NOTE

Alkylated alkali lignin for compatibilizing agents of carbon fiber-reinforced plastics with polypropylene

Hiroki Sakai[1] · Kosuke Kuroda[1] · Shiori Muroyama[1] · Takayuki Tsukegi[2] · Ryohei Kakuchi[1] · Kenji Takada[1] ·
Ayano Hata[1] · Ryosuke Kojima[3] · Tomoki Ogoshi[3] · Masaaki Omichi[1] · Kazuaki Ninomiya[4] · Kenji Takahashi[1]

Abstract

As an alternative to petroleum-based compatibilizing agents, we developed lignin derivatives for compatibilizing agents of carbon fiber-reinforced plastics that have thermoplasticity. In this study, alkyl chains were introduced into alkali lignin at various ratios to optimize the compatibility of the lignin derivatives with both polypropylene and carbon fiber. The interfacial shear strength between the two materials was improved from 8.2 to 17.2 MPa by mixing with the optimized lignin derivative. The value is comparable to that achieved with a typical petroleum-based compatibilizing agent (18.3 MPa).

Introduction

Polysaccharides derived from plant biomass have been highlighted as resources of ethanol, material building blocks, and plastics [1, 2]. Although lignin is also known to be a major component of plant biomass, its applications have not been well developed. Lignin has been suggested for use in various fields, such as a water reducer for concrete [3] and as an aromatic chemical source, e.g., vanillin [4, 5], and strong demand exists for further valuable applications.

Hiroki Sakai and Kosuke Kuroda contributed equally to this work.

Electronic supplementary material The online version of this article (https://doi.org/10.1038/s41428-017-0009-3) contains supplementary material, which is available to authorized users.

✉ Kosuke Kuroda
    kkuroda@staff.kanazawa-u.ac.jp

✉ Kenji Takahashi
    ktkenji@staff.kanazawa-u.ac.jp

1   Division of Natural System, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

2   Innovative Composite Center, Kanazawa Institute of Technology, Yatsukaho, Kanazawa 924-0838, Japan

3   Division of Material Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

4   Institute for Frontier Science Initiative, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

We focused on the aromatic rings of lignin to develop useful materials. Aromatic polymers are known to be compatible with carbon nanotubes via $\pi-\pi$ interactions [6], and lignin is also compatible with carbon materials such as carbon nanotubes [7, 8] and graphene [9], exhibiting similar interactions. Because lignin is, therefore, expected to be compatible with carbon fiber (CF), it was applied as a compatibilizing agent of carbon fiber-reinforced plastics (CFRPs) in this study.

We selected polypropylene (PP) as a matrix of the CFRP in this study. PP is a typical thermoplastic used for a range of materials applications, such as in automobile bumpers [10], because of its good chemical and mechanical properties and good processibility [11]. PP, therefore, appears to be a suitable polymer for CFRPs. However, the compatibility of CF and PP is known to be poor, which prevents the preparation of a homogeneous composite. Maleic-anhydride-modified polypropylene (MAPP) is used as a compatibilizing agent [12], but it is a petroleum-based polymer. In the present study, we proposed using lignin as an alternative to MAPP.

Experimental procedure

Materials

Alkali lignin and dimethyl sulfoxide were purchased from Sigma-Aldrich Co., Llc. (St. Louis, MO, USA) and used as received. 1-Ethyl-3-methylimidazolium acetate was purchased

from Iolitec Ionic Liquids Technologies GmbH (Heilbronn, Germany) and used after drying. Isopropenyl acetate, vinyl butyrate, vinyl hexanoate, vinyl decanoate, and vinyl palmitate were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received. Methanol and xylene were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and used as received. PP (Novatech FY-6) was purchased from the Japan Polypropylene Corporation (Tokyo, Japan) and used as received. Carbon fiber (T700/12 K) was purchased from Toray Industries, Inc. (Tokyo, Japan) and used after washing with acetone under sonication, followed by washing with methanol and water without sonication.

