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# Butylated lignin as a compatibilizing agent for polypropylene–based carbon fiber reinforced plastics

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## **RUNNING HEAD**

Lignin as compatibilizing agent of CFRP

## **ABSTRACT**

Lignin is known to be a renewable resource but is also considered a waste or very low value-added material. Herein we propose a lignin-derived compatibilizing agent as an alternative to the current compatibilizing agents. We prepared a polypropylene-based carbon fiber-reinforced plastic (CFRP) with butylated lignin (C<sub>4</sub> lignin). Upon the addition of C<sub>4</sub> lignin, the dispersion of carbon fiber into the matrix, and the adhesion between carbon fiber and the matrix were greatly improved. As a result, the tensile strength of the CFRP prepared with C<sub>4</sub> lignin increased from 37.1 to 40.2 MPa. This value is close to that of a CFRP prepared with maleic anhydride-modified polypropylene (40.9 MPa), an existing compatibilizing agent. C<sub>4</sub> lignin is a promising candidate for biomass-derived compatibilizing agents for polypropylene-based CFRPs.

## **KEYWORDS**

Biomass / Carbon fiber-reinforced plastic / Compatibilizing agent / Lignin / Polypropylene / Tensile strength

## INTRODUCTION

Plant biomass, especially polysaccharides such as cellulose, has been highlighted as a resource for biofuels and bio-plastics over the last few decades.<sup>1, 2</sup> On the other hand, the applications of lignin, which is also a main component of plant biomass, have not been well developed, as opposed to the case of polysaccharides. There is currently a strong demand for further applications because a part of lignin is still considered waste, although lignin has been proposed as a water reducer for concrete<sup>3</sup> and as an aromatic chemical source such as vanillin.<sup>4</sup> <sup>5</sup> In this study, we paid special attention to the aromatic rings of lignin in order to find new and useful materials. Aromatic polymers are compatible with carbon materials such as carbon nanotubes via  $\pi$ - $\pi$  interactions.<sup>6</sup> Lignin has also been reported to be compatible with carbon nanotubes<sup>7, 8</sup> and graphene<sup>9</sup> due to similar interactions. We propose that lignin would also be compatible with CF and thus be applicable as a compatibilizing agent for CFRPs.

Polypropylene (PP) was selected as the matrix for CFRPs in this study. PP is a typical thermoplastic and has advantages such as good chemical and mechanical properties and good processibility.<sup>10</sup> Thus, PP is used in various applications, e.g., automobile bumpers.<sup>11</sup> PP is therefore expected to be a suitable matrix for CFRPs. However, its compatibility with CF is poor, thus hindering the preparation of a homogeneous composite. To improve the

compatibility, maleic anhydride-modified polypropylene (MAPP) is often used as a compatibilizing agent.<sup>12</sup> We propose lignin as a bio- and waste-derived alternative to MAPP.

We have performed a preliminary study on the potential of lignin as a compatibilizing agent using microbond test.<sup>13</sup> Microbond test<sup>14</sup> is a conventional method to investigate the interfacial shear strength between polymer matrices and CF, which is roughly related to their compatibility. The most valuable advantage of microbond test is that only a few hundred milligrams of the samples are needed for measurements, i.e., it is the best method for initial screening. We have synthesized ~200 mg of several kinds of alkylated lignin and optimized the structure of lignin as a compatibilizing agent. The lignin whose 70% of the OH groups were substituted with butyl groups (C<sub>4</sub> lignin, shown in Figure 1) showed the highest interfacial shear strength. The derivatization is necessary to efficiently increase the interfacial shear strength because raw lignin is immiscible with PP due to the differentiation of the polarities of PP and the raw lignin. In addition, the residual 30% OH groups in C<sub>4</sub> lignin was found to enhance the interfacial shear strength, presumably because of interaction with the OH groups of the CF existing as defects. We report the preparation of CFRP with the optimized C<sub>4</sub> lignin after synthesis on a several-gram scale, and the mechanical properties of the CFRPs. We also compare the properties of CFRP prepared with C<sub>4</sub> lignin with those of CFRP prepared with MAPP.

