Moldable Material from ε-Poly-L-lysine and Lignosulfonate: Mechanical and Self-Healing Properties of a Bio-Based Polyelectrolyte Complex

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ABSTRACT: A moldable material from a natural cationic polyelectrolyte, ε-poly-L-lysine (ε-PL), was prepared by mixing with two lignosulfonates a reagent for research (L-SO3Na) and a commercially available purified lignosulfonate (Pearllex NP). The obtained ε-PL/lignosulfonate complexes demonstrated the ability to be tuned from a rigid form, such as polystyrene or poly(methyl methacrylate), to a soft elastomer form such as silicone by varying the lignosulfonate species and composition. The maximum toughness of the complex (8.4 MJ/m3) was superior to that of ε-PL or lignosulfonate-derived polyelectrolyte complexes. In addition, the ε-PL/lignosulfonate complex showed self-healing properties due to the many reversible ionic bonds in the complex. The preparation process for the novel complex was simple, involving the mixing and drying of an aqueous solution of the polyelectrolyte without any extra reagents (organic solvents, condensation reagents, and cross-linker). Thus, given these many advantages and the excellent biodegradability of the components, the ε-PL/lignosulfonate complex is expected to be useful as a sustainable structural material.

INTRODUCTION

The extensive use of polymers in the modern world has prompted an urgent need for clean, sustainable biomass resources to replace fossil-based polymers. Polymer compounds from microorganisms, which can be obtained from renewable biomass sources via an environmentally friendly fermentative process, show great promise as alternatives to fossil-based complexes and have attracted the attention of many researchers. ε-Poly-L-lysine (ε-PL), a commercially available polymer produced by the Streptomyces strain, is composed of 25–35 L-lysine residues. ε-PL exhibits strong antimicrobial activity against a wide range of bacteria, due to the cationic nature of the primary amino groups hanging on its side chain. This, combined with its low toxicity against mammalian cells, allows ε-PL to be used as a food preservative.

Another potential application of ε-PL is its use as a structural material, given that the chemical structure of ε-PL is similar to that of nylon 6, which has no primary amine groups on its side chain. In fact, the glass transition temperature (Tg at 88 °C) and melting temperature (Tm at 173 °C) of ε-PL imply that it may possess the ideal thermoplastic properties for structural applications. To date, the low molecular weight of ε-PL has resulted in low moldability, thus limiting its use in structural components, with the exception of soft hydrogel materials.

In a previous study, we focused on the strong ionic interactions between amino groups and sulfonation groups and prepared a thermoplastic from ε-PL via formation of an ionic complex with a sulfonate surfactant. The complex formation introduced a networking structure between the ε-PL chain via ionic bonds, allowing it to be prepared as a free-standing sheet and as other forms. To our knowledge, this was the first example of an ε-PL-based thermoplastic. From a practical point of view, the tensile strength and toughness of this ε-PL-derived complex was insufficient compared with commodity plastics or elastomers and required further improvement before being applied as a structural component.

To this end, we considered a complex formed using ε-PL and an anionic polyelectrolyte, as opposed to low molecular weight anionic compounds. In recent studies, good mechanical performance was demonstrated in polyelectrolyte complexes composed of both anionic and cationic polymers. In contrast to low-molecular-weight complexes, the introduction of an anionic polymer to a ε-PL-derived complex dramatically introduces a cross-linking network in the complex that provides improved mechanical properties and elasticity.

Lignosulfonate, a wood-derived polyelectrolyte produced in sulfate pulping processes, has excellent biodegradability and is especially promising as it contains many sulfonate groups to...
strongly interact with amino groups, as mentioned earlier. We recently reported on moldable complexes obtained from lignosulfonate and cationic polyelectrolytes.16 In this earlier study, we produced free-standing sheets from the lignosulfonate/synthetic cationic polyelectrolyte mixture via a simple process of mixing and drying the mixture. The obtained complexes showed good mechanical and self-healing properties.

Based on our earlier findings, here, we created a novel complex by combining the ε-PL polyelectrolyte individually with two lignosulfonates, L-SO3Na and Pearllex NP. The resulting bio-based complexes demonstrated tunable mechanical properties, good moldability, self-healing, and a maximum toughness (8.4 MJ/m3) superior to those known for ε-PL or lignosulfonate-derived polyelectrolyte complexes alone.

