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Cellulose esters as compatibilizers in wood/poly(lactic acid) composite

Received: July 26, 2006 / Accepted: July 26, 2007 / Published online: October 7, 2007

Abstract One of the important issues relevant to wood/plastic composite molding is the compatibility between hydrophilic wood and hydrophobic plastic. Polyolefins modified with maleic anhydride, which have been frequently used for wood and polyolefin composites, are not effective for poly(lactic acid) composites. Because compounds with both hydrophilic and hydrophobic groups are potential compatibilizers, cellulose esters of several carboxylic acids, RCOO-cellulose ($R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_5\text{H}_{11}, \text{C}_{11}\text{H}_{23}$), were synthesized and their effects as compatibilizers of wood/poly(lactic acid) composites (WPLC) were examined in this study. The mechanical properties of WPLC were improved with a small amount of added cellulose esters, especially cellulose butyrate or cellulose valerate. The relevant effect of added cellulose esters on the thermal properties of wood/PLA composite was analyzed by measuring dynamic viscoelasticity.

Key words WPC · Wood/plastic composite · Cellulose ester · Compatibilizer · Poly(lactic acid)

Introduction

The compatibility of the natural environment with human life is an important issue, and the establishment of a sustainable recycling society with low environmental stress is crucial for that compatibility to occur. In particular, the development of materials that can replace fossil resources is necessary. Wood/plastic composites (WPC) have attracted

attention in this context, because WPC are regarded as an effective means of using waste wood and/or plastic. Furthermore, wood acquires one of the important characteristics of plastic, that of easy molding, in WPC.^{1,2}

When hydrophilic wood and hydrophobic plastic are mixed, their interfacial adhesion is not good because of their poor compatibility, leading to poor mechanical properties of the composite. To improve their compatibility, various compounds have been tested and reported so far; in general, a small amount of polyolefin modified with maleic anhydride (MAPO) was found to be an effective compatibilizer, and many kinds of maleic anhydride-modified polyethylene (MAPE) or polypropylene (MAPP) are now commercially available.^{1–5} As the mechanism of the compatibilizing effect, Qui et al.⁶ reported covalent interfacial interaction in a composite of cellulose prepared in the presence of MAPP by novel mechanochemical mixing. This composite showed an ester peak in the Fourier transform-infrared (FT-IR) spectra. In addition, there exists a patent that describes poly(lactic acid) (PLA) modified with maleic anhydride (MAPLA), which is claimed to improve the properties of wood/PLA composite by its addition.⁷ However, Plackett⁸ reported that the addition of MAPLA decreased the tensile strength of compression-molded jute/PLA composite. Huda et al.⁹ investigated the effect of MAPP in wood/PLA composite (WPLC), and reported that the modulus of rupture (MOR) of wood/PLA composite decreased by the addition of 5% (w/w) MAPP. In addition, the modulus of elasticity (MOE) and notched Izod impact strength were not improved.⁹ We also confirmed the effect that MAPP (Toyotach H-1100P, Toyokasei) effectively improved the MOR and water resistance of wood/PP composite; in particular, H-1100P increased MOR more than three times, although the MOR of a WPLC did not increase so much by the addition of H-1100P.^{3,4} In addition to the concern that MAPO is a fossil product, this material is not a very effective compatibilizer as a PLA composite. Many scientists have already studied compatibilizers to replace MAPO. Geng et al.¹⁰ reported a commercial paper wet-strength agent (Kymene 557H, Hercules) and stearic anhydride as a compatibilizer for wood/high-density PE composites. This combination

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Part of this report was presented at the 56th Annual Meeting of Japan Wood Research Society, Akita, August 2006 and the 9th International Conference on Frontiers of Polymers and Advanced Materials, Cracow, Poland, July, 2007

demonstrated almost the same degree of effect as MAPP. Marcovich et al.¹¹ studied the effect of chemically modified wood flour on the properties of composites using unsaturated polyester as the plastic. They found that composites prepared with MA-treated wood flour had better performance under compressive loads. These results suggest that derivatives of natural products might be promising compatibilizers of WPC. In this work, we focused on cellulose, which is a major component of wood, synthesized cellulose esters of several carboxylic acids, and examined their compatibilizing abilities for WPLC. It is notable that this composite is made from completely bio-based materials.

Experimental

Materials

Lignocel C300G, a softwood flour prepared mainly from spruce (*Picea* spp.) with an average particle size of 300 μm (100 mesh pass 14.6%, 60–100 mesh 17.8%, 20–60 mesh 57.7%, 10–20 mesh 9.9%, Rettenmeyer) was used as the wood raw material and a PLA (PL002, Kuraray) was used as the thermoplastic polymer for WPLC preparation. Wood cellulose fiber (Arbocel BE600-10, average size 18 μm long \times 15 μm diameter; Rettenmeyer) was used as the raw material for the synthesis of cellulose esters. Acetic anhydride (97.0%; Nacalai Tesque), propionic acid (99.0%; Kanto Chemical), butanoic acid (98%; Merck), valeric acid (98%; Merck), hexanoic acid (99%; Aldrich), lauric acid (98%; Aldrich) were used for the synthesis of cellulose esters. Commercial cellulose acetates [Wako C2C, degree of substitution (DS) 1.5; Daicel, DS 2.4] were also used.