Synthesis of lignin derivatives

Lignin derivatives were synthesized through a transesterification reaction [13]. Alkali lignin (200 mg) was dissolved in 2.4 mL of a mixed solution of dimethyl sulfoxide/1-ethyl-3-methylimidazolium acetate (1/0.04, v/w) and heated to 80 °C for 16 h with an excess amount of ester-donating agents under an Ar atmosphere. The obtained lignin derivatives ($n = 2$–16; C_2–C_{16} lignin, see Fig. 1) were purified through dialysis in methanol. The yields of C_2, C_4, C_6, C_{10}, and C_{16} lignin were 75%, 77%, 59%, 71%, and 73%, respectively. The OH content of the lignin derivatives was measured by ^{31}P NMR as previously reported [14]. The OH contents of C_4, C_6, C_{10} and C_{16} lignin were 10%, 11%, 13%, and 11%, respectively, unless otherwise noted, while that of C_2 lignin could not be determined because it was not soluble in any solvents. Lignin derivatives containing greater amounts of hydroxyl groups were synthesized by reducing the reaction time.

Preparing composites of PP and lignin derivatives and their microscopic observation

PP (2.0 g) and lignin derivatives (60 mg) were dissolved in xylene (100 mL) at 130 °C. Composite pellets were prepared by solution casting, followed by kneading at 180 °C (MC5, DSM Xplore Instruments BV, Sittard, Netherlands). Microscopy images were captured using an ECLIPSE 50i microscope (Nikon Instruments Inc., Tokyo, Japan). A composite of PP and MAPP was prepared by the same method.
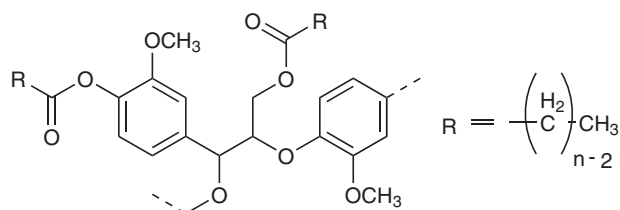

Fig. 1 Structures of lignin derivatives ($n = 2, 4, 6, 10, 16$; C_2, C_4, C_6, C_{10}, C_{16} lignin)

Microbond test

A microbond test [15] was performed using a MODEL HM410 (Tohei Sangyo Co., Ltd., Fukushima, Japan) to determine the interfacial shear strength (IFFS) between CF and PP with and without lignin derivatives. Microdroplets with a diameter of ~80 μm were selected, and a loading rate of 2.0 μm/s was applied to obtain the interfacial debonding load. The IFFS was an average of ≥ 30 measurements.

Results and discussion

The miscibility of alkali lignin and PP was investigated as a preliminary study. After alkali lignin (3 wt%) and PP were kneaded, the composite was examined under an optical microscope (Fig. 2). Agglomerates of alkali lignin (brown parts) and pure PP (transparent parts) were observed; they were clearly immiscible. This immiscibility was due to the different polarities of alkali lignin and PP: alkali lignin has hydroxyl groups in addition to aromatic rings and, therefore, is partly polar, while PP is composed of only hydrocarbons and is completely nonpolar.

We capped the hydroxyl groups of alkali lignin by acetylation to decrease the polarity of the alkali lignin (C_2 lignin). Acylation of the alkali lignin was performed using a method we have developed involving the use of an ionic liquid as both a solvent and catalyst [13]. The C_2 lignin was also observed under an optical microscope after being kneaded together with PP (see Fig. 2). Agglomerates of C_2 lignin and pure PP were clearly observed; they were
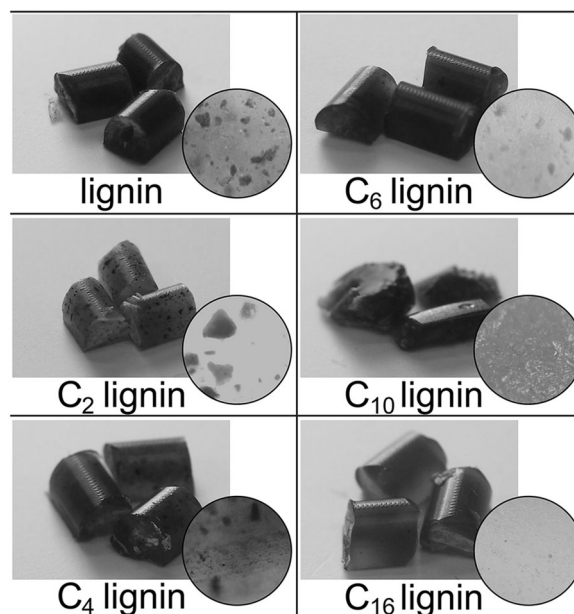

Fig. 2 Macroscopic and microscopic images of composites of PP and alkali lignin or lignin derivatives (Color figure online)

immiscible. This result indicated that capping the hydroxyl groups is not sufficient to make it miscible with PP.