## RESULTS AND DISCUSSION

### Preparation of the ε-PL/Lignosulfonate Complex

We prepared ε-PL/lignosulfonate complexes using two lignosulfonates individually; a research reagent L-SO3Na purchased from Tokyo Chemical Industry and a commercialized, purified lignosulfonate, Pearllex NP, which has a high molecular weight (10 000–20 000 g/mol). Notably, Pearllex NP is a fractionated product of higher molecular weight components from industrial lignosulfonates manufactured by Nippon Paper Industries Co., Ltd. The mixtures of ε-PL with L-SO3Na and Pearllex NP were homogeneous solutions; no precipitate or aggregate was observed. The homogeneous mixture, ranging from ε-PL/lignosulfonate = 40:60 to 60:40, was cast and dried in a poly(tetrafluoroethylene) (PTFE) mold, from which homogeneous, sheetlike samples were obtained. It should be noted that the cast sheet from only ε-PL or Pearllex NP cracked during the drying process; additionally, L-SO3Na by itself was too brittle to form the intended shape (Table 1). The ionic cross-linking between ε-PL and the lignosulfonates improved the material toughness via a "sacrificial bond" mechanism,17,18 which effectively prevented the corruption of the sample during the preparation of a sheet or dumbbell-shaped test piece.

In our previous study, we fabricated an ε-PL-based thermoplastic by combining ε-PL and a sulfonate surfactant [sodium bis(2-ethylhexyl)sulfosuccinate, BEHS];11 notably, the ε-PL/BEHS complex was obtained as a water-insoluble precipitate. Despite using a similar preparation method to that used in a previous study,11 the ε-PL/lignosulfonate complexes of the present study were distributed homogeneously throughout the aqueous solution. Lignosulfonate is highly soluble in water; for example, L-SO3Na can dissolve more than 500 g/L of water, compared with BEHS (∼8.2 g/L of water, based on the material data sheet from the supplier). Therefore, the homogeneity of the ε-PL/lignosulfonate mixture would be derived from the water solubility of the components.

We also reported recently on a moldable complex from poly(2-diallyldimethylammonium chloride) (PDADMACl) and L-SO3Na.16 The viscosity of the PDADMACl/L-SO3Na mixture increased sharply during mixing. In contrast, in the current study, the viscosity of the ε-PL/lignosulfonate complex did not change significantly. We speculate that the lower molecular weight of ε-PL (3000–4500 g/mol) compared with that of PDADMACl (200 000–350 000 g/mol) is insufficient to form a large molecular weight complex in the mixture, leading to the observed low viscosity. Despite the differences in water solubility and viscosity, a sheetlike material was obtained from both the ε-PL/lignosulfonate and PDADMACl/L-SO3Na complexes. Therefore, we speculated that the ionic networks in the ε-PL/lignosulfonate complex would be sufficient to improve the moldability of this material.

### Mechanical Properties of the ε-PL/L-SO3Na Complex

The as-fabricated ε-PL/lignosulfonate complexes were cut into dumbbell-shaped test pieces after sample equilibration at 50% relative humidity. Tensile tests were performed as a function of the composition ratio of ε-PL to L-SO3Na. The results are shown in Figure 1a and Table 1. The ε-PL/L-SO3Na complexes became hard and brittle with increasing L-SO3Na content, as with the previously reported PDADMACl/L-SO3Na complex16 and other lignin/polymer composites.19,20 A maximum stress of 28.9 MPa was attained for the ε-PL/L-SO3Na complex, using a weight ratio of ε-PL/L-SO3Na of 40:60; this value was 14.8-fold higher than that of the ε-PL/B DHS complex,11 which is the only moldable material from ε-PL referenced to date to our knowledge. Thus, the ε-PL/L-SO3Na complex may be the strongest ε-PL-based moldable material currently available. In addition, the maximum stress of the ε-PL/L-SO3Na complex was 7.0 times that of the PDADMACl/L-SO3Na complex (4.1 MPa) and other reported complexes of cationic-polyelectrolyte/lignosulfonate.16 The maximum stress, Young’s modulus, and strain at break of the ε-PL/L-SO3Na complex (28.9 MPa, 1652.0 MPa, and 3%, respectively, at ε-PL/L-SO3Na = 40:60) were similar to those of polystyrene (39 MPa, 1600 MPa, and 3%, respectively), poly(methyl methacrylate) (20 MPa, 1800 MPa, and 3%, respectively).22