Instruments and procedure

FT-IR spectra were measured with a Shimadzu FT-IR 8200D instrument using the KBr tablet method. A Super Mixer (Kawata), a hot press (Shinto Kinzoku Kogyo Seisakujo; Oil pressure hot press Shinto type F), and a bending machine (Shinko Tushin; TCM500) were used for preparation of test samples and analyses.

Synthesis of cellulose carboxylates

C2C (DS 2.8) was synthesized according to the literature¹² and DS was determined by FT-IR analysis.^{13,14} Syntheses of other cellulose esters, such as propionate (C3C), butyrate (C4C), valerate (C5C), capurate (C6C), and laurate (C12C) were carried out as follows.

Carboxylic acid (8 equivalents) was put in a flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel. Thionyl chloride (8 equivalents) was added dropwise to the flask at room temperature. The mixture was then warmed up to 78°C and stirred at about 130 rpm for 4 h. Pyridine (32 equivalents) was added dropwise to the mixture and the solution was stirred for 1 h. Cellulose fiber was then added to the flask and stirring was

continued at 78°C for 20 h. The product was isolated by filtration, washed with ethanol four times, dried, and analyzed by FT-IR spectroscopy. DS values were estimated by weight increase using the following equation:

$$DS = \frac{\frac{W_p \times 162}{W_r}}{M_{wA} - 17}$$

where, W_p , W_r , and M_{wA} represent the weight of products, weight of raw cellulose, and the molecular weight of carboxylic acid, respectively.

WPLC molding

C300G was dried to a moisture content of 3%–4% in an oven at about 60°C for more than 24 h before use. A cellulose ester, PL002, and dried C300G were blended using a Henschel-type mixer (Super Mixer, Kawata). Mixing was carried out at a blade speed of 1500 rpm and continued until the temperature of the mixture reached 180°C to give an agglomerated product. Agglomerates of C300G/PL002 (80/20) and C300G/PL002/Arbocel (80/20/2) were also prepared similarly for comparison. The prepared agglomerate (24 g) was placed in a mold of 80 \times 100 mm, and compression molded at 13 MPa at 200°C for 15 min to make a 2.5-mm-thick board. Four WPLC boards were prepared for the test.

Mechanical strength and water resistance

The mechanical properties of the WPLC board were evaluated in accordance with JIS A5741 by the three-point static bending test with a loading speed of 5 mm/min. Twelve specimens of 25 \times 95 \times 2.5 mm were used to evaluate MOR and MOE. The results of the mechanical properties are shown divided by the density (d). The water resistance of the composite was determined by measuring 12 specimens of about 25 \times 45 \times 2.5 mm for water absorption (WA), thickness swelling (TS), and linear expansion (LE) after immersion of the board in water at 23° \pm 2°C for 1, 2, 3, and 24 h.

Dynamic viscoelasticity test

To investigate the thermal properties of WPLCs, dynamic viscoelasticity was measured with a Rheovibron DDV-25FP instrument (Orientec) at 1 Hz in temperature ranges from 0° to 150°C with a programming rate of 2.0°C/min. The size of the specimen was about 5.0 \times 60 \times 2.5 mm.

Results and discussion

FT-IR of cellulose ester

FT-IR spectra of Arbocel, C2C (DS 1.5, 2.4, or 2.8), and other cellulose esters are shown in Fig. 1. All cellulose esters

have peaks due to carbonyl groups of esters at around 1750cm^{-1} . The decrease of hydroxyl peaks (over 3000cm^{-1}) can be monitored for all cellulose esters through an esterification reaction that can be accepted as reflecting the DS below. Furthermore, all cellulose esters show strong C–H stretching peaks due to a methyl and/or methylene group(s) ($2850\text{--}2990\text{cm}^{-1}$) of the acyl part.

DS values and yields of cellulose esters

DS values and product yields are summarized in Table 1. The DS values of cellulose esters were calculated from the product yield except for C2Cs (DS 1.5, 2.4, or 2.8), which were estimated based on the linear relationship of product yield with $\nu_{\text{C=O}}/\nu_{\text{OH}}$ absorbance peak ratios of FT-IR

