

# Functionalization of Lignin: Synthesis of Lignophenol-graft-Poly(2-ethyl-2-oxazoline) and Its Application to Polymer Blends with Commodity Polymers

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**ABSTRACT:** Lignophenol (LP)-graft-poly(2-ethyl-2-oxazoline) (POZO) was prepared to reuse lignin, an industrial waste material, and to produce novel LP-based polymer blends with poly(vinyl chloride) (PVC), poly(bisphenol A carbonate) (PC), polyvinylpyrrolidone (PVP), and polystyrene (PSt) as commodity polymers. The resulting graft polymer was soluble in various types of organic solvents such as chloroform, THF, acetone, and methanol, unlike LP. The miscibility of LP-graft-POZO with commodity polymers was measured by differential scanning calorimetry (DSC) to determine the glass transition temperatures ( $T_g$ ). In the cases of the blends of LP-graft-POZO with PVC, PC, and PVP, the  $T_g$  values decreased during the second scan. Moreover, in the cases of the blends with PVC and PVP, the  $T_g$  values were not detected during the

third scan. Therefore, it was inferred that LP-graft-POZO was miscible with PVC, PC, and PVP while forming single phases; in particular, the blends of LP-graft-POZO with PVC and PVP exhibited a secondary miscibility because the  $T_g$  values were not detected. Furthermore, the blend of LP-graft-POZO with PC exhibited better thermostability than LP and LP-graft-POZO. These results indicated that LP blended with POZO could be used as a polymer additive and as an adhesive to combine different polymers, organic-inorganic polymers, etc. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2636–2642, 2012

**Key words:** lignin; lignophenol; polyoxazoline; polymer blend; phenolic resin

## INTRODUCTION

With the advancement in human civilization and the accompanying technological advancements, energy consumption has increased considerably. Consequently, the reserves of fossil fuel deposits such as those of petroleum, coal, and methane hydrate are in danger of being exhausted; therefore, it is necessary to explore alternative energy resources. Recently, renewable energy sources such as bioethanol, which is produced from biomass,<sup>1,2</sup> have attracted considerable attention as alternatives to fossil fuels. Lignocellulose, one of the constituents of a biopolymer composite found in plant cells, can be

decomposed to cellulose and lignin.<sup>3</sup> Cellulose is one of the most important natural materials used in the manufacture of paper. Lignin<sup>4–20</sup> contains polyphenol and is often disposed off as an industrial waste. Lignin has excellent potential as an aromatic polymer despite its poor solubility in organic solvents. Therefore, many attempts have been made to produce organosoluble lignin derivatives. We succeeded in developing a phase-separation system (2-step process II) that can produce processable and organosoluble lignophenol (LP).<sup>21–26</sup> The structure of LP is similar to that of artificial phenolic resins,<sup>27–37</sup> which are often used as plastics, adhesives, cures, etc. Being a natural polymer-based plastic, LP is considered to be a substitute for commodity polymers derived from fossil fuels. We have been studying the manufacturing procedure and the applications of organosoluble phenolic resins derived from phenol derivatives and aldehydes and the advantages of these organosoluble phenolic resins over artificial phenolic resins.<sup>36–51</sup> By developing novel LP-based materials, it may be possible to reduce the consumption of fossil fuels and recycle valuable industrial materials from waste.

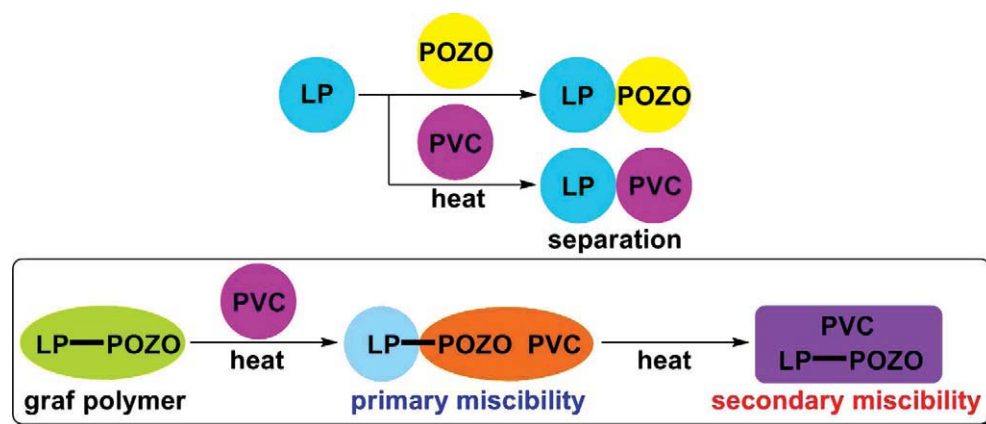
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**Chart 1** Miscibility mechanism between LP-graft-POZO and PVC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

