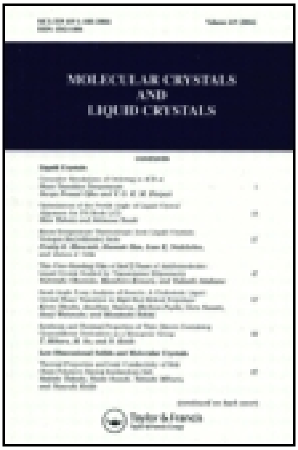

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Wood/Plastic Composite of High Filler Content

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Wood/Plastic Composite of High Filler Content

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Preparation and properties of wood/plastic composite (WPC) with high content of wood filler around 80% are reported focusing at: effects of high filler content, preparation of all bio-based composite by using poly(lactic acid) (PLA) as plastic material and cellulose esters as compatibilizer, and method for improving weather resistance of wood/PP composite. Addition of about 2% of cellulose esters of C4-C6 aliphatic carboxylic acids was effective for improving the bending strength of high wood content WPC of PLA by slowing down the crystallization rate of plastic. For improving weather resistance of wood/PP composite, top-coating was found most effective.

Keywords: cellulose esters; crystallization rate of plastic; poly(lactic acid); wood/plastic composite

INTRODUCTION

Construction of a sustainable society with low environmental stress is an important issue in this Century. Wood material plays an important role in this context since wood is abundant and sustainable. Effective utilization procedure of wood material should be developed extensively. We report here on the preparation and properties of a wood/plastic composite with high filler content of wood flour around 80%, which can be accepted as a new wood material.

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Effect of High Wood Filler Content in Composite

Generally, composite reflects the characteristics of constituting components shown in Figure 1, the total dependence of performance of composite on the composition of components may be linear in some cases and nonlinear in others. However, it is accepted that the characteristics of a component develop more with its increasing composition in the composite. Therefore, for wood plastic composite of high wood content, the molded product strongly reflects the characteristics of wood material, such as easy painting and bonding, moisture control, and so on, for example. In other words, the composite has characteristics like wood. Today in response to the demand of market for high performance wood material, the amount of adhesive used for preparation of engineered wood is increasing, and the amount above 15% is not rare especially for amino-type adhesives. Then the high wood content of WPC using about 20% of thermoplastic resin, reporting here, has almost similar wood/polymer ratio with some engineered wood in the market, and it will be possible to be classified as a type of engineered wood. Since WPC is prepared by extrusion or injection molding, this means preparation of wood material by such molding processes as have been used extensively in the manufacturing processes of plastic material. Now it will be accepted that a long-waited manufacture of wood material by extrusion or injection molding has been realized.

All-Biobased Composite [1]

When poly(lactic acid) (PLA) is used as the matrix, WPC of almost bio-based material can be prepared. However, WPC in general does

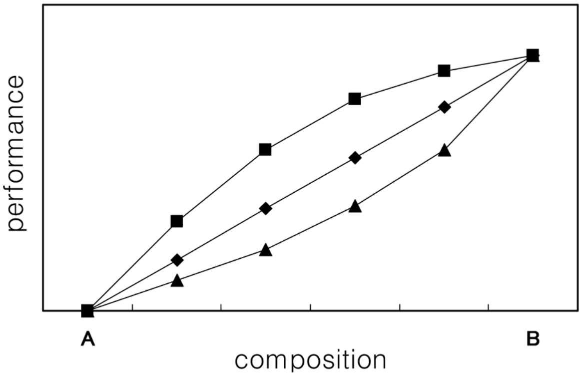


FIGURE 1 Performance of composite dependent on the content of components.

not show sufficient strength without compatibilizer. This is the case also for WPC with PLA as plastic (WPLC) reported here. When hydrophilic wood and hydrophobic plastic are mixed together, their interfacial adhesion does not develop well because of their poor compatibility, leading to poor mechanical properties of the composite. To improve their compatibility, various compounds have been examined and reported so far; in general, a small amount of polyolefin modified with maleic anhydride (MAPO) was found to be effective, and many kinds of maleic anhydride modified polyethylene (MAPE) or polypropylene (MAPP) are now commercially available [2–5]. Although MAPO was well accepted for its excellent effect in the composite of polyolefin as the plastic, there is controversy in the case of PLA [6–8]. We also confirmed the effect that MAPP (Toyotach H-1100P, Toyokasei) improved the MOR and water resistance of wood/PP composite effectively; in particular, H-1100P increased MOR more than three times. However, MOR of a WPLC did not increase so much by the addition of H-1100P [3]. Many scientists have already proposed compatibilizers replacing MAPO. The results in literature [9,10] suggest that derivatives of natural products might be promising for WPLC. So, we focused on cellulose, which is a major component of wood, synthesized cellulose esters of several carboxylic acids [11], such as acetate (C2C of DS 2.8), propionate (C3C), butyrate (C4C), valerate (C5C), capurorate (C6C), and laurate (C12C), and examined their abilities for compatibilizer of WPLC. It is notable that this WPLC composite is made from fully bio-based materials.