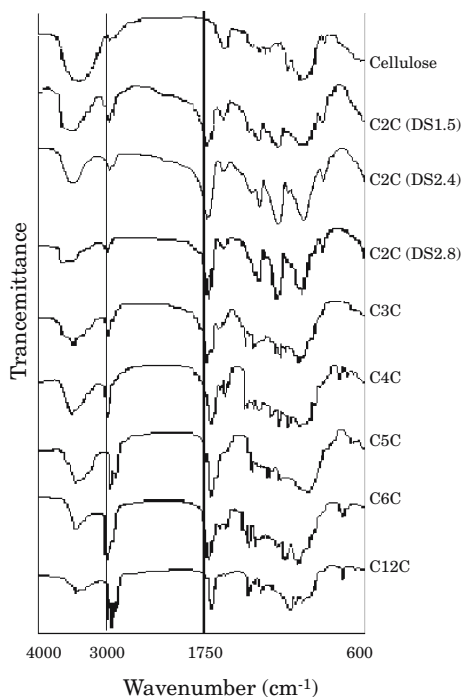
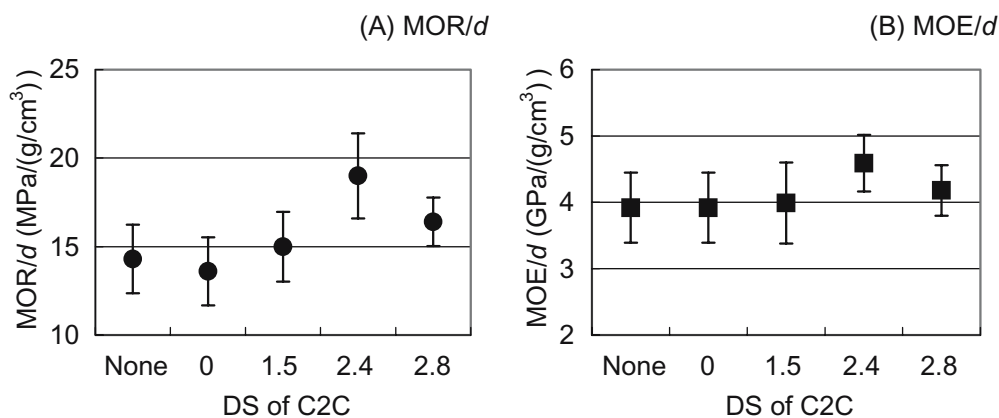


Fig. 1. Fourier transform-infrared (FT-IR) spectra of cellulose esters. DS, Degree of substitution; C2C, cellulose acetate; C3C, cellulose propanoate; C4C, cellulose butanoate; C5C, cellulose pentanoate; C6C, cellulose hexanoate; C12C, cellulose dodecanoate

Fig. 2A, B. Effect of DS of C2C on mechanical properties of wood/poly(lactic acid) composites (WPLC) expressed as **A** MOR/ d (modulus of rupture relative to density), and **B** MOE/ d (modulus of elasticity relative to density) for composite mixture lignocel C300G/poly(lactic acid) PL002/C2C (DS 1.5, 2.4, 2.8) in 80/20/2 weight ratio. Density of wood/plastic composite (WPC): None, $d = 1.22\text{g/cm}^3$; DS0, $d = 1.18\text{g/cm}^3$; DS1.5, $d = 1.22\text{g/cm}^3$; DS2.4, $d = 1.19\text{g/cm}^3$; DS2.8, $d = 1.22\text{g/cm}^3$



spectra.^{13,14} A comparison of FT-IR spectra of several C2Cs showed that C2C (DS 2.8) had the strongest 1750cm^{-1} peak and the weakest peak over 3000cm^{-1} , suggesting that the DS of C2C (DS 2.8) is the highest; similarly, the DS of C2C (DS1.5) is estimated as the lowest (Fig. 1).

Mechanical properties and water resistance

Effect of the DS of C2Cs used as a compatibilizer

To compare the effect of the DS of C2C as a compatibilizer, WPLCs were prepared with the formulation of C300G/PL002/C2C (DS 1.5, 2.4, or 2.8), 80/20/2 by weight. The effects on MOR/ d and MOE/ d of WPLC are shown in Fig. 2, which indicates that C2C (DS 2.4) is effective for improving MOR and MOE of WPLC. The effect of C2C (DS 2.4) on increasing the strength of composites was the most significant, and the highest MOR of WPLC of 22.6MPa was observed for the composite of C2C (DS 2.4) with a density of 1.2g/cm^3 . The MOR of pure PLA board was determined to be about 39MPa , indicating that the strength of WPLC was less than half that of pure PLA board. However, the addition of C2Cs improved the MOR of WPLC a little. On the other hand, WPLC had a higher MOE than pure PLA board, which was about 2.9GPa , and the addition of C2C further improved the MOE of WPLC board as illustrated. The effects on the water resistance (WA, TS, and LE) of WPLCs are shown in Fig. 3, which indicates that C2C could not contribute much to WA, LE, and TS, contrary to the mechanical properties. It is thought that C2Cs are more

Table 1. Degree of substitution and yields of cellulose carboxylates

Cellulose carboxylate	Yield (%)	Degree of substitution
C2C	143	2.8
C3C	185	2.4
C4C	208	2.4
C5C	230	2.5
C6C	264	2.7
C12C	330	2.1

C2C, Cellulose acetate; C3C, cellulose propanoate; C4C, cellulose butanoate; C5C, cellulose pentanoate; C6C, cellulose hexanoate; C12C, cellulose dodecanoate