From this viewpoint, we focused on preparing graft polymer structures containing poly(2-ethyl-2-oxazoline) (POZO). Poly(2-alkyl-2-oxazoline)s [poly(*N*-acylethylenimine) and poly(2-oxazoline)],<sup>52–58</sup> including POZO derived from the ring-opening polymerization of 2-alkyl-2-oxazoline, are miscible with various types of commodity polymers.<sup>59</sup> Saegusa and coworkers modified bovine liver catalase enzyme using poly(2-oxazoline) and examined its enzymatic activity in an aqueous solution and in organic media.<sup>60</sup> Aoi et al. prepared chitosan-graft-poly(2-methyl-2-oxazoline) and chitin-graft-poly(2-alkyl-2-oxazoline) to design biopolymer hybrids, and they also investigated the miscibility of these compounds with poly(vinyl alcohol).<sup>61–63</sup> If mixed polymer composites derived from LP-graft-POZO are successfully prepared, it would be possible to explore various novel uses of LP, for example, as recyclable natural phenolic resins, high-performance polymer blends, etc.

In this study, we synthesized a functional Japanese-cedar-based LP by carrying out the Williamson ether synthesis of  $\alpha,\alpha'$ -dihalo-*p*-xylene to investigate the use of LP as a reactive polymer. The resulting functional LP was used as an initiator for the cationic ring-opening polymerization of 2-ethyl-2-oxazoline to produce a new class of LP-based polymers. To evaluate the miscibility of LP-graft-POZO with various types of commodity polymers, the glass transition temperatures ( $T_g$ ) of the mixtures derived from LP-graft-POZO and poly(vinyl chloride) (PVC), polycarbonate (PC), or polystyrene (PSt) were determined by differential scanning calorimetry (DSC). The  $T_g$  values of the mixture of LP-graft-POZO and PVC were found to be lower than those of PVC during the second DSC scan. However, interestingly, the  $T_g$  value of the mixture was not detected during the third scan. This behavior probably originates

from the specific miscibility of the mixture, as shown in Chart 1.

## EXPERIMENTAL

### Materials

Unless otherwise noted, all reagents and chemicals were used without further purification. Lignophenol (LP) was obtained from Japanese cedar (*Cryptomeria japonica*)-based lignin by means of the phase-separation system (2-step process II) according to the previous report ( $M_n = 2400$ ,  $M_w/M_n = 3.24$ , eluent: THF, polystyrene standards).<sup>22</sup>  $\alpha,\alpha'$ -Dichloro-*p*-xylene and  $\alpha,\alpha'$ -dibromo-*p*-xylene were purchased from TCI. Potassium iodide and polyvinylpyrrolidone (PVP,  $M_w = 24,500$ ) were obtained from Nacalai tesque, Inc. Potassium carbonate and poly(vinyl chloride) (PVC,  $M_w = 68,800$ ) were purchased from Wako Pure Chemical, Ltd. 2-Ethyl-2-oxazoline, polystyrene (PSt,  $M_w = 35,000$ ), and poly(bisphenol A carbonate) (PC,  $M_w = 64,000$ ) were obtained from Aldrich. 2-Ethyl-2-oxazoline was distilled under the argon atmosphere after dehydration with potassium hydroxide.  $\alpha,\alpha'$ -Diiodo-*p*-xylene was prepared according to the previous report.<sup>64</sup>

