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

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RUNNING HEAD

Lignin derivatives for compatibilizing agents

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 to alkali lignin at various ratios to optimize the compatibility of the lignin derivatives with both polypropylene and carbon fiber. Interfacial shear strength between both materials was improved from 8.2 to 17.2 MPa by mixing with the optimized lignin derivative. The value was comparable to that achieved with a typical petroleum-based compatibilizing agent (18.3 MPa).

KEYWORDS

Carbon fiber reinforced plastic / Compatibilizing agent / Interfacial shear strength / Lignin / Microbond test / Polypropylene

INTRODUCTION

Polysaccharides derived from plant biomass have been highlighted as resources of ethanol, 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 use has been suggested in few fields, such as water reducers for concrete[3] and aromatic chemical sources, e.g. vanillin,[4,5] and

strong demand exists for further valuable applications. We focused on the aromatic rings of lignin to develop useful materials. Aromatic polymers are known to be compatible with carbon nanotube via π-π interaction,[6] and lignin is also compatible with carbon materials such as carbon nanotube[7,8] and graphene,[9] with similar interaction. Since 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 material applications, such as in automobile bumpers[10], because of its good chemical and mechanical properties, and good processibility.[11] PP therefore seems to be a suitable polymer for CFRPs. However, the compatibility of CF and PP is known to be poor, which prevents 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 propose 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 (T700/12K) 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 transesterification reaction.[13] Alkali lignin (200 mg) was dissolved in 2.4 mL of dimethyl sulfoxide/1-ethyl-3-methylimidazolium acetate (1/0.04, v/w) mixed solution and heated at 80 °C for 16 hours 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 Figure 1) were purified through dialysis in methanol. The yield of C_2, C_4, C_6, C_{10}, and C_{16} lignin was 75, 77, 59, 71, and 73%, respectively. The OH content of the lignin derivatives was measured with ^{31}P NMR as reported.[14] The OH content of C_4, C_6, C_{10} and C_{16} lignin was 10, 11, 13 and 11%, respectively, while C_2 lignin could not be determined because it was not soluble in any solvents. Lignin derivatives that had higher amounts of hydroxyl groups were synthesized through reduction of the reaction time.

Preparing composites of PP and lignin derivatives and its microscopic observation

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

Microbond test

A microbond test[15] was performed using 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 subjected to optical microscopy (Figure 2). Agglomerates of alkali lignin (brown parts) and pure PP (transparent parts) were observed; they

were clearly immiscible. This is 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 hydrocarbon and is totally apolar.

We capped the hydroxyl groups of alkali lignin by acetylation to decrease polarity of the alkali lignin (C_2 lignin). Acylation of the alkali lignin was performed using a method we have developed with an ionic liquid used as both a solvent and catalyst.[13] The C_2 lignin was also subjected to optical microscopy after being kneaded together with PP (see Figure 2). Agglomerates of C_2 lignin and pure PP were clearly observed; they were immiscible. This result indicated that capping of hydroxyl groups is not sufficient to be miscible with PP.

To increase 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 Figure 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 viewed by optical microscopy. The results showed that alkali lignin can be miscible with PP, at least partly, through capping hydroxyl groups of alkali lignin with acyl groups that have a hydrocarbon chain length of four and more.

The C_4–C_{16} lignins were subjected to a microbond test to investigate their compatibilizability. The test revealed interfacial shear strength (IFSS) between CF and PP/lignin derivative composites (lignin derivative content in PP: 3 wt%). The IFSS between CF and PP without lignin derivatives was 8.2 MPa (Figure 3). The IFSS was 14.1, 13.4, and 12.3 MPa when adding C_4, C_6, and C_{10} lignin, respectively. This clearly showed a considerable increase of IFSS. These values did not much differ from that found 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 discussing the reasons, by using differential scanning calorimetry. Figure S1 shows 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 suggests that all PP interacted with the lignin derivatives, while some agglomerates of the lignin derivatives were observed in optical microscopy. On the other hand, the melting peak was observed at the melting point of pure PP with regard to the PP/C_{16} lignin composite, suggesting a part of PP does not interact with the 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 interaction between C_{16} lignin molecules. It is noted that C_2 lignin was also subjected to a microbond test although C_2 lignin does not miscible with PP. It is confirmed that there was no increase in the IFFS (8.4 MPa). From these results, the miscibility of alkali lignin and PP at both micro- and molecular levels are key factors underlying 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 has a hydroxyl group and carboxyl group as defects (Figure S2). The residual OH content increased stepwise to 50%, and the IFSS between CF and PP with lignin derivatives was measured (Figure 4). The experiment was conducted with C_4 lignin because it showed the highest IFSS among lignin derivatives (see Figure 3). When the residual OH content was 10% (same sample shown in Figure 3), the IFSS was 14.2 MPa. While the IFSS between CF and C_4 lignin with the residual OH content of 21% was similar to that with 10% (14.1 MPa), that with 28% considerably increased to 17.2 MPa. Increase of the OH content of alkali lignin was