### Table 1. Mechanical Figures of Merit of ε-PL/Lignosulfonate Complexes Obtained by Varying the Weight Ratio of ε-PL to Lignosulfonates

| Lignosulfonate | weight ratio of ε-PL/lignosulfonate | maximum stress (MPa) | strain at break (%) | Young’s modulus (MPa) | toughness (MJ/m3) | water content (w/w %) |
|---------------|---------------------------------|---------------------|--------------------|----------------------|------------------|---------------------|
| L-SO3Na       | 100:0                           | a                   | a                  | a                    | a                | 14.1                |
|               | 60:40                           | 3.1 ± 0.1           | 139 ± 7            | 70.5 ± 5.4           | 3.3 ± 0.3        | 13.7                |
|               | 50:50                           | 10.0 ± 0.5          | 82 ± 3             | 556.2 ± 35.5         | 7.5 ± 0.1        | 12.2                |
|               | 40:60                           | 27.9 ± 3.4          | 3 ± 0.3            | 1652.0 ± 263.4       | 0.4 ± 0.02       | 11.6                |
|               | 0:100                           | b                   | b                  | b                    | b                | 16.7                |
| Pearllex NP   | 60:40                           | 3.8 ± 0.3           | 207 ± 19           | 86.7 ± 3.4           | 6.0 ± 0.8        | 11.6                |
|               | 50:50                           | 17.5 ± 2.3          | 64 ± 13            | 760.8 ± 96.9         | 8.4 ± 1.6        | 9.7                 |
|               | 40:60                           | b                   | b                  | b                    | b                | 6.7                 |
|               | 0:100                           | a                   | a                  | a                    | a                | 11.8                |

"The sample was cracked during the drying process. The sample was too brittle and a dumbbell-shaped test piece could not be prepared. All samples were equilibrated at 30 °C and 50% relative humidity for 5 days. Results are averages ± standard deviation of at least three samples.
The toughness of the ε-PL/L-SO₃Na complex was maximized at a weight ratio of 50:50 (7.5 MJ/m³). The molar ratio of the amino groups of ε-PL and the anionic functional groups of L-SO₃Na in this complex was estimated as 2.5:1, based on the elemental analysis data of L-SO₃Na from a previous study. This value is close to that previously reported for the PDADMAC/L-SO₃Na complex, in which the cationic/anionic group ratio of the complex (3:0.1) was similar. The lignosulfonate molecule has a rigid structure and a small molecular radius, due to a phenolic backbone and covalent cross-linking. The excess amount of flexible ε-PL chains would bridge the small, rigid lignosulfonate molecules, which would be necessary to attain the desired strength, as with the PDADMAC/L-SO₃Na complex. The molar ratio of functional groups in ε-PL/L-SO₃Na and PDADMAC/L-SO₃Na complexes is similar, however, the toughness of the former was 2.1-fold higher (7.5 vs 3.6 MJ/m³, respectively). The ε-PL complex showed higher toughness than the PDADMACI complex, despite the lower molecular weight of ε-PL (3000–4500 g/mol) with respect to PDADMACI (200 000–350 000 g/mol). Comparing the chemical structures of these two cationic polyelectrolytes, ε-PL has a primary amino group, whereas PDADMACI has a quaternary ammonium group. It has been reported that the interaction between sulfonate and primary amino groups in a polyelectrolyte complex is stronger than that with quaternary ammonium groups. In fact, the ε-PL/BEHS complex is a water-insoluble complex, however, the PDADMACI/BEHS complex is a small micellar complex that dissociates at low BEHS concentration. These findings imply a stronger interaction between sulfonate and a primary amino group than with a quaternary ammonium group. The stronger interaction between L-SO₃Na (sulfonate group) and ε-PL (primary amino group) than with PDADMACI (quaternary ammonium group) may contribute to superior stress at break and a high Young’s modulus and toughness, despite the lower molecular weight of ε-PL. Further studies are underway in an attempt to better understand the mechanisms responsible for the high toughness of the L-SO₃Na/ε-PL complex, to be reported in future work.