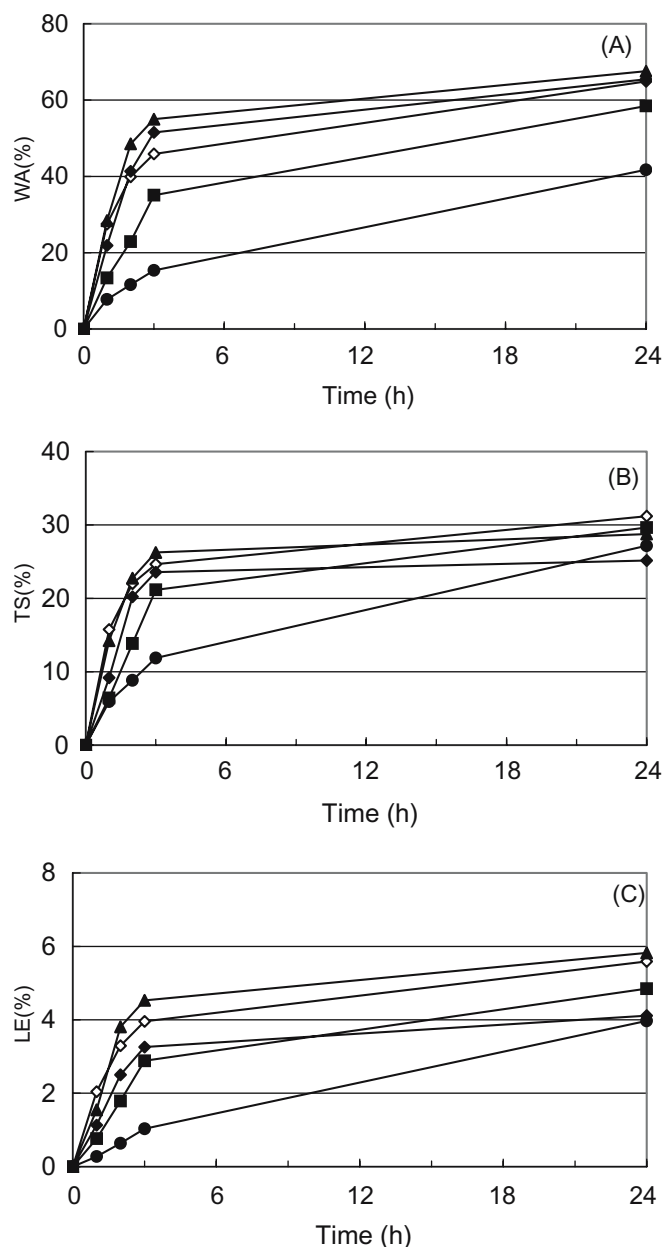


Fig. 3A–C. Effect of DS of C2C on water resistance of WPLC expressed in terms of **A** water absorption (WA), **B** thickness swelling (TS), and **C** linear expansion (LE) for composite mixture C300G/PL002/C2C (DS 1.5, 2.4, 2.8) in 80/20/2 weight ratio. Density of WPC is shown in Fig. 2. *Open diamonds*, None; *squares*, DS0; *triangles*, DS1.5; *circles*, DS2.4; *filled diamonds*, DS2.8

hydrophobic than wood and more hydrophilic than PLA. They therefore work as compatibilizers and the hydrophobicity of C2Cs might be dependent on DS. Mechanical strength can be controlled by equalizing the hydrophilic–hydrophobic balance between the components, that is, by DS. However, the water resistance test did not show this tendency, indicating the presence of other controlling factor(s) for this property. Although we have no conclusive evidence on this point at present, the results might suggest the importance of some physical properties and/or kinetic

factors for increasing water resistance rather than the chemical properties such as the hydrophilic–hydrophobic balance, or the equilibrated thermodynamic factor.

Effect of the amount of C2C (DS 2.4) on WPLC

To compare the effect of the amount of C2C (DS 2.4) as a compatibilizer, WPLC boards were prepared with a formulation of C300G/PL002/C2C (DS 2.4) of 80/20/2, 4, 6, or 8 by weight. The effect of a small amount of added C2C (DS 2.4) on MOR/*d* and MOE/*d* of WPLC is shown in Fig. 4. The addition of 6 parts of C2C (DS 2.4) gave the best mechanical strength and 8 parts of added C2C (DS 2.4) decreased the mechanical properties of the composite. The effects of C2C (DS 2.4) addition on WA, TS, or LE are shown in Fig. 5, suggesting that the addition of C2C (DS 2.4) slightly improved WA, TS, and LE of WPLCs.

Effects of acyl chain lengths of cellulose esters

The effects of C2–C12 cellulose esters as compatibilizers of WPLC were studied with a formulation of C300G/PL002/cellulose ester as 80/20/2 by weight. The effects of the carbon chain length on MOR/*d* and MOE/*d* of WPLC are shown in Fig. 6. In this experiment C2C prepared in the laboratory (DS 2.8) was used to eliminate a possible effect of difference in the raw materials. The addition of C2C, C3C, C4C, and C5C improved the mechanical properties, and C4C and C5C were most effective for MOR. It is noteworthy that the addition of only 2 parts of cellulose esters resulted in about a 30% increase of MOR in three-point bending strength. For MOE, C3C showed the best modulus, but the effect was less significant. The addition of C6C and C12C decreased MOR and MOE of WPLC. The effects on WA, TS, and LE of WPLC are shown in Fig. 7. The addition of C3C, C4C, or C5C improved WA in parallel with the strength above.