## **EXPERIMENTAL PROCEDURE**

### **Materials**

Vinyl butyrate (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was purchased and used as received. Lignin alkali and dimethyl sulfoxide (Sigma-Aldrich Co., LLC., St. Louis, MO, USA) were purchased and used as received. 1-Ethyl-3-methylimidazolium acetate (Iolitec Ionic liquids Technologies GmbH, Heilbronn, Germany) was purchased and used after drying. Methanol, acetone, and xylene (Kanto Chemical Co., Inc., Tokyo, Japan) were purchased and used as received. PP (Novatech FY-6; Japan Polypropylene Corporation, Tokyo, Japan) was purchased and used as received. CF (T700/12K; Toray Industries, Inc., Tokyo, Japan) was purchased and used after washing with acetone under sonication, followed by washing with methanol and water without sonication.

### **Synthesis of butylated lignin**

Butylated lignin was synthesized through a transesterification reaction as reported.<sup>13, 15</sup> Lignin alkali (3.00 g) was added in a solution (31.5 mL) containing 1-ethyl-3-methylimidazolium acetate and dimethyl sulfoxide (0.04:1.00, w/v) and stirred at 80 °C for 2 h with vinyl butyrate (2.79 g) under an Ar atmosphere. The butylated lignin was purified through dialysis with methanol. The structure was confirmed by <sup>1</sup>H NMR (Figure S1). The OH content of the

butylated lignin was determined by  $^{31}\text{P}$  NMR, as reported.<sup>16</sup> The OH content of the C<sub>4</sub> lignin used in this study was  $29\pm 3$  mol%. It has certain error because fine control of the OH content is very difficult. In addition, the conversion ratio of aliphatic OH and phenolic OH was  $25\pm 3$  and  $30\pm 3$  mol%, respectively.

### **Determination of flow beginning temperature**

A capillary rheometer (CFT-500EX, Shimadzu Corporation, Kyoto, Japan) was used to measure the flow beginning temperature. 1 g of the sample was loaded into the barrel and extruded with increasing temperature at 3 °C/min. The extrusion was carried out using a die (diameter: 1.0 mm, length: 10.0 mm).

### **Preparation of PP/CF/C<sub>4</sub> lignin composites**

PP (46.0 g) and C<sub>4</sub> lignin (1.5 g) were mixed and stirred in hot xylene (600 mL, 130 °C). Short CF (2.5 g) (diameter: 7 μm, average fiber length: 2 mm) was added to a PP/C<sub>4</sub> lignin mixture and stirred for 1 h. The PP/CF/C<sub>4</sub> lignin composite was dried in a fume hood for 1 day and in an oven at 55 °C for 5 h. The dried composite was cut (1 cm × 1 cm) and dried again under reduced pressure for 1 day. A twin-screw extruder (KZW20TW-45MG-NH; Technovel corporation, Osaka, Japan; L/D: 45, screw diameter: 20 mm, unidirectional rotation) was used

to prepare homogeneous PP/CF/C<sub>4</sub> lignin pellets with a pelletizer. The twin-screw extruder includes kneading elements, unlike the case in our previous report.<sup>13</sup> The extrusion temperature and screw speed were 180 °C and 150 rpm, respectively. PP, PP/CF, and PP/CF/MAPP samples were prepared using similar procedures.

### **Tensile and Bending tests**

Specimens for tensile tests and bending tests were molded with an injection molding machine (IMC-5705, Imoto Machinery Co., Ltd., Kyoto, Japan). The sample and mold temperatures were 180 °C and 60 °C, respectively. Dumbbell-shaped specimens (JIS K7161) and strip specimens (thickness: 2 mm, width: 10 mm, length: 75 mm) were prepared. The tensile strength and flexural strength of the samples were measured by tensile test and three-point bending test using a universal testing machine (AG-5kNX plus, Shimadzu Corporation, Kyoto, Japan). The tensile test was carried out at a speed of 5.0 mm/min with a distance of 58 mm between the two grips. The three-point bending test was carried out at a speed of 5.0 mm/min with a distance of 40 mm between the two supports. The tests were repeated seven times, and the data shown in the manuscript were averaged from the middle five values after excluding the maximum and minimum strength. The elastic modulus of the samples was calculated from the relation between tensile stress and tensile strain under a tensile stress of 10–20 N. The fracture surfaces of the specimens were investigated using scanning electron



microscopy (SEM, JSM-6510LV, JEOL Ltd., Tokyo, Japan) to evaluate the adhesion between PP and CF.