### Mechanical Properties of the ε-PL/Pearllex NP Complex

Using the same combination of polyelectrolytes, our previous study indicated that the molecular weight of the polyelectrolyte affected the mechanical properties of the complex; a certain degree of molecular weight is necessary for the material to exhibit good toughness. Thus, we attempted to further improve the mechanical properties of the ε-PL-based complex using another lignosulfonate, Pearllex NP, a commercially available lignosulfonate with high molecular weight. We prepared the ε-PL/Pearllex NP complex and evaluated its mechanical properties using the same methods described for the ε-PL/L-SO₃Na complex. Tensile test results for ε-PL/Pearllex NP are given in Figure 1b and Table 1. The complex became hard and brittle with increasing Pearllex NP content, similar to the ε-PL/L-SO₃Na complex. At the composition ratio of ε-PL/Pearllex NP of 40:60, the sample was too brittle to form a dumbbell-shaped test piece. With increasing ε-PL content, the complex became softer. The mechanical properties of ε-PL/Pearllex NP at 60:40 showed the values for maximum stress, strain at break, Young’s modulus, and toughness values of 3.8 MPa, 207%, 86.7 MPa, and 6.0 MJ/m³, respectively; these were comparable to those of hard silicone rubber (6.7 MPa, 198%, 6.4 MPa, and 8.0 MJ/m³, respectively), with the exception of Young’s modulus. This means that simply by changing the lignosulfonate species and composition ratio, the ε-PL/lignosulfonate complex could take the forms of either a rigid polymer or a soft material, depending on the desired configuration.

Focusing on the difference between Pearllex NP and L-SO₃Na, the ε-PL/Pearllex NP complex revealed a higher maximum stress value and a higher Young’s modulus and toughness than the ε-PL/L-SO₃Na complex, at comparable compositions (Table 1). The complex with a ε-PL/lignosulfonate weight ratio of 50:50 showed the maximum stress and Young’s modulus values, which were improved 1.8 (from 10.0 to 17.5 MPa) and 1.4 (from 556.2 to 760.8 MPa) times, respectively, by the use of Pearllex NP. Replacing L-SO₃Na with Pearllex NP (ε-PL/lignosulfonate = 60:40) also provided a higher maximum stress (from 3.1 to 3.8 MPa, improved 1.2 times) and Young’s modulus (from 70.5 to 86.7 MPa, 1.2 times) (Table 1).

Most currently available industrial-grade lignosulfonates and research reagents contain impurities, such as sugars. Thus, we suspected the presence of these impurities in L-SO₃Na. Considering the same amount of L-SO₃Na and Pearllex NP, the impurity sugars in L-SO₃Na reduce the amount of lignosulfonate per weight basis compared with Pearllex NP. It is presumed that the increased effective lignosulfonate in the complex achieved by the use of Pearllex NP would stiffen the complex (i.e., increase the maximum stress and Young’s modulus) to a greater degree than L-SO₃Na. In addition, the toughness of the complex was improved by the use of Pearllex NP (from 7.5 to 8.4 and 3.3–6.0 MJ/m³ at ε-PL/lignosulfonate = 50:50 and 60:40, respectively). We considered that the higher toughness of the ε-PL/Pearllex NP complex derives from the high molecular weight of Pearllex NP. In fact, the strain at break with the ε-PL/Pearllex NP = 60:40 complex was higher than the corresponding complex using L-SO₃Na (207 vs 139%, Table 1). The improvement in strain at break could not be explained in terms of the increasing effective

![Figure 1](image-url)
lignosulfonate content, as this causes a reduction in the strain at break (Table 1). Thus, this implies that the improved strain at break originates from the high molecular weight of Pearlex NP, in which the molecular network and degree of molecular entanglement are enhanced. This also agrees with the results of our previous study with PDADMACl that has a high molecular weight.16

Effects of Relative Humidity on the Mechanical Properties of ε-PL/L/SO3Na and ε-PL/Pearllex NP Complexes. In a previous study, the PDADMACl/L-SO3Na complex softened as the relative humidity increased due to water absorption.16 On this basis, we speculated that the mechanical properties of ε-PL/lignosulfonate complexes would also be changed by relative humidity. The complexes with a fixed ε-PL/lignosulfonate composition of 50:50 were equilibrated at different relative humidity values for 5 days, after which tensile tests were performed (Figure 2 and Table 2).