In these results, the miscibility of the additive with the polymer matrix was noted. Nishio et al.^{15–18} reported the miscibility of plastic polymers such as poly(ϵ -caprolactone (PCL), poly(*N*-vinyl pyrrolidone) (PVP), poly(vinyl acetate) (PVAc), and several cellulose esters. In particular, they studied the miscibility of PCL and several cellulose esters in terms of the side-chain length and the DS through thermal analysis by differential scanning calorimetry.¹⁵ They reported that a pair, C4C/PCL, showed the highest miscibility. They also reported that more DS of C4C increased miscibility, and C5C had good miscibility with PCL.¹⁶ Esters of a short acyl group such as C2C or C3C did not show miscibility with PCL. Esters of long alkyl chains (e.g., C6C) showed decreased miscibility and were partially miscible. It is also suggested that cellulose esters are miscible with PVP. These results are similar to our results. With both PLA and PCL being polyesters, it is highly probable that the improved mechanical properties observed in this study are given by good miscibility of the components. However, we mixed materials using a Henschel-type mixer (Super mixer) under melt conditions, which is contrary to the work of Nishio and

Fig. 4A, B. Effect of additional amount of C2C (DS 2.4) on mechanical properties of WPLC expressed as **A** MOR/*d*, and **B** MOE/*d* for composite mixture C300G/PL002/C2C (DS 2.4) in variable 80/20/0–8 weight ratios. Density of WPC: C2C none, $d = 1.18 \text{ g/cm}^3$; C2C 2 parts, $d = 1.19 \text{ g/cm}^3$; C2C 4 parts, $d = 1.19 \text{ g/cm}^3$; C2C 6 parts, $d = 1.20 \text{ g/cm}^3$; C2C 8 parts, $d = 1.21 \text{ g/cm}^3$

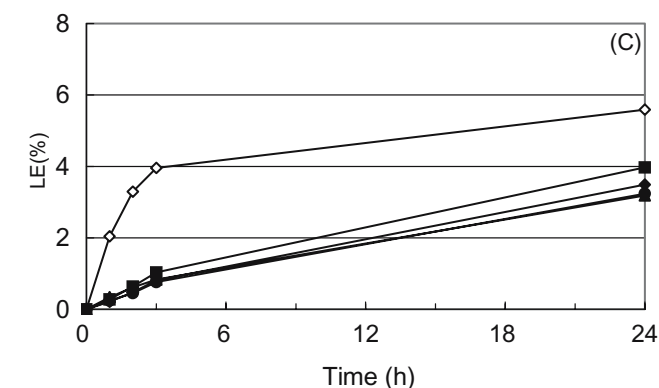
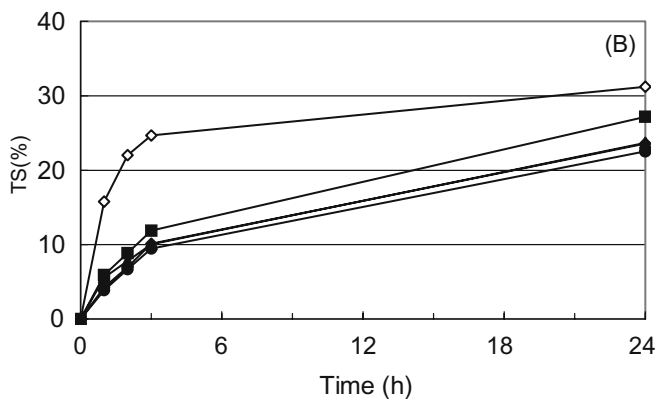
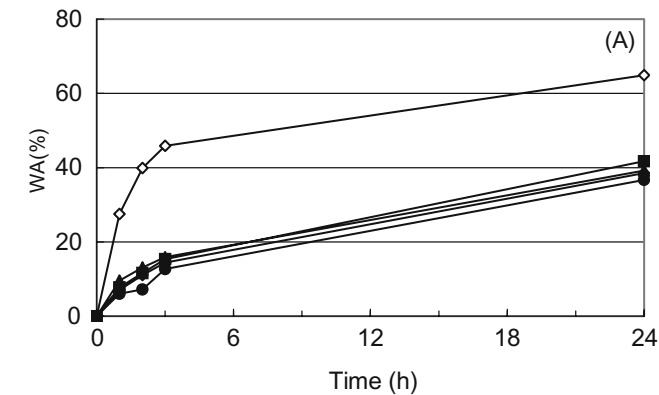
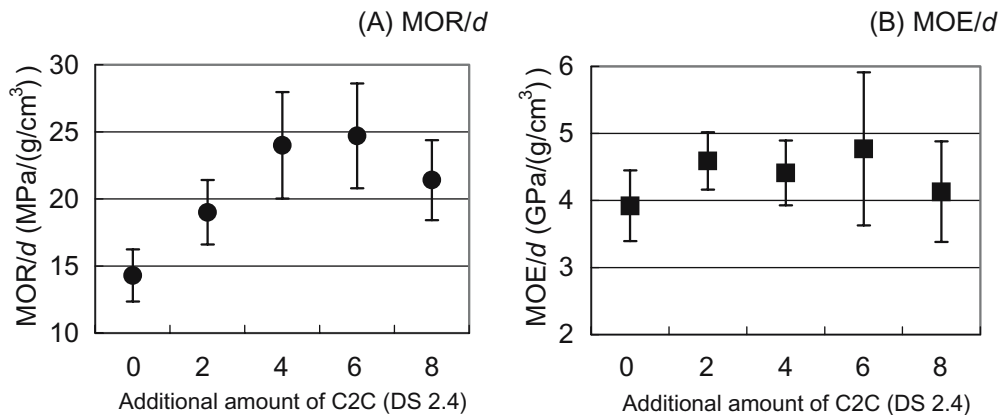