confirmed as effective in increasing IFSS. On the other hand, the IFSS was 14.1 MPa when residual OH content was 50%. This may be explained by a decrease of CH-π interaction[16] between alkyl chains in C_4 lignin and CF surface. From these results, the IFSS between PP and CF can be improved by controlling the OH content of the lignin derivatives, considering the hydrogen bond. The highest IFSS in this study (17.2 MPa; residual OH content is 28%) was comparable to the IFSS with MAPP (18.3 MPa). The lignin derivative is, thus, a strong candidate as an alternative to MAPP, being made from petroleum.

CONCLUSION

Alkali lignin derivatives were developed for 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 seen in 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 C_4 lignin is a clearly viable candidate among alternatives in petroleum-based compatibilizing agents.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

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Titles and legends to figures

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

Figure 2 Macroscopic and microscopic images of composites of PP and alkali lignin or lignin derivatives.

Figure 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.

Figure 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.

DISPLAY ITEMS (Figures)

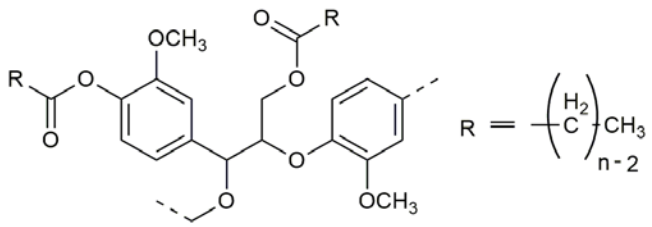

Figure 1

Figure 2

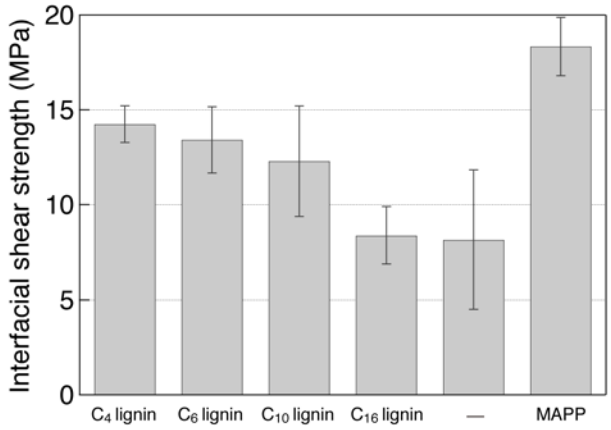

Figure 3

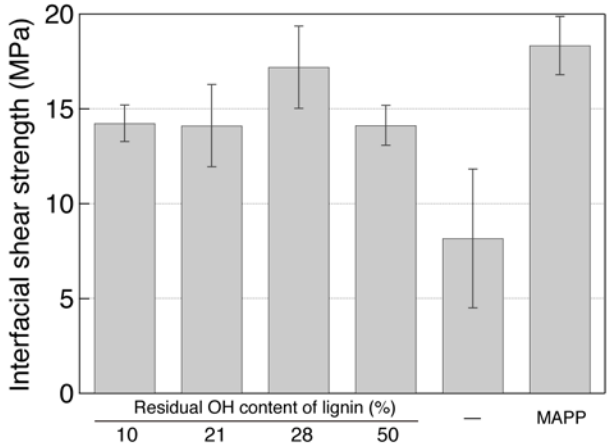

Figure 4