### Instruments

All the <sup>1</sup>H-NMR spectra (in CDCl<sub>3</sub>) and the <sup>13</sup>C-NMR spectra (in CDCl<sub>3</sub>) were recorded by a 400 MHz JEOL LNM-EX400 instrument with tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were recorded using a JASCO FT-IR 460 plus spectrometer. Gel permeation chromatography (GPC) was carried out by a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSKgel G3000H<sub>XL</sub> or G4000H<sub>XL</sub> column) using tetrahydrofuran

(THF) as the eluent after calibration with polystyrene standards, or was carried out by a JASCO UV-1570 detector and a JASCO RI-1530 detector (TOSOH TSKgel GMH<sub>XL</sub> and TSKgel G2000H<sub>XL</sub> columns) using 0.12 mM LiBr-containing *N,N*-dimethylformamide (DMF) as the eluent after calibration with polystyrene standards. Thermogravimetric analysis (TGA) was performed using a SII TG/DTA 6200 with a heating rate of 10°C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out on a SII DSC 6220 at a heating rate of 10°C/min in a nitrogen atmosphere.

#### Preparation of phenolic hydroxyl groups of lignophenol (LP) with $\alpha,\alpha'$ -dihalo-*p*-xylene

The typical procedure is as follows. To a 200-mL round bottom-flask, LP (2.0 g),  $\alpha,\alpha'$ -dihalo-*p*-xylene (30 mmol), potassium carbonate (73 mmol), and acetone (50 mL) were added in an open system. This mixture was heated at 60°C and stirred for 2 days under the argon atmosphere. The mixture was filtered to remove insoluble parts, and then the filtrate was poured into excess amount of hexane. The crude product was reprecipitated with chloroform/hexane three times to give the objective product. The yields and characterization of the products were listed below.

#### LP with $\alpha,\alpha'$ -dibromo-*p*-xylene (LP-Br)

Yield: 28%; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 7.52–7.27, 7.03–6.08 (aromatic protons from lignophenol), 7.23–7.03 (aromatic protons from the moieties of  $\alpha,\alpha'$ -dibromo-*p*-xylene), 5.22–4.60 (–O–CH<sub>2</sub>–Ph), 4.60–4.14 (Ph–CH<sub>2</sub>–Br), 4.02–3.05 (Ph–CH<sub>2</sub>–Ph, Ph–O–CH<sub>3</sub>) 2.40–2.05 (Ph–CH<sub>3</sub>); FT-IR (KBr, cm<sup>-1</sup>): 3503 (phenolic or alkyl hydroxyl groups), 3030 (aromatic C–H), 2938, 2875 (aliphatic C–H), 1229, 1142 (C–O–C), 609 (C–Br); Elemental analysis for estimation of Br content (Found): C: 66.31, H: 5.70, Br: 12.06.

#### LP with $\alpha,\alpha'$ -dichloro-*p*-xylene (LP-Cl)

Yield: 27%; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 7.64–7.27, 7.09–6.18 (aromatic protons from lignophenol), 7.23–7.09 (aromatic protons from the moieties of  $\alpha,\alpha'$ -dichloro-*p*-xylene), 5.29–4.66 (–O–CH<sub>2</sub>–Ph), 4.66–4.20 (Ph–CH<sub>2</sub>–Cl), 4.07–3.69 (Ph–CH<sub>2</sub>–Ph), 3.69–3.00 (Ph–O–CH<sub>3</sub>), 2.48–1.90 (Ph–CH<sub>3</sub>); FT-IR (KBr, cm<sup>-1</sup>): 3491 (hydroxyl group), 3053 (aromatic C–H), 2931, 2868 (aliphatic C–H), 1222, 1139 (C–O–C); Elemental analysis for estimation of Cl content (Found): C: 70.50, H: 5.82, Cl: 6.92.

#### LP with $\alpha,\alpha'$ -diiodo-*p*-xylene (LP-I)

The product was insoluble in any organic solvents after reaction.