Fig. 5A–C. Effect of additional amount of C2C (DS 2.4) on water resistance of WPLC expressed in terms of **A** WA, **B** TS, and **C** LE for composite mixture C300G/PL002/C2C (DS 2.4) in variable 80/20/0–8 weight ratios. Density of WPC is shown in Fig. 4. *Open diamonds*, no C2C; *squares*, 2 parts C2C; *triangles*, 4 parts C2C; *circles*, 6 parts C2C; *filled diamonds*, 8 parts C2C

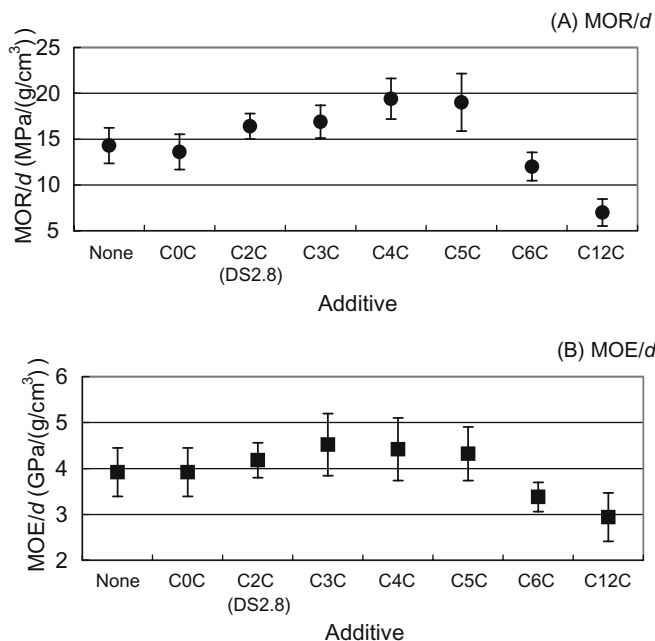


Fig. 6A, B. Effect of carbon chain length on mechanical properties of WPLC expressed as **A** MOR/*d*, and **B** MOE/*d* for composite mixtures C300G/PL002/cellulose ester [C0C (raw cellulose), C2C (DS 2.8), C3C, C4C, C5C, C6C, or C12C] with 80/20/2 weight ratio. Density of WPC: None, $d = 1.18 \text{ g/cm}^3$; C0C, $d = 1.18 \text{ g/cm}^3$; C2C (DS2.8), $d = 1.20 \text{ g/cm}^3$; C3C, $d = 1.22 \text{ g/cm}^3$; C4C, $d = 1.19 \text{ g/cm}^3$; C5C, $d = 1.20 \text{ g/cm}^3$; C6C, $d = 1.16 \text{ g/cm}^3$; C12C, $d = 1.23 \text{ g/cm}^3$

coworkers^{15–18} who prepared films by casting homogeneous solutions of cellulose esters and PCL.

Dynamic viscoelasticity

The results of dynamic viscoelasticity measured in a tensile mode are summarized in Fig. 8. Figure 8A shows storage modulus, E' . E' of WPLC containing C5C or C6C decreased rapidly at about 60°C, showed the lowest value at about 80°C, and then increased up to about 90°C. C4C showed a similar tendency. Long acyl carbon chains of carboxylic acid would induce these changes. Mathew and Oksman¹⁹ and Yoshioka²⁰ suggested that this type of change in E' of PLA is ascribed to crystallization of WPLC. Then, the present results of dynamic viscoelasticity tests indicate an increase in crystallization at the stage in response to the slowdown

