form of HSAL is soluble in these solvents, except for chloroform. The easy solubilization of HSAL in CL is useful for preparing the homogeneous copolymer of CL and HSAL.

Thermal properties of poly(ϵ -caprolactone) containing HSAL

The acid form of HSAL was dissolved in CL at various ratios (CL:HSAL = 20:1, 15:1, 10:1, 5:1, and 3:1 w/w) and the mixture was heated to obtain poly(ϵ -caprolactone) (PCL) containing HSAL (PCL-HSAL). The prepared PCL-HSAL was subjected to differential scanning calorimetric analysis and the results are shown in Fig. 1. The melting point (T_m) of PCL was around 60°C . In PCL-HSAL, an endothermal peak corresponding to the crystalline fusion of the PCL segment was observed. The peak was shifted to a lower temperature and the peak area was smaller with increasing HSAL content in PCL-HSAL. de Oliveira and Glasser¹⁹ reported a similar phenomenon in a copolymer using hydroxypropyl kraft lignin and CL. They described how the thermal behavior of the copolymers was affected by the molecular weight of PCL, and the T_m increased with the length of PCL. In this experiment, it seems that HSAL interfered with the homopolymerization of CL, leading to the low molecular weight of crystalline PCL and a decrease in the area of the PCL segment in PCL-HSAL. This resulted in lower T_m and smaller peak areas in PCL-HSAL.

The prepared PCL-HSAL was heated at 80°C in an oven. The PCL-HSALs with low HSAL content (CL:HSAL =

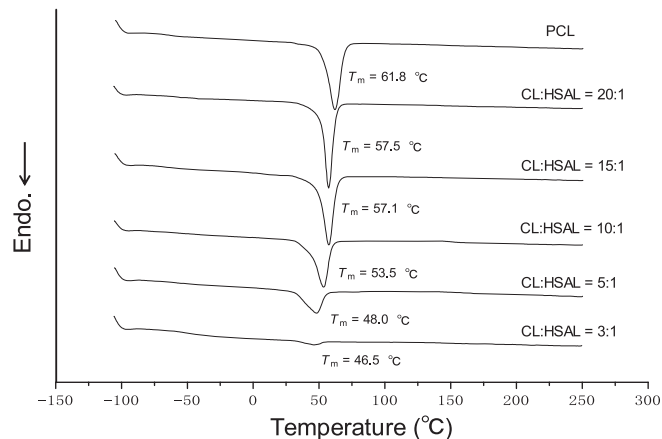


Fig. 1. Differential scanning calorimetry curves of poly(ϵ -caprolactone) (PCL) containing the polymer obtained when sulfuric acid lignin undergoes hydrothermal reaction under alkali conditions (HSAL). T_m , melting point

Table 2. Swellability of PCL-HSAL in organic solvents

	CL:HSAL			
	3:1	5:1	10:1	15:1
Water	0	0	0	0
MeOH	0.2	0.4	0.4	0.4
Chloroform	4.7	9.6	8.0	— ^a
Toluene	0.8	4.3	3.6	— ^a

PCL, poly(ϵ -caprolactone)

^aDissolved

20:1 and 15:1) melted; however, PCL-HSALs with high HSAL content did not melt and instead transformed into gelatinous materials. This was accounted for by the anchoring of HSAL to the melted PCL at high temperature.

Swelling property of PCL-HSAL

The swelling property is an important characteristic in cross-linked polymers; Table 2 shows the results of swelling tests. All prepared PCL-HSALs exhibited no swellability in water because of the hydrophobic property of PCL-HSAL. PCL-HSALs with low HSAL content dissolved in organic solvents chloroform and toluene, whereas those with high HSAL content became swollen by imbibition. The organic solvents most likely penetrated into the PCL segment in PCL-HSAL. When the number of HSAL molecules, which act as an anchor, was low, PCL-HSAL could be dissolved. In contrast, PCL-HSALs with a greater number of anchor molecules did not dissolve and exhibited a high swelling property. However, the swellability of PCL-HSAL decreased when the HSAL content was too high (CL:HSAL = 3:1). The reason seems to be that the reduction of the PCL area led to a decrease in the amount of imbibed organic solvent; furthermore, higher levels of HSAL caused PCL-HSAL to become rigid because of the increase in the number of anchors.