![Figure 2](image)

**Figure 2.** Effects of relative humidity on the mechanical properties of ε-PL/lignosulfonate complexes. The complexes were prepared from ε-poly-l-lysine (ε-PL) and sodium lignosulfonates (a) L-SO3Na and (b) Pearllex NP at the weight ratio of ε-PL to lignosulfonate was 50:50. All samples were equilibrated at 30 ± 3°C and at each relative humidity for 5 days. The same data are summarized in Table 2.

The strain at break of both complexes increased at higher relative humidity, whereas their maximum stress and Young’s modulus decreased. This behavior is consistent with those previously reported for PDADMACl/L-SO3Na16,26,27 and other polyelectrolytes.28 However, the water content in ε-PL-based complexes is lower than that of PDADMACl/L-SO3Na under comparable humidity. The water content of each complex at 60, 50, and 40% relative humidity, respectively, is as follows: ε-PL/L-SO3Na: 13.7, 12.2, and 11.6 w/w%; ε-PL/Pearllex NP: 11.6, 9.7, and 6.7 w/w%; and PDADMACl/L-SO3Na: 25.2, 16.9, and 14.2 w/w% (Table 2 and previous study16). The higher water content of the PDADMACl/L-SO3Na complex compared with that of the ε-PL/lignosulfonate complex is attributable to the presence of chloride ions. The presence of salt softens the polyelectrolyte—surfactant29 and polyelectrolyte—polypelectrolyte12,13 complexes, due to weakening of the ionic interaction. Similar phenomena would be induced in ε-PL/L-SO3Na and PDADMACl/L-SO3Na complexes by the presence of chloride ions. To check this, we added HCl to the ε-PL/L-SO3Na mixture during preparation, which increased the water content and softened the complex (Supporting Information Table S2). Focusing on the difference between L-SO3Na and Pearllex NP, the change in the material toughness between 50 and 60% humidity was smaller for Pearllex NP. The ε-PL/Pearllex NP complex retained 71% of its toughness after the humidity change from 50 to 60%, whereas the toughness of the ε-PL/L-SO3Na complex declined to 27% under the same conditions. Impurity sugars in L-SO3Na, as discussed earlier, would hydrate; the hydrated water weakens the ε-PL/L-SO3Na complex by increasing the water content in the complex (Table 2). Given that humidity resistance is important for practical use of these complexes in a wide range of environments, we continue to work toward further improvements in humidity resistance via chemical modification of the primary amino group of ε-PL.

Self-Healing Properties of ε-PL/Lignosulfonate Complexes. Many studies have demonstrated that reversible bonds in polymer materials promote self-healing properties in the material. For example, a self-healing material using hydrogen bonds30 reversible covalent bonds,31 and ionic bonds13,16 has been reported. The ε-PL/lignosulfonate complex includes many ionic bonds; therefore, it is expected to have self-healing properties. The two cut surfaces of the complex were reunited, incubated at a specific humidity for 24 h, and re-equilibrated at 50% humidity before undergoing tensile tests to assess self-healing (Table 3). To achieve a high healing efficiency, the ratio of ε-PL/lignosulfonate was fixed at 60:40 (the softest composition in this study, Table 1) to promote healing.13,16 The first self-healing test was conducted at 60% relative humidity, which is identical to the self-healing conditions of the previously reported PDADMACl/L-SO3Na complex.16 The healing efficiency, determined based on the toughness