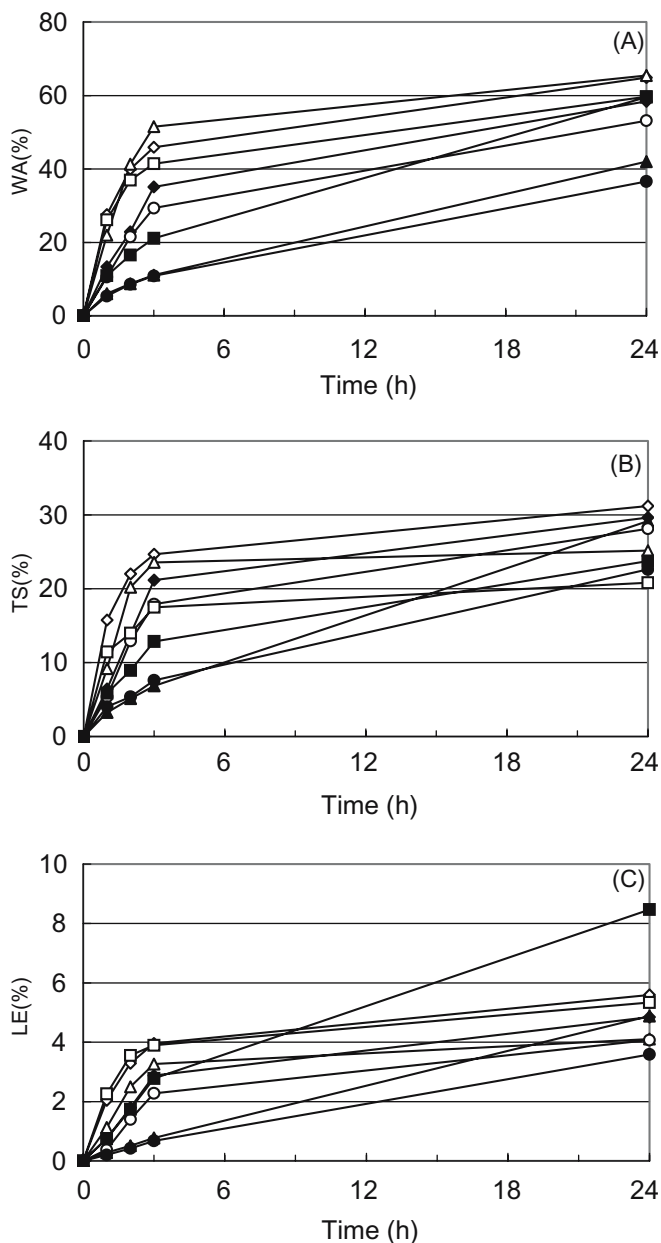


Fig. 7A–C. Effect of carbon chain length on water resistance of WPLC expressed in terms of **A** WA, **B** TS, and **C** LE for composite mixtures C300G/PL002/cellulose ester [C0C, C2C (DS 2.8), C3C, C4C, C5C, C6C, or C12C] with 80/20/2 weight ratio. Density of WPC is shown in Fig. 6. *Open diamonds, none; filled diamonds, C0C; open triangles, C2C (DS 2.8); filled triangles, C3C; open circles, C4C; filled circles, C5C; open squares, C6C; filled squares, C12C*

of crystallization rate of WPLC by the addition of C4C, C5C, or C6C. Although there are reports that crystallization of PLA increases the MOR of composite, decreases in MOR of composite are also reported in other cases. Park et al.²¹ suggested that the quasi-static fracture strength of PLA decreases with increase of crystallinity. On the other hand, the impact fracture toughness was improved with increase of crystallinity. Therefore, when crystallization induces the increase of defects in the composite that behave as the points of stress concentration, crystallization of composite

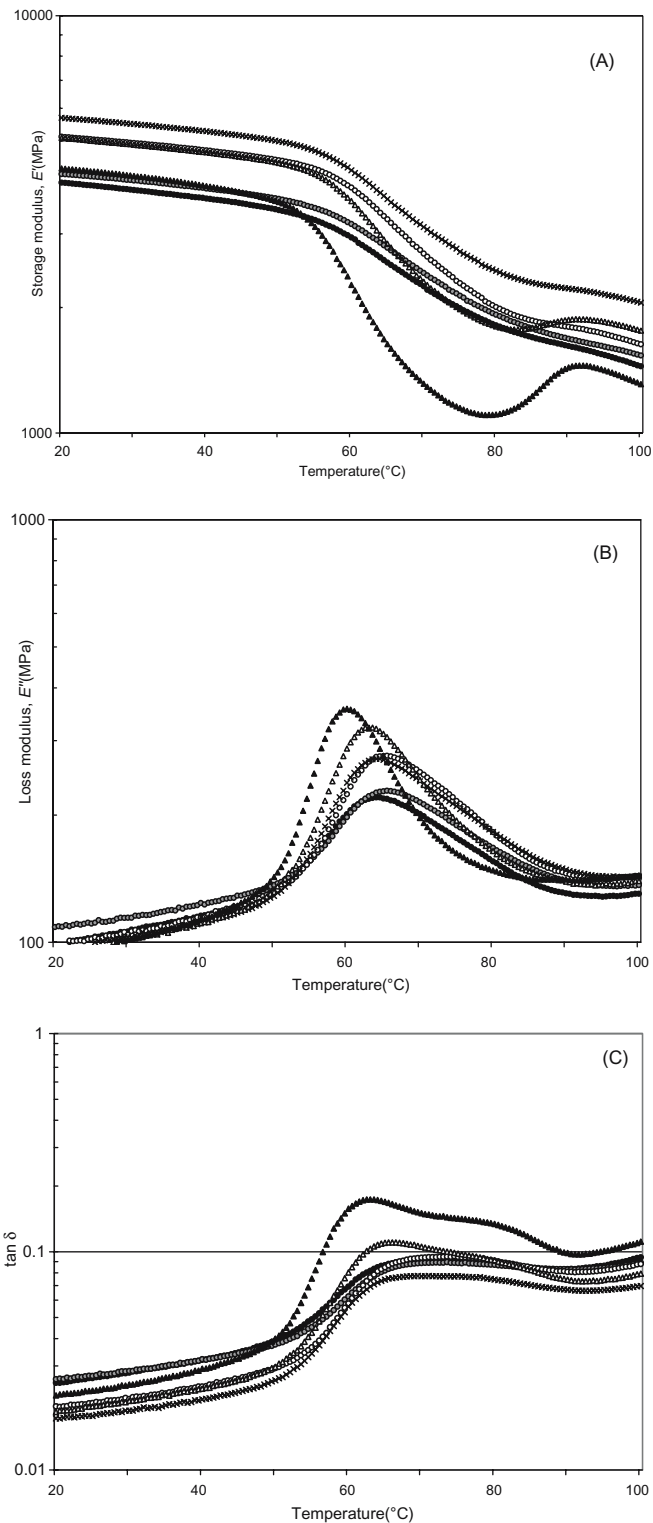
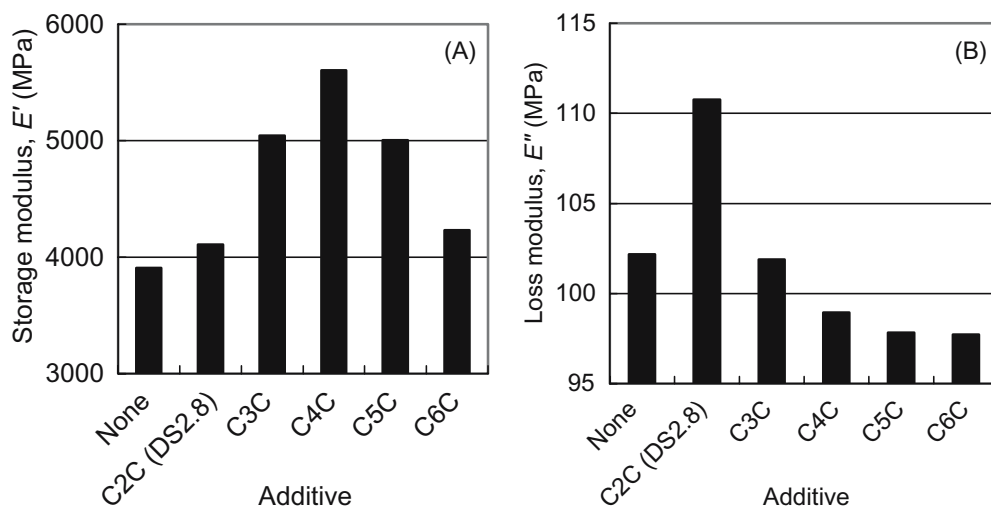