To increase the interaction between alkali lignin and PP, the alkyl chain of the acyl group was extended (C_4, C_6, C_{10}, and C_{16} lignin, see Fig. 1), and the miscibility with PP was investigated. C_4, C_6, and C_{10} lignins were partly miscible, and C_{16} lignin was completely miscible, at least as indicated by optical microscopy. The results showed that alkali lignin can be miscible with PP, at least partly, by capping the hydroxyl groups of alkali lignin with acyl groups that have a hydrocarbon chain length of at least four.

The C_4–C_{16} lignins were subjected to a microbond test to investigate their compatibilizability. The test revealed the IFSS between the CF and PP/lignin derivative composites (lignin derivative content in PP: 3 wt%). The IFSS between the CF and PP without lignin derivatives was 8.2 MPa (Fig. 3). The IFSS values were 14.1, 13.4, and 12.3 MPa when adding C_4, C_6, and C_{10} lignin, respectively. This result clearly demonstrated a considerable increase in the IFSS. Moreover, these values did not differ greatly from the strength observed with MAPP, a petroleum-derived compatibilizing agent (18.3 MPa). There was no increase in IFSS when adding C_{16} lignin (8.3 MPa). We focused on the miscibility of PP and C_{16} lignin at the molecular level in determining the reasons for these findings by using differential scanning calorimetry. Supplementary Fig. S1 presents the results. Concerning the composites of PP and C_4–C_{10} lignins, a melting peak was not observed at the melting point of pure PP (164 °C) but was observed at a lower temperature. This finding suggests that all PP interacted with the lignin derivatives, while some agglomerates of the lignin derivatives were observed by optical microscopy. On the other hand, the melting peak was observed at the melting point of pure PP for the PP/C_{16} lignin composite, suggesting that a portion of PP does not interact with C_{16} lignin, whereas agglomerates of the C_{16} lignin were not

observed via optical microscopy. The immiscibility of PP and the C_{16} lignin may be attributed to aggregation of the C_{16} lignin in PP at the molecular level, which is caused by interactions between C_{16} lignin molecules. It is noted that C_2 lignin was also subjected to a microbond test, although C_2 lignin is not miscible with PP. It was confirmed that the IFFS did not increase (8.4 MPa). Based on these results, the miscibility of alkali lignin and PP at both the micro- and molecular levels is a key factor in the suitable design of lignin derivatives, and C_4–C_{10} lignins were found to be suitable lignin derivatives as compatibilizing agents.

Exploiting the hydrogen bond between lignin derivatives and CF is one method for increasing IFSS because CF contains a hydroxyl group and carboxyl group as defects (Fig. S2). The residual OH content increased stepwise to 50%, and the IFSS between CF and PP with lignin derivatives was measured (Fig. 4). The experiment was conducted with C_4 lignin because it showed the highest IFSS among the lignin derivatives (see Fig. 3). When the residual OH content was 10% (same sample shown in Fig. 3), the IFSS was 14.2 MPa. While the IFSS between CF and C_4 lignin with a residual OH content of 21% was similar to that of the composite containing 10% OH (14.1 MPa), the IFSS of the composite containing 28% OH increased considerably to 17.2 MPa. Increasing the OH content of alkali lignin was confirmed to be an effective way of increasing the IFSS. On the other hand, the IFSS was 14.1 MPa when the residual OH content was 50%. This result may be explained by a decrease in CH–π interactions [16] between alkyl chains in C_4 lignin and the CF surface. Based on these results, the IFSS between PP and CF can be improved by controlling the OH content of the lignin derivatives, considering the effects of the hydrogen bond. The highest IFSS obtained in this study (17.2 MPa; residual OH content is 28%) was comparable to the IFSS of the composite
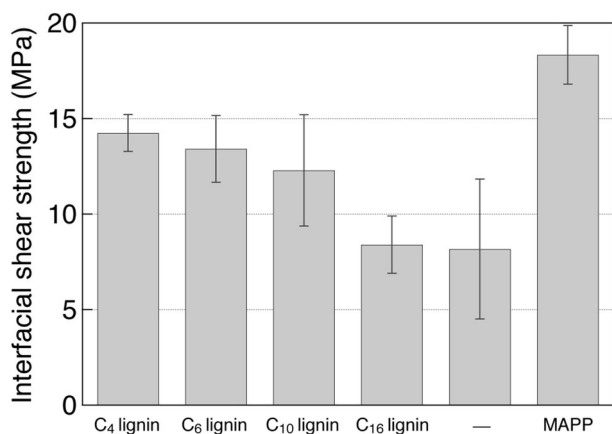