| Lignosulfonate | Equilibrated Relative Humidity | Maximum Stress (MPa) | Strain at Break (%) | Young’s Modulus (MPa) | Toughness (MJ/m^3) | Water Content (w/w%) |
|---------------|-------------------------------|-----------------------|---------------------|----------------------|-------------------|----------------------|
| L-SO3Na       | 60                            | 2.4 ± 0.1             | 130 ± 5             | 28.8 ± 2.0           | 2.0 ± 0.2         | 16.8                 |
|               | 50                            | 10.0 ± 0.5a           | 82 ± 3a             | 556.2 ± 35.5a        | 7.5 ± 0.1a         | 12.2a                |
|               | 40                            | 26.1 ± 3.2            | 2 ± 0.2             | 1622.3 ± 183.6       | 0.4 ± 0.1         | 11.7                 |
| Pearllex NP   | 60                            | 7.2 ± 0.2             | 91 ± 5              | 367.4 ± 5.2          | 6.0 ± 0.2         | 11.2                 |
|               | 50                            | 17.5 ± 2.3a           | 64 ± 13a            | 760.8 ± 96.9a        | 8.4 ± 1.6a         | 9.7a                 |
|               | 40                            | b                     | b                   | b                    | b                 | 8.8                  |

*aThe data are the same as in Table 1. bThe sample was too brittle, and a dumbbell-shaped test piece could not be prepared. cThe weight ratio of lignosulfonate and ε-PL is 50:50. dAll samples were equilibrated at 30 °C and at each relative humidity for 5 days. eResults are averages ± standard deviation of at least three samples.
which can achieve completely (approximately 100% healing). Young's modulus is crucial for achieving high healing efficiency and a high healing property arising from ionic interactions between the healing complex. In future investigations, we will focus on the healing efficiency, due to the low mobility of the molecular chains in the materials. A recent study showed the coexistence of high healing and a high healing efficiency, with 40% in ε-PL/Lignosulfonate complex before cutting and after healing, was 40% in ε-PL/L-SO3Na complex, which can achieve completely (approximately 100% healing). The ε-PL/lignosulfonate complex has a much higher stiffness (Young's modulus, 28.8 and 367.4 MPa in the complex using L-SO3Na and Pearllex NP at 60% humidity, Table 1) than the PDADMAC/L-SO3Na complex (0.1 MPa at 60% humidity). In general, in a polymer material with a high Young's modulus, it is difficult to achieve a high healing efficiency, due to the low mobility of the molecular chains in the materials. A recent study showed the coexistence of high healing and a high Young's modulus (>1 GPa) using a unique hydrogen bond (ether-thioure). As described in the section on humidity resistance experiments, the primary amino group of ε-PL/lignosulfonate complex can be modified chemically, which allows the introduction of unique reversible bonds into the complex. The chemical modifications can help to create an “evolved” ecological material that combines sustainability, biodegradability, excellent and tunable mechanical properties, and self-healing ability based on the ε-PL/lignosulfonate complex in this study.

### CONCLUSIONS

We prepared a new moldable polyelectrolyte complex from ε-PL and lignosulfonates by taking advantage of its ionic functional group. To our knowledge, the mechanical properties of this complex are superior to those of any moldable ε-PL-based materials. In addition, the present ε-PL/lignosulfonate complex can be prepared from only ε-PL, lignosulfonate, and water; thus, this complex is an excellent environmentally compatible material, composed of biodegradable, sustainable resources and prepared using an eco-friendly production process. The mechanical properties of the ε-PL/lignosulfonate complex are tunable from a rigid form [similar to polystyrene or poly(methyl methacrylate)] to a soft form (similar to silicone rubber), simply by varying the lignosulfonate type/species and composition of the complex. The sustainability, biodegradability, and tunable mechanical properties of the ε-PL/lignosulfonate complex should help to overcome various environmental problems, such as those associated with microplastics. Furthermore, the complex revealed a self-healing property arising from ionic interactions between ε-PL and lignosulfonate, which is a promising function to improve the lifetime and safety of structural materials using this complex. In future investigations, we will focus on the healing efficiency of the complex to further exploit this property. Thus, the ε-PL/lignosulfonate complex is expected to expand the application field of ε-PL, as a sustainable structural material for various commodities, building components, and agricultural materials.