## **RESULTS AND DISCUSSION**

The flow beginning temperatures of the samples were determined. The temperatures of PP and PP/CF were 180 and 176 °C. Here, we do not think that CF addition affects the actual flow beginning temperature of PP. We used a capillary rheometer to determine flow beginning temperature, and the flow beginning temperature was measured by extruding the samples with continuously increasing temperature at 3 °C/min. Therefore, the thermal conductivity of the sample slightly affects the flow beginning temperature, i.e., samples which have high thermal conductivity show slightly low flow beginning temperature. CF has high thermal conductivity, and it may slightly decrease apparent flow beginning temperature of PP. The sample with C<sub>4</sub> lignin as a compatibilizing agent (PP/CF/C<sub>4</sub> lignin) showed a flow beginning temperature of 175 °C, indicating that C<sub>4</sub> lignin has very little effect on the flow beginning temperature. This is due to the amount of C<sub>4</sub> lignin added is only 3 wt% because the sample with 5 wt% showed the flow beginning temperature at 171 °C. MAPP did not affect the flow beginning temperature either (176 °C). From these results, we chose the temperature for molding to be 180 °C.

The tensile strength of pure PP was 35.1 MPa (Figure 2). The addition of CF slightly increased the tensile strength to 37.1 MPa because of the poor compatibility between PP and CF. Under SEM observation, CF did not disperse well in PP without compatibilizing agents, and consequently, around 70% of CFs aggregated (Figure S2a). PP/CF/C<sub>4</sub> lignin showed further increase in tensile strength to 40.2 MPa. It corresponds to that of MAPP (40.9 MPa), a well-known oil-derived compatibilizing agent for PP/CF composites. This increase was attributed to the compatibility of C<sub>4</sub> lignin with both PP and CF; presumably, hydrophobic interactions/Van der Waals interactions between PP and C<sub>4</sub> lignin, and  $\pi$ - $\pi$  interactions between CF and the aromatic rings of C<sub>4</sub> lignin. CF dispersed well in the PP/C<sub>4</sub> lignin composite, and no aggregates were found in the SEM images (Figure S2b). The trend observed in the tensile test is consistent with that observed in the microbond test<sup>13</sup>. The interfacial shear strength between CF and PP, PP/C<sub>4</sub> lignin, and PP/MAPP measured by microbond tests was 8.2, 17.2, and 18.3 MPa, respectively. This clearly suggests that increasing the interfacial shear strength between PP and CF is important and that C<sub>4</sub> lignin, consequently, works as a compatibilizing agent by improving the interfacial shear strength.

Figure 3 shows the elastic modulus of each sample. The elastic modulus of PP was 1631 MPa. The addition of CF increased the elastic modulus to 3223 MPa because CF is harder than PP. On the other hand, PP/CF/C<sub>4</sub> lignin showed an elastic modulus of 2534 MPa, which was lower than that of PP/CF. The elastic modulus of PP/CF/C<sub>4</sub> lignin was not much different

from that of PP/CF/MAPP (2807 MPa, CF is also well dispersed in the matrix). Elastic modulus generally increases by addition of compatibilizing agents unlike our case.<sup>17-19</sup> On the other hand, in some cases, the elastic modulus increases by addition of compatibilizing agents despite good dispersion of nanofillers although the mechanism is not described in the literature.<sup>18</sup> Further investigation is required to clarify the mechanism. Figure 4 shows the flexural strength of each sample. The flexural strength of PP and PP/CF was 50.9 and 51.1 MPa, respectively, showing that the addition of CF did not affect the flexural strength. The addition of C<sub>4</sub> lignin slightly improved the flexural strength (53.2 MPa), while the value was still less than that of PP/CF/MAPP (56.9 MPa).

The fracture surfaces of the samples were investigated by SEM after tensile test to monitor the adhesion between PP and CF. On the fracture surface of PP/CF, there was no adhesion and small voids between PP and CF were seen, as shown in Figure 5a, confirming the incompatibility between these components. In the PP/CF/C<sub>4</sub> lignin composite, PP/C<sub>4</sub> lignin matrix adheres to CF as well as PP/MAPP matrix (Figures 5b and c). The adhesion of the PP/C<sub>4</sub> lignin matrix to CF was not observed in all CFs, but the ratio of CFs covered by PP/C<sub>4</sub> lignin was similar to the ratio of CFs covered by PP/MAPP (~50%). This observation is consistent with the previous results of microbond test<sup>13</sup> and directly supports the mechanism underlying the increase in the tensile strength by the addition of C<sub>4</sub> lignin: the compatibility between PP and CF increased, consequently increasing the adhesion and the interfacial shear strength.