#### LP-graft-POZO

To a schlenk flask was added LP-Br (0.2 g) and 2-ethyl-2-oxazoline (26.9 mmol, 2.67 g, 89 equiv. for Br-content in LP-Br (1.5 mmol/1.0 g)) under an argon atmosphere. After stirring for a while at room temperature, the mixture was heated at 100°C in a closed system for 12 h. After cooling to ambient temperature, the solid was dissolved in chloroform (10 mL), accordingly the solution was poured into diethyl ether (100 mL) to give the crude product. The reprecipitation was carried out two times with chloroform and diethyl ether to obtain the objective polymer in 74% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  (ppm)): 7.63–7.27, 7.19–6.23 (aromatic protons), 5.22–4.62 (–O–CH<sub>2</sub>–Ph), 3.94–3.22 (Ph–CH<sub>2</sub>–Ph, Ph–O–CH<sub>3</sub>, –CH<sub>2</sub>–N(COEt) –CH<sub>2</sub>–), 2.52–2.02 (CH<sub>3</sub>–CH<sub>2</sub>–CO–), 1.18–1.00 (CH<sub>3</sub>–CH<sub>2</sub>–CO–); FT-IR (KBr, cm<sup>-1</sup>): 3543 (hydroxyl group), 2980, 2938, 2883 (aliphatic C–H), 1640 (tertiary amide moiety), 1239, 1201 (C–O–C).

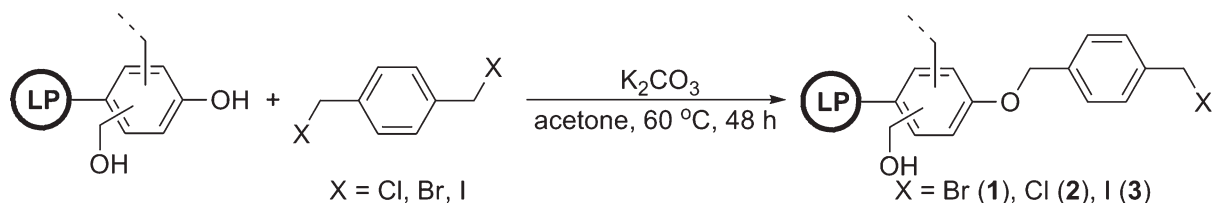
Polymer blends between LP-graft-POZO and commodity polymers (PVC, PC, PVP, or PSt)

The typical procedure is as follows. LP-graft-POZO (0.1 g) and commodity polymer (0.1 g) were dissolved in CHCl<sub>3</sub> or THF. After stirring at room temperature for an hour, the solution was poured into excess amount of hexane to obtain the objective product. Differential scanning calorimetry (DSC) was carried out to evaluate the miscibility of the blended polymers.

## RESULTS AND DISCUSSION

#### Preparation of lignophenol (LP)-graft-poly(2-ethyl-2-oxazoline) (POZO)

To prepare LP-graft-POZO, we synthesized a halomethylphenyl-group-modified LP by carrying out the Williamson ether synthesis of  $\alpha,\alpha'$ -dibromo-*p*-xylene (Scheme 1). As a result of this, an organosoluble polymer (LP-Br) was obtained in 28% yield. The plausible reasons of a low yield are as follows: (1) the formation of crosslinked structure prepared by bifunctional linker ( $\alpha,\alpha'$ -dibromo-*p*-xylene), (2) hydrophilic impurities in starting material (lignophenol) was transformed into hydrophobic materials and then they were removed by reprecipitation. On the basis of elemental analysis, the bromomethyl moiety of LP-Br was estimated to be 1.50 mmol/g. The FT-IR spectrum of LP-Br exhibited peaks attributable to phenolic and alkyl hydroxyl groups (3503 cm<sup>-1</sup>), benzene rings (3030 cm<sup>-1</sup>), aliphatic C–H bonds (2938 and 2875 cm<sup>-1</sup>), C–O–C bonds (1229 and 1142 cm<sup>-1</sup>), and C–Br bonds (609 cm<sup>-1</sup>). From the <sup>1</sup>H-NMR spectrum of LP-Br, the peaks of