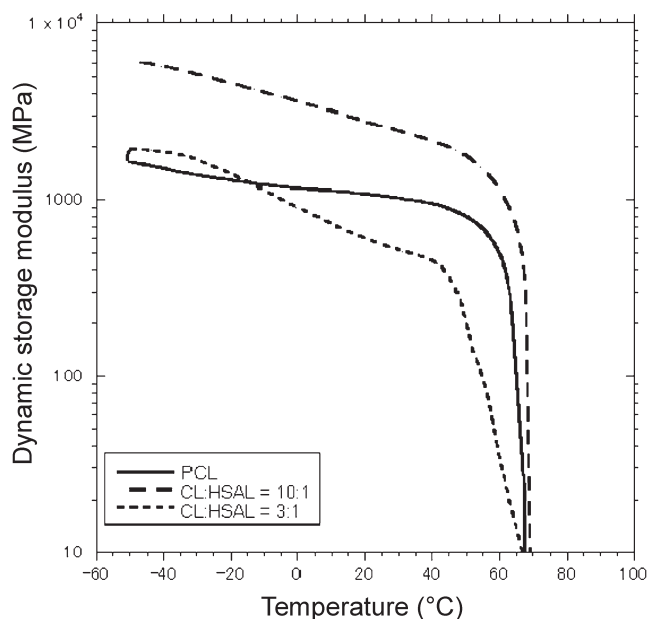


Fig. 2. Dynamic storage modulus of PCL-HSAL

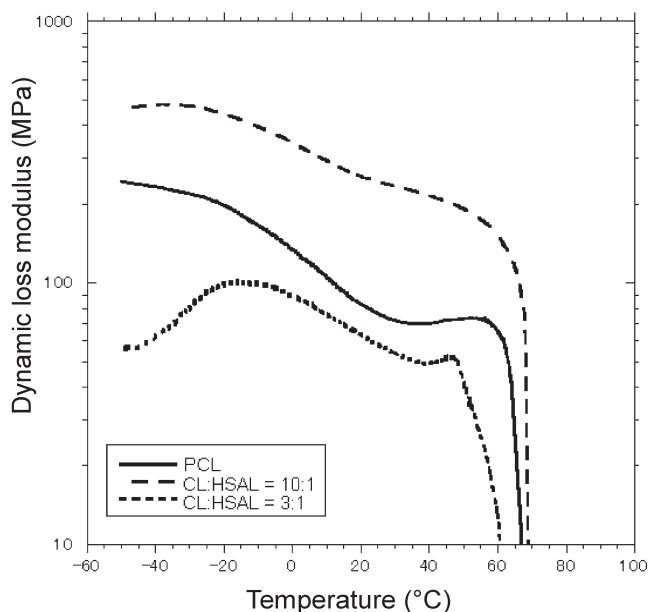


Fig. 3. Dynamic loss modulus of PCL-HSAL

Dynamic mechanical thermal analysis of PCL-HSAL

Changes in the dynamic storage modulus and the dynamic loss modulus were obtained by DMA analysis; the results are shown in Figs. 2 and 3. The dynamic storage modulus and the dynamic loss modulus of PCL-HSAL were affected by the formation of a three-dimensional network and a decrease in crystalline PCL. The moduli were increased by