In the present method, C<sub>4</sub> lignin was first mixed with PP in hot xylene, followed by drying and kneading. C<sub>4</sub> lignin was only partially dissolved in hot xylene (dissolved part: 17 wt%) because lignin is a very complex natural polymer and does not have a homogeneous structure. Nonetheless, we used the mixture without removing the xylene-insoluble C<sub>4</sub> lignin because C<sub>4</sub> lignin has a softening point of 160 °C; therefore, the xylene-insoluble C<sub>4</sub> lignin is also expected to be homogeneous after kneading at 180 °C and have a positive effect on the tensile strength. To clarify this, we prepared PP/CF/C<sub>4</sub> lignin after removing the xylene-insoluble C<sub>4</sub> lignin by filtration. The composite showed a tensile strength of 38.2 MPa, which was lower than that of the unfiltered composite (40.2 MPa), as shown in Figure 6. This result suggests that xylene-insoluble lignin has a positive effect on the tensile strength. Furthermore, considering that the tensile strength of PP/CF was 37.1 MPa, the xylene-insoluble C<sub>4</sub> lignin made a greater contribution to the increase in tensile strength than did the xylene-soluble C<sub>4</sub> lignin.

We further investigated whether xylene-insoluble C<sub>4</sub> lignin was well dispersed in PP after kneading and molding at 180 °C. A specimen of PP/CF/C<sub>4</sub> lignin (without filtration) for tensile test was sonicated in methanol, which is a good solvent for C<sub>4</sub> lignin, for 3 h, and then, the resulting sample was subjected to SEM observations (Figure 7). A smooth sample surface was observed; there were no lignin aggregates or pores resulting from the removal of lignin.

This indicated that not only xylene-soluble C<sub>4</sub> lignin but also xylene-insoluble C<sub>4</sub> lignin is homogeneous in the matrix and should be an important factor in increasing the tensile strength.

## **CONCLUSION**

C<sub>4</sub> lignin, a derivative of a waste biomass polymer, was tested for use as a compatibilizing agent for polypropylene-based CFRP. C<sub>4</sub> lignin improved the tensile strength of the CFRP from 37.1 to 40.2 MPa, which corresponded to that of MAPP (40.9 MPa), a well-known oil-based compatibilizing agent. While PP/CF had the highest elastic modulus (3223 MPa), the value for PP/CF/C<sub>4</sub> lignin was similar (2534 MPa) to that of PP/CF/MAPP (2807 MPa). Good dispersion and adhesion of PP/C<sub>4</sub> lignin could be confirmed through SEM observations. C<sub>4</sub> lignin was categorized as xylene-soluble and xylene-insoluble C<sub>4</sub> lignin, and both contributed to the increase in tensile strength. From these results, it is confirmed that C<sub>4</sub> lignin is applicable as an alternative to the current compatibilizing agent, MAPP.

## **CONFLICT OF INTEREST**

The authors declare no conflict of interest.

## **ACKNOWLEDGEMENTS**

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## REFERENCES

- 1 Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). *Prog. Polym. Sci.* 2008;33:820–52.
- 2 Ragauskas J, Williams CK, Davison HB, Britovsek G, Cairney J, Eckert AC, Frederick Jr. JW, Hallett PJ, Leak JD, Liotta LC, Mielenz RJ, Murphy R, Templer R, Tschaplinski T. The Path Forward for Biofuels and Biomaterials. *Science* 2006;311:484–89.
- 3 Uchikawa H, Sawaki D, Hanehara, S. Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste. *Cem. Concr. Res.* 1995;25:353–64.
- 4 Mialon L, Pemba GA, Miller AS. Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid. *Green Chem.* 2010;12:1704–06.