**Scheme 1** Modification of LP with  $\alpha,\alpha'$ -dihalo-*p*-xylene and a structure of LP.

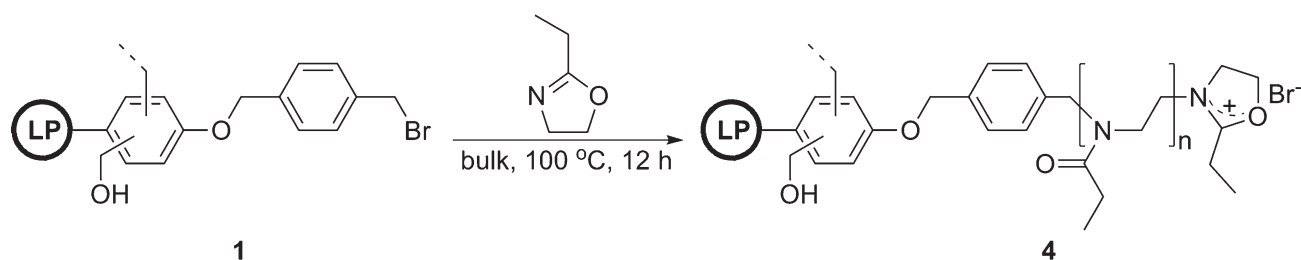
aromatic and bromomethyl protons were confirmed to be at 7.03–7.23 and 4.14–4.60 ppm, respectively. The peaks of the methylene and methoxy protons were detected at 3.05–4.02 ppm; furthermore, the proton peaks of the methyl groups attached to benzene rings were confirmed to be at 2.05–2.40 ppm. These results suggest that the structure of LP-Br depends on the LP structure, the protected phenolic hydroxyl groups with  $\alpha,\alpha'$ -dibromo-*p*-xylene, and the cresol moieties. However, it is difficult to estimate the conversion ratio of phenolic hydroxyl groups to protected moieties. The reaction of LP with  $\alpha,\alpha'$ -dichloro-*p*-xylene also afforded an organo-soluble objective product (LP-Cl) in 27% yield. By carrying out elemental analysis, the content of the chloromethyl moiety in LP-Cl was estimated to be 1.95 mmol/g. From the FT-IR (Supporting Information Fig. S1) and  $^1\text{H-NMR}$  (Supporting Information Fig. S2) spectra, it was observed that the structure of LP-Cl is similar to that of LP-Br. When  $\alpha,\alpha'$ -diiodo-*p*-xylene was used for the polymer reaction, an insoluble gel was obtained owing to the higher reactivity of  $\alpha,\alpha'$ -diiodo-*p*-xylene; therefore,  $\alpha,\alpha'$ -diiodo-*p*-xylene was considered to act as a crosslinking agent.

LP-based functional polymers (**1**, **2**) with benzyl halide moieties in their side chains were successfully prepared, as described above. These polymers can initiate the cationic ring opening polymerization of 2-ethyl-2-oxazoline. If the ring-opening polymerization of 2-ethyl-2-oxazoline is initiated by benzyl bromide moieties of LP-Br to prepare an LP graft polymer, it is possible that LP-Br could exhibit a different behavior than those exhibited by typical phenolic resins, including LP.

The graft polymer was prepared by the cationic ring-opening polymerization of 2-ethyl-2-oxazoline,

initiated by the bromomethyl group-modified LP (LP-Br) (26.9 mmol, 89 equiv. for Br content in LP-Br (1.5 mmol/1.0 g)) (Scheme 2). Graft polymer LP-graft-POZO was obtained at 74% yield. The solubility properties of LP-graft-POZO were quite different from those of LP-Br and LP-Cl. Graft polymer LP-graft-POZO was soluble in chloroform, THF, and methanol, whereas LP was poorly soluble in these solvents (Table I).