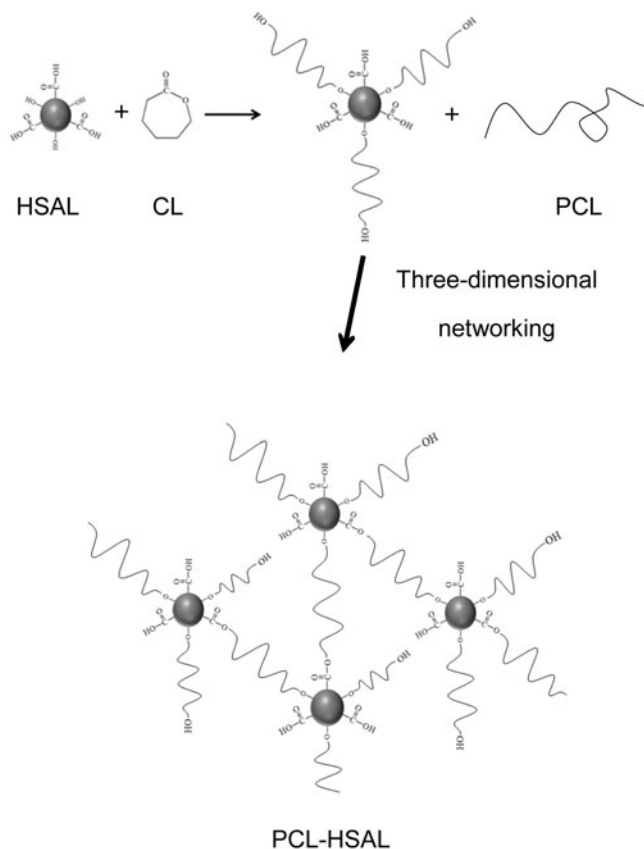


Fig. 4. Copolymerization between HSAL and PCL to generate three-dimensional networked PCL-HSAL

adding a small amount of HSAL (CL:HSAL = 10:1). This was because a three-dimensional network was generated in PCL-HSAL by the anchoring of HSAL on PCL, which is discussed later. However, these dynamic moduli both decreased with increasing content of HSAL in PCL-HSAL (CL:HSAL = 3:1). The reason was believed to be the decrease of crystalline PCL in PCL-HSAL.

Putative structure of PCL-HSAL

The hydroxyl group in HSAL participated in ring-opening polymerization of CL and formed a copolymer. Based on the results of DSC, swelling tests, and DMA, the structure of PCL-HSAL was presumed to be the three-dimensional structure illustrated in Fig. 4. When the HSAL content was low, the generated polymer was mainly PCL and binding between the copolymers did not occur, which resulted in the dissolution of the polymer in organic solvents. In the case of high HSAL content, the terminal hydroxyl group of PCL on the copolymer was bound to the carboxyl group of other copolymers to form a three-dimensional gelatinous material by a dehydration–condensation reaction at a high reaction temperature (150°C) and a long reaction time (12 h). Thus, the generated polymer did not dissolve in organic solvents and did not melt at high temperature.

Conclusions

Polyesters (PCL-HSAL) were prepared from CL and HSAL, with the latter produced by the hydrothermal reaction of sulfuric acid lignin. The characteristic properties of the polymers were as follows:

- PCL-HSAL formed three-dimensional networked substances.
- PCL-HSAL with a high proportion of HSAL did not dissolve in organic solvents, did not melt at high temperature, and showed a high swelling property.
- PCL-HSAL showed a high swelling property by choosing a suitable ratio of CL to HSAL.
- The storage modulus and the loss modulus of PCL were increased by adding a small amount of HSAL.

Acknowledgments The present study was conducted with the support of a Grant-in-Aid for Scientific Research (21380109) from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT). This study was also partially supported by MEXT under the program Asia Science and Technology Cooperation Promotion Strategy.