Fig. 8A–C. Effect of carbon chain length of cellulose ester on dynamic viscoelasticity of composite in terms of **A** storage modulus E' , **B** loss modulus E'' , and **C** $\tan \delta$ for composite mixtures C300G/PL002/cellulose ester [C2C (DS 2.8), C3C, C4C, C5C, or C6C] with 80/20/2 weight ratio. *Filled circles, none; shaded circles, C2C (DS 2.8); open circles, C3C; crosses, C4C; open triangles, C5C; filled triangles, C6C*

Fig. 9A, B. Effect of chain length on **A** storage modulus E' , and **B** loss modulus E'' at 25°C for composite mixtures C300G/PL002/cellulose ester [C2C (DS 2.8), C3C, C4C, C5C, or C6C] with 80/20/2 weight ratio



would decrease the mechanical properties of composite. In the present results, it is suggested that adding C4C or C5C slows down the crystallization rate, and the composites have fewer weak points. Figure 8B shows that the peak temperature of loss modulus, E'' , of the composite tends to shift slightly to a higher temperature by the addition of C2C (DS2.8) or C3C than that of a composite of wood and PLA. On the other hand, for composites involving C4C, C5C, or C6C as the additive, the peak temperature decreased gradually in this order. The specimen of added C12C was not measurable because it failed in the early stage of the testing process. It is known that the glass transition temperature, T_g , is dependent on several factors such as molecular weight, cross-linking, plasticizer, and so on.²² In this study, the amount of added cellulose ester was as low as 2%, and the molecular weights of cellulose esters were not expected to change significantly because they were prepared from the same cellulose raw material with the same procedure. Furthermore, the increase of strong bonding between molecules and particles in the composite, which induces cross-linking, is hardly expected by the addition of less-polar cellulose esters to a composite of wood and PLA polyester mixture. It is proposed that the shift of the peak temperature of E'' and $\tan \delta$, and also the increase in the mechanical property of the composite are accounted for by the plasticizing effect of cellulose esters, C4C, C5C, and C6C. The results of C2C or C3C composites indicate an insufficient plasticizing effect because of the poor miscibility of esters in the matrix. In Fig. 9, the storage modulus, E' , and loss modulus, E'' , at 25°C are summarized. The decrease of the loss modulus, E'' , for composites C4C, C5C, and C6C can be accounted for as reflecting their plasticizing effects.

Conclusions

The addition of acyl esters of cellulose to wood/PLA composites as compatibilizers was studied. The addition of C2C improved the mechanical properties of composites regardless of DS. When the DS of C2Cs was compared, C2C (DS

2.4) was the most effective for MOR and MOE of WPLC. The most effective amount of C2C (DS 2.4) in a composite of wood/PLA 80/20 was 6% (w/w). There was a significant effect of the carbon chain length of the acyl group on the mechanical property of WPLC, and the most effective additives for MOR and MOE of WPC were C4C and C5C, respectively. The viscoelastic property of composite suggested that C4C, C5C, or C6C restrains crystallization of WPLC and functions as a plasticizer, and the results of added cellulose esters of various aliphatic acids were assessed, at least in part, by the miscibility of cellulose esters with the matrix.

Acknowledgments The authors thank Kawata Co. for the loan of a Super-mixer, Kuraray Co. for raw materials, and Professor Hiroyuki Yano of Kyoto University for permitting us the measurement of dynamic viscoelasticity.

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