The FT-IR spectrum of LP-graft-POZO exhibited peaks attributable to the hydroxyl groups and tertiary amide moieties at  $3543\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$ , respectively. The  $^1\text{H-NMR}$  spectrum of LP-graft-POZO exhibited peaks attributable to methylene protons in ethylenimine moieties (3.22–3.68 ppm), methylene protons in propionyl groups (2.02–2.52 ppm), and methyl protons in propionyl groups (1.00–1.18 ppm). Furthermore, the peaks of the aromatic protons of LP-Br were confirmed to be at around 7.00 ppm, and those of the bromomethyl protons of LP-Br disappeared almost completely at around 4.50–4.60 ppm. These results indicated that almost all the bromomethyl groups of LP-Br initiated the ring-opening polymerization of 2-ethyl-2-oxazoline. GPC measurements (UV detector, polystyrene standards) revealed that the number-average molecular weight ( $M_n$ ) and the polydispersity index ( $M_w/M_n$ ) of LP-graft-POZO were 38,900 and 4.4, respectively. These values of LP-graft-POZO were larger than those of LP ( $M_n = 2400$ ,  $M_w/M_n = 3.2$ ). From the integral ratio of methylene protons of polyoxazoline and benzylic protons of initiator, the molecular weight of each POZO unit was estimated to be  $\sim 6400$ . Therefore, LP-graft-POZO apparently formed polyoxazolines that branched at multiple points on LP-Br.



**Scheme 2** Cationic ring-opening polymerization of 2-ethyl-2-oxazoline initiated by **1**.

TABLE I  
Solubility of LP and 4

	CHCl <sub>3</sub>	THF	Hexane	Acetone	DMF	Methanol	Water
LP	–	++	–	+	++	+–	–
4	++	++	–	++	++	++	+–

++, Well soluble; +, soluble; +–, fairly insoluble; –, insoluble.

### Thermal degradation property of LP-graft- POZO

Lignin (precursor of LP) is known to be firm and inflexible. Its polymer main chain consists of aromatic rings that are similar to those of phenolic resins. Therefore, LP can be regarded as a polymer material with good thermal stability and mechanical properties. Thermogravimetric (TG) analysis of LP carried out under a nitrogen atmosphere revealed that LP started decomposing at 30°C and that its  $T_{10}$  (temperature for 10% loss in mass) value was 168°C. We want to comment about this phenomenon. LP as a starting material in this study may have hydrophilic impurity which can not be removed by reprecipitation or column chromatography; therefore, the early decomposition might be caused by impurity. In contrast, the  $T_{10}$  value of LP-graft-POZO increased to 334°C. At least, no decomposition occurs after heating at 140°C (Supporting information Fig. S6). These results indicated that the thermal degradation properties of LP could be improved by branching the poly(2-oxazoline) units on the polymer chains, whose moieties protected the main chain of LP, causing thermal decomposition to occur at a high temperature.

### Miscibility of LP-graft-POZO with commodity polymers

LP-graft-POZO was blended with different commodity polymers such as poly(bisphenol A carbonate) (PC), polyvinylpyrrolidone (PVP), polystyrene (PSt), and poly(vinyl chloride) (PVC) (Table II). The glass transition temperatures ( $T_g$ ) of the resulting products were measured by differential scanning calorimetry (DSC) to evaluate the miscibility of LP-graft-POZO with the commodity polymers. In the case of a polymer blend of LP-graft-POZO with PVC (LP-graft-

POZO-PVC, Fig. 1), the  $T_g$  values of LP-graft-POZO-PVC and PVC were found to be 63 and 81°C, respectively, during the second scan of the DSC measurement (Table II, run 1). These results clearly indicated that LP-graft-POZO and PVC were completely miscible, forming a single phase. Kobayashi et al. reported that poly(2-oxazoline) is slightly basic and highly polar because of the amide groups present on their side chains.<sup>30</sup> Therefore, poly(2-oxazoline)s may be miscible with PVC (primary miscibility), where PVC is slightly acidic and PVC is derived from chloride groups. The blend of poly(2-oxazoline) and PVC have a lower  $T_g$  value than PVC.<sup>65</sup>