References

1. Yasuda S, Tachi M, Takagi Y (1989) Phenolization of red pine sulfuric acid lignin and guaiacyl sulfuric acid lignin model in the presence of sulfuric acid catalyst. *Mokuzai Gakkaishi* 35:513–520
2. Yasuda S, Ito K, Hamaguchi E, Matsushita Y (1997) Ready chemical conversion of acid hydrolysis lignin into water-soluble lignosulfonate. I. Successive treatment of acid hydrolysis lignin by phenolation, hydroxymethylation and sulfonation. *Mokuzai Gakkaishi* 43:68–74
3. Matsushita Y, Yasuda S (2003) Preparation of anionic-exchange resins from pine sulfuric acid lignin, one of the acid hydrolysis lignins. *J Wood Sci* 49:423–429
4. Matsushita Y, Yasuda S (2003) Reactivity of a condensed-type lignin model compound in the Mannich reaction and preparation of cationic surfactant from sulfuric acid lignin. *J Wood Sci* 49:166–171
5. Matsushita Y, Iwatsuki A, Yasuda S (2004) Application of cationic polymer prepared from sulfuric acid lignin as a retention aid for usual rosin sizes to neutral papermaking. *J Wood Sci* 50:540–544
6. Matsushita Y, Yasuda S (2005) Preparation and evaluation of lignosulfonates as a dispersant for gypsum paste from acid hydrolysis lignin. *Bioresour Technol* 96:465–470
7. Matsushita Y, Imai M, Tamura T, Fukushima K (2005) Preparation and evaluation of a dispersant for gypsum paste from acid hydrolysis lignin. *J Appl Polym Sci* 98:2508–2516
8. Matsushita Y, Imai M, Iwatsuki A, Fukushima K (2008) Relationships between surface tension and industrial performance of water-soluble polymers prepared from acid hydrolysis lignin, a saccharification by-product from woody materials. *Bioresour Technol* 99:3024–3028
9. Tai S, Nakano J, Migita N (1966) Studies on utilization of lignin. II. Preparation of anion exchanger from wood hydrolysis lignin. *Mokuzai Gakkaishi* 12:108–112
10. Watanabe M, Meshitsuka G, Ishizu A (1992) Radical sulfonation of lignin. III. Application to various lignins. *Mokuzai Gakkaishi* 38:173–179
11. Matsushita Y, Inomata T, Hasegawa T, Fukushima K (2009) Solubilization and functionalization of sulfuric acid lignin generated during bioethanol production from woody biomass. *Bioresour Technol* 100:1024–1026
12. Hatakeyama H (2002) Thermal analysis of environmentally compatible polymers containing plant components in the main chain. *J Therm Anal Cal* 70:755–795
13. Hatakeyama T, Izuta Y, Hirose S, Hatakeyama H (2002) Phase transitions of lignin-based polycaprolactones and their polyurethane derivatives. *Polymer* 43:1177–1182
14. Hirose S, Hatakeyama T, Hatakeyama H (2005) Glass transition and thermal decomposition of epoxy resins from the carboxylic acid system consisting of ester-carboxylic acid derivatives of alcoholysis lignin and ethylene glycol with various dicarboxylic acids. *Thermochem Acta* 431:76–80
15. Bonin C, D'Auria M, Emanuele L, Ferri R, Puccariello R, Sabia ARJ (2005) Polyurethanes and polyesters from lignin. *Appl Polym Sci* 98:1451–1456
16. Teramoto Y, Lee SH, Endo T (2009) Phase structure and mechanical property of blends of organosolv lignin alkyl esters with poly(ϵ -caprolactone). *Polym J* 41:219–227
17. Cavalli G, Shooter AG, Pears DA, Steinke JHG (2003) Non-PEG-derived polyethers as solid supports. 1. Synthesis, swelling studies, and functionalization. *J Comb Chem* 5:637–644
18. Chen CP, Ko BT, Lin SL, Hsu MY, Ting C (2006) Hydrophilic polymer supports grafted by poly(ethylene glycol) derivatives via atom transfer radical polymerization. *Polymer* 47:6630–6635
19. de Oliveira W, Glasser WG (1994) Multiphase materials with lignin. 11. Starlike copolymers with caprolactone. *Macromolecules* 27:5–11