### EXPERIMENTAL SECTION

**Materials.** ε-PL (25 w/v% aqueous solution, 25-35 mer; molecular weight = 3000–4500 g/mol) was kindly provided by JNC Corporation (Tokyo, Japan) as a gift. L-SO3Na containing approximately 3.1 mmol/g-sample of anionic functional groups, including 1.8 mmol/g-sample of sulfonate groups based on an elemental analysis, was purchased from Tokyo Chemical Industry (Tokyo, Japan). Pearllex NP (molecular weight: 10 000–20 000 g/mol, highly purified sodium lignosulfonate, with a higher molecular weight) was kindly provided by Nippon Paper Industries Co., Ltd. (Tokyo, Japan) as a gift. Hard silicone rubber (thickness: 1 mm; catalog No. 2-9321-01) was purchased from AS ONE (Osaka, Japan).

**Preparation of the Complexes.** The ε-PL/lignosulfonate complex was prepared by mixing an ε-PL aqueous solution (25 w/v%) with powder forms of L-SO3Na or Pearllex NP. For the preparation with high lignosulfonate content, some amount of pure water was added to the mixture to dissolve L-SO3Na or Pearllex NP completely (composition details are provided in the Supporting Information Table S1). The mixture was cast onto a poly(tetrafluoroethylene) (PTFE) mold, dried in air, and then peeled from the mold. The peeled equilibrated sample was then equilibrated under controlled conditions in a humidity chamber (THR030FA; Advantec Toyo, Tokyo, Japan). The water content of each sample was determined by subtracting the amount of solid polymer that had been used in the cast solution from the weight of the equilibrated sample.

**Mechanical Tests.** The equilibrated ε-PL/lignosulfonate complexes (thickness: ~1 mm) were cut into dumbbell-shaped test pieces according to the International Organization for Standardization (ISO) standard 37-3 [equivalent to the Japan Industrial Standard (JIS) K-6251-8]. The test speed was 50 mm/min (EZ-LX; Shimadzu, Kyoto, Japan), and the test was performed under ambient conditions. The toughness of the sample was determined by the total area of the stress–strain curve.

**Self-Healing Tests.** Equilibrated dumbbell-shaped test pieces of the ε-PL/lignosulfonate complex (weight ratio of ε-PL/lignosulfonate: 60:40) were cut into two separate pieces using a razor blade. The cut surfaces of the pieces were then gently pressed back together. The reunited sample was placed into a dumbbell-shaped PTFE mold to avoid slippage during healing. The sample in the PTFE mold was incubated in a humidity-controlled chamber at 30 °C under a relative humidity of 60% or 90% for 24 h of healing. After healing, the sample was re-equilibrated at 30 °C and 50% relative humidity for 5 days. Tensile tests of the healed samples were carried out.

### Table 3. Mechanical Figures of Merit of the ε-PL/Lignosulfonate Complexes in Self-Healing Tests

| lignosulfonate | healing procedure | maximum stress (MPa) | strain at break (%) | toughness (MJ/m3) | healing efficiencyb |
|---------------|-----------------|----------------------|--------------------|------------------|---------------------|
| L-SO3Na       | before cutting  | 3.1 ± 0.1            | 139 ± 7            | 3.3 ± 0.3        | 40%                 |
|               | healed at 60% RH for 24 h | 1.7 ± 0.2  | 120 ± 13           | 1.3 ± 0.3        | 40%                 |
|               | healed at 90% RH for 24 h | 1.8 ± 0.1  | 106 ± 13           | 1.2 ± 0.1        | 37%                 |
| Pearllex NP   | before cutting  | 3.8 ± 0.3            | 207 ± 19           | 6.0 ± 0.8        | 29%                 |
|               | healed at 60% RH for 24 h | 2.2 ± 0.3  | 93 ± 19            | 1.7 ± 0.4        | 31%                 |
|               | healed at 90% RH for 24 h | 1.8 ± 0.1  | 132 ± 15           | 1.9 ± 0.2        | 31%                 |

Notes: bRH: relative humidity. Healing efficiency is calculated from the toughness of samples before cutting and after healing. The data are the same as in Table 1. All samples were healed at 30 °C and each relative humidity for 24 h and then re-equilibrated at 30 °C and 50% RH for 5 days. Results are averages ± standard deviation of at least three samples.
using the same method described above. The healing efficiency of the sample was determined from the toughness of the samples before cutting and after healing.

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