Next, the  $T_g$  value of the sample was not detected during the third DSC scan (Table II, run 1, Fig. 1). This is probably because of the presence of LP, which was incorporated with POZO, and also because of the secondary miscibility between the LP moieties and poly(2-oxazoline) chain-PVC complexes. The secondary miscibility can be attributed to the fact that phenolic resins (including LPs) having complicated structures<sup>21</sup> such as branched polymer usually have no glass transition points between room temperature and ~100°C. This thermal behavior of LP-graft-POZO-PVC is extremely interesting; however, there is a possibility that LP exhibits a glass transition point at a temperature lower than room temperature. To confirm this possibility, DSC measurements were performed; however, the mass loss of LP was confirmed to occur in a low temperature range (from –100 to 100°C). TG analysis revealed that the decomposition of LP started at 30°C, and hence, it was difficult to perform DSC measurements of LP. It is noted that LP played a

TABLE II  
Polymer Blends of 4 With PVC, PC, PVP, or PSt

Run	4 (g)	Polymer (g)	$T_g^a$ (°C) 2nd scan	$T_g^a$ (°C) 3rd scan
1	0.1	PVC (0.1)	62.6	<sup>b</sup>
2	0.1	PC (0.1)	53.3, 141.8	142.1
3	0.1	PVP (0.1)	<sup>b</sup>	<sup>b</sup>
4	0.1	PSt (0.1)	50.2, 97.1	48.1, 98.1

<sup>a</sup> Glass transition temperature.

<sup>b</sup> Not detected.

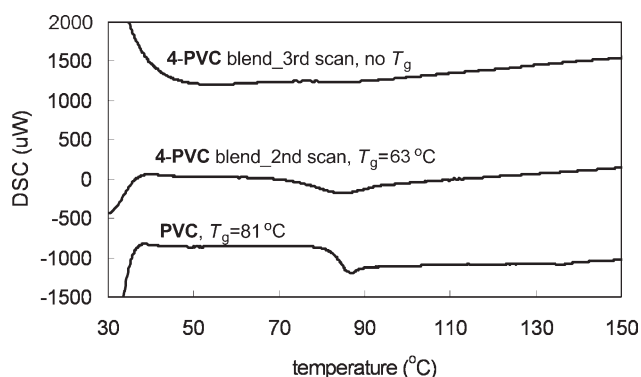


Figure 1 DSC analyses of PVC and 4-PVC blend.

significant role in secondary miscibility, although LP was low content in the blend.

The DSC analyses of the mixtures (**M1** and **M2**) composed of LP-graft-POZO and PVC (feed ratio based on weight: **M1** = 1 : 2, **M2** = 1 : 5) were carried out to determine the optimum feed ratio of LP-graft-POZO and PVC. Even after the fifth DSC scan, the  $T_g$  value of each sample was 81°C. These values were same as that of PVC; therefore, this behavior was clearly dependent on the feed ratio of LP-graft-POZO and PVC. Moreover, LP-graft-POZOs with different side-chain lengths of POZO were prepared to examine the effects of these lengths on the miscibility of LP-graft-POZO with PVC (feed ratio of LP-Br : 2-ethyl-2-oxazoline = 1 : 10, 1 : 20, and 1 : 50). However, DSC analyses revealed that not all samples were miscible with PVC at different feed ratios. This indicated that the side-chain length of POZO in LP-graft-POZO should at least be equivalent to that of **4** for LP-graft-POZO to perform as a compatible polymer.

In the case of run 2, the  $T_g$  value of **4-PC** during the third scan was lower than that of PC; moreover, TG analysis revealed that the  $T_{10}$  value of LP-graft-POZO-PC was 344°C. These results suggested that **4** could act as a polymer additive to PC without causing any deterioration in the thermal stability. Meanwhile, the  $T_g$  value of the LP-graft-POZO-PVP blend polymer (Table II, run 3, Fig. 2) was not detected. The reason for this behavior might be the same as the reason why the  $T_g$  value of the LP-graft-POZO-PVC was not detected in run 1. These results suggested that LP-graft-POZO was miscible with both PC and PVP. Therefore, it can be inferred that LP-graft-POZO, which is a highly polar polymer, is readily miscible with all polar materials. The  $T_g$  values of the LP-graft-POZO-PSt blend polymer detected during the second and third scans (Fig. 3) were very similar to that of PSt (89°C), which is, 97°C during the second scan and 98°C during the