- 5 Borges da Silva AE, Zabkova M, Araujo DJ, Cateto AC, Barreiro FM, Belgacem NM, Rodrigues EA. An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin. *Chem. Eng. Res. Des.* 2009;87:1276–92.
- 6 Umeyama T, Kadota N, Tezuka N, Matano Y, Imahori H. Photoinduced energy transfer in composites of poly[(*p*-phenylene-1,2-vinylene)-*co*-(*p*-phenylene-1,1-vinylidene)] and single-walled carbon nanotubes. *Chem. Phys. Lett.* 2007;444:263–67.
- 7 Teng YN, Dallmeyer I, Kadla, FJ. Effect of Softwood Kraft Lignin Fractionation on the Dispersion of Multiwalled Carbon Nanotubes. *Ind. Eng. Chem. Res.* 2013;52:6311–17.
- 8 Liu Y, Gao L, Sun J. Noncovalent Functionalization of Carbon Nanotubes with Sodium Lignosulfonate and Subsequent Quantum Dot Decoration. *J. Phys. Chem. C* 2007;111:1223–29.
- 9 Yang Q, Pan X, Huang X, Li K. Fabrication of High-Concentration and Stable Aqueous Suspensions of Graphene Nanosheets by Noncovalent Functionalization with Lignin and Cellulose Derivatives. *J. Phys. Chem. C* 2010;114:3811–16.
- 10 Valentini L, Biagiotti J, Kenny MJ, Santucci S. Morphological characterization of single-walled carbon nanotube-PP composites. *Compos. Sci. Technol.* 2003;3:1149–53.
- 11 Lloyd MS, Vave B. Life Cycle Economic and Environmental Implications of Using Nanocomposites in Automobiles. *Environ. Sci. Technol.* 2003;37:3458–66.
- 12 Karsli GN, Aytac A. Effects of maleated polypropylene on the morphology, thermal and mechanical properties of short carbon fiber reinforced polypropylene composites. *Mater. Des.*

2011;32:4069–73.

- 13 Sakai H, Kuroda K, Muroyama S, Tsukegi T, Kakuchi R, Takada K, Hata A, Kojima R, Ogoshi T, Omichi M, Ninomiya K, Takahashi K. Alkylated alkali lignin for compatibilizing agents of carbon fiber reinforced plastics with polypropylene. *Polym. J.* 2018;50:281–84.
- 14 Wong HK, Mohammed SD, Pickering JS, Brooks R. Effect of coupling agents on reinforcing potential of recycled carbon fiber for polypropylene composite. *Compos. Sci. Technol.* 2012;72:835–44.
- 15 Kakuchi R, Yamaguchi M, Endo T, Shibata Y, Ninomiya K, Ikai T, Maeda K, Takahashi K. Efficient and rapid direct transesterification reactions of cellulose with isopropenyl acetate in ionic liquids. *RSC Adv.* 2015;88:72071–74.
- 16 Granata A, Argyropoulos DS. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins. *J. Agric. Food Chem.* 1995;43:1538–44.
- 17 Kada D, Koubaa A, Tabak G, Migneault S, Garnier B, Boudenne A. Tensile Properties, Thermal Conductivity, and Thermal Stability of Short Carbon Fiber Reinforced Polypropylene Composites. *Polym. Compos.* (2016) DOI: 10.1002/pc.24093
- 18 Lin J-H, Huang C-L, Liu C-F, Chen C-K, Lin Z-I, Lou C-W. Polypropylene/Short Glass Fibers Composites: Effects of Coupling Agents on Mechanical Properties, Thermal Behaviors, and Morphology, *Materials* 2015;8:8279–91.



- 19 Bhaskar J, Haq S, Yadaw SB. Evaluation and testing of mechanical properties of wood plastic composite. *J. Thermoplastic Compos. Mater.* 2011;25:391–401.

## **Titles and legends to figures**

**Figure 1** A structure of C<sub>4</sub> lignin.

**Figure 2** Tensile strength of PP, PP/CF, PP/CF/C<sub>4</sub> lignin and PP/CF/MAPP.

**Figure 3** Elastic modulus of PP, PP/CF, PP/CF/C<sub>4</sub> lignin and PP/CF/MAPP.

**Figure 4** Flexural strength of PP, PP/CF, PP/CF/C<sub>4</sub> lignin and PP/CF/MAPP.

**Figure 5** SEM images of the fracture surface of (a) PP/CF, (b) PP/CF/C<sub>4</sub> lignin, and (c) PP/CF/MAPP after tensile test. Magnification ratio was appropriately adjusted to show clear images.

**Figure 6** Tensile strength of CFRP with only xylene-soluble C<sub>4</sub> lignin as compatibilizing agent. Tensile strength of CFRP with entire lignin and without lignin is shown for comparison.

**Figure 7** A SEM image of the surface of CFRP with C<sub>4</sub> lignin as a compatibilizing agent.