Fig. 3 IFSS between CF and PP with and without lignin derivatives. IFSS between CF and PP with MAPP (3 wt%) is also shown as a reference
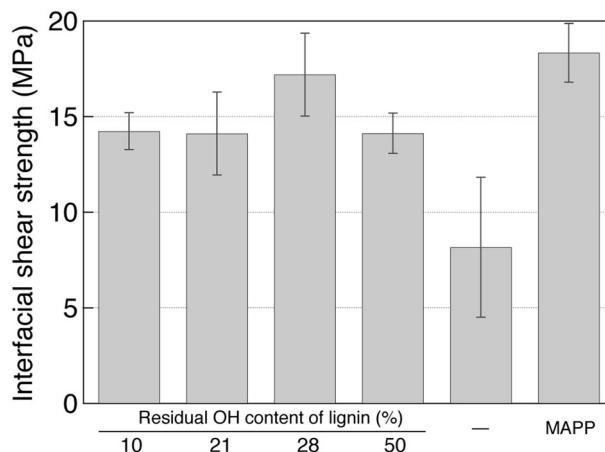

Fig. 4 IFSS between CF and PP with C_4 lignin whose residual OH content was 10–50%. IFSS between CF and PP with and without MAPP (3 wt%) is also shown as a reference

containing MAPP (18.3 MPa). The lignin derivative is thus a strong candidate for substituting for MAPP, which is made from petroleum.

Conclusion

Alkali lignin derivatives were developed to serve as compatibilizing agents of CFRPs. While alkali lignin and C_2 lignin were not miscible with PP, C_4-, C_6-, and C_{10} lignins were partly miscible and C_{16} lignin was completely miscible, as indicated by optical microscopy. The IFSS between CF and PP increased from 8.2 to 14.1, 13.4, and 12.3 MPa when adding C_4, C_6, and C_{10} lignin, respectively. The IFSS was further improved to 17.2 MPa by increasing the OH content in C_4 lignin. The highest IFSS with C_4 lignin was comparable to that with MAPP (18.3 MPa), suggesting that C_4 lignin is a viable candidate for substituting for petroleum-based compatibilizing agents.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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 JW Jr, Hallett PJ, Leak JD, Liotta LC, Mielenz RJ, Murphy R, Templer R, Tschaplinski T. The path forward for biofuels and biomaterials. Science. 2006;311:484–9.

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;12:1704–6.

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-1,1vinylidene)] and single-walled carbon nanotubes. Chem Phys Lett. 2007;444:263–7.

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;52:6311–7.

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;111:1223–9.

9 Yang Q, Pan X, Huang X, Li K. Fabrication of high-concentration and stable aqueous suspensions of graphene nanosheets by non-covalent functionalization with lignin and cellulose derivatives. J Phys Chem C. 2010;114:3811–6.

10 LloyL MS, Vave B. Life cycle economic and environmental implications of using nanocomposites in automobiles. Environ Sci Technol. 2003;37:3458–66.

11 Valentini L, Biagiotti J, Kenny MJ, Santucci S. Morphological characterization of single-walled carbon nanotube-PP composites. Compos Sci Technol. 2003;63:1149–53.

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 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;88:72071–4.

14 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.

15 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.

16 Gupta J, Keddie JD, Wan C, Haddleton MD, McNally T. Functionalisation of MWCNTs with poly(lauryl acrylate) polymerised by Cu(0)-mediated and RAFT methods. Polym Chem. 2016;7:3884–96.