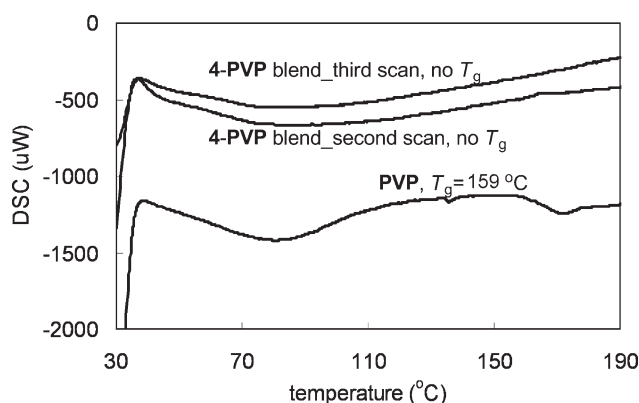


Figure 2 DSC analyses of PVP and 4-PVP blend.

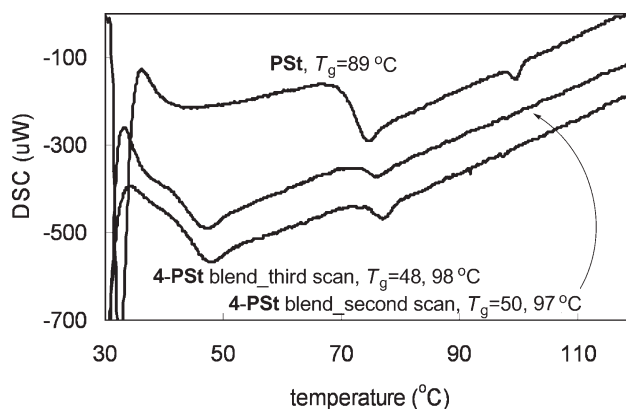


Figure 3 DSC analyses of PSt and 4-PSt blend.

third scan. This similarity was apparently because of the immiscibility of LP-graft-POZO with PSt.

To verify the efficiency of the graft structure of POZO, the blends of LP, POZO (Aldrich,  $M_w$  = 50,000), and the commodity polymers were prepared by mixing them in a mortar with a pestle and TG and DSC analyses were carried out. The TG analyses of LP-POZO, LP-POZO-PVC, LP-POZO-PC, and LP-POZO-PVP revealed that the decomposition of these blends commenced at temperatures below 100°C and that their  $T_{10}$  values were 322°C (LP-POZO), 253°C (LP-POZO-PVC), 340°C (LP-POZO-PC), and 343°C (LP-POZO-PVP), respectively. These  $T_{10}$  values were less than those of LP-graft-POZO and LP-graft-POZO-commodity polymer blends. These results suggested that the polymer blends prepared in a mortar with a pestle did not exhibit any improvements in thermal stability. DSC analyses revealed that the degradation of polymer blends started at temperatures below the glass transition temperatures.

## CONCLUSIONS

We successfully prepared lignophenol (LP)-graft-poly(2-ethyl-2-oxazoline) (POZO) by means of the cationic ring-opening polymerization of 2-ethyl-2-oxazoline initiated by LP, which was modified using  $\alpha,\alpha'$ -dibromo-*p*-xylene. DSC measurements revealed that LP-graft-POZO was miscible with the commodity polymers PVC, PVP, and PC. In particular, the polymer blends of LP-graft-POZO/PVC and LP-graft-POZO/PVP did not reveal any glass transition temperature ( $T_g$ ) values during the third DSC scan, regardless of the existence of the individual  $T_g$  values during the second scan. This behavior was attributed to the secondary miscibility between the LP moieties and poly(2-oxazoline) chain-commodity polymer complexes. Further, TG analysis revealed that LP-graft-POZO was more thermostable than LP. This result suggested that the addition of POZO can

improve the thermal stability of LP and can act as a polymer compatibilizer. Thus, a novel LP-based material was successfully prepared. LP-graft-POZO can be used as a polymer additive. It is also expected that LP blended with poly(2-oxazoline) will be used as an adhesive to combine different polymers, organic-inorganic polymers, etc.

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