For preparation of WPLC, wood flour (C300G, J. Rettenmeyer & Sohn, moisture content 3–4%), a cellulose ester, and PL002, were blended using a Henschel-type mixer (Super Mixer, Kawata). The agglomerate thus prepared (24 g) was placed in a mold of 80 × 100 mm, and compression molded at 13 MPa at 200°C for 15 min to make a 2.5 mm thick board. Degree of substitution of cellulose esters (DSs) were adjusted as much as possible about 2.4, as follows: C2C DS = 2.8, C3C 2.4, C4C 2.4, C5C 2.5, C6C 2.5, C12C 2.1. The DSs of cellulose esters were calculated on the basis of the product yields except for C2Cs (DS 1.5 (a commercial product), 2.4 (a commercial product), or 2.8 (prepared in the lab.)), which were estimated based on the linear relationship of product yield with absorbance peak intensity ratios of FT-IR spectra ($I_{C=O}/I_{OH}$) [12]. A comparison of FT-IR spectra of several C2Cs (Fig. 2) showed that C2C (DS 2.8) has the strongest $1750\,\mathrm{cm}^{-1}$ peak and the weakest over $3000\,\mathrm{cm}^{-1}$ peak, suggesting that the DS of C2C (DS 2.8) is the highest; similarly, the DS of C2C (DS1.5) is estimated as the lowest.

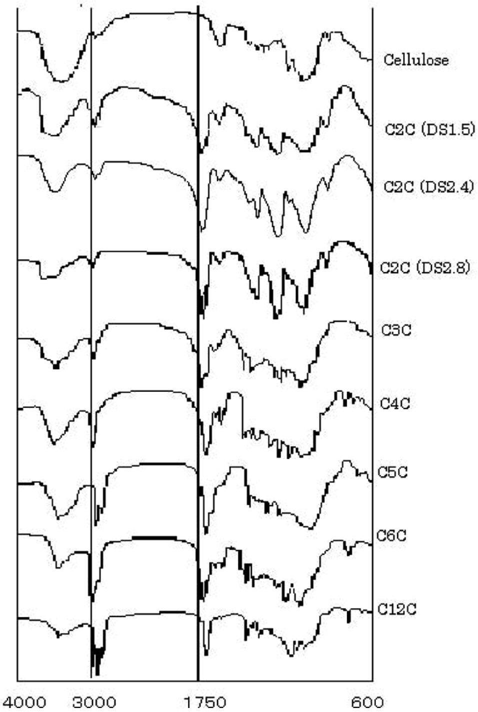


FIGURE 2 FT-IR spectra of cellulose esters.

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 Figure 3, 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 22.6 MPa was observed for the composite of C2C (DS 2.4) with a density of 1.2 g/cm^3. Since the MOR of pure PLA board was determined to be about 39 MPa, the strength of WPLC was less than a half 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 2.9 GPa, and the addition of C2C further improved the MOE of WPLC board as illustrated. The effects on the water resistance showed that C2C do not contribute much to water absorption (WA), linear expansion (LE), and thickness swell (TS), contrary to the mechanical properties.

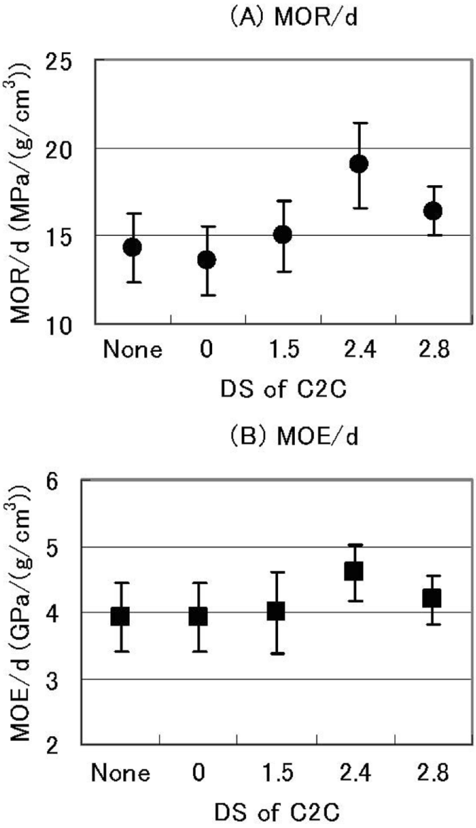


FIGURE 3 Effect of DS of C2C on mechanical properties of WPLC. (A) MOR/d, (B) MOE/d C300G/PL002/C2C (DS 1.5, 2.4, 2.8), 80/20/2; density of WPC, None d = 1.22, DS0 d = 1.18, DS1.5 d = 1.22, DS2.4 d = 1.19, DS2.8 d = 1.22 g/cm^3. Solid circle: MOR/d, Solid square: MOE/d.

It is thought that C2Cs are more 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; the water resistance test, however, 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. The effect of a small amount of added C2C (DS 2.4) on MOR/d and MOE/d of WPLC is shown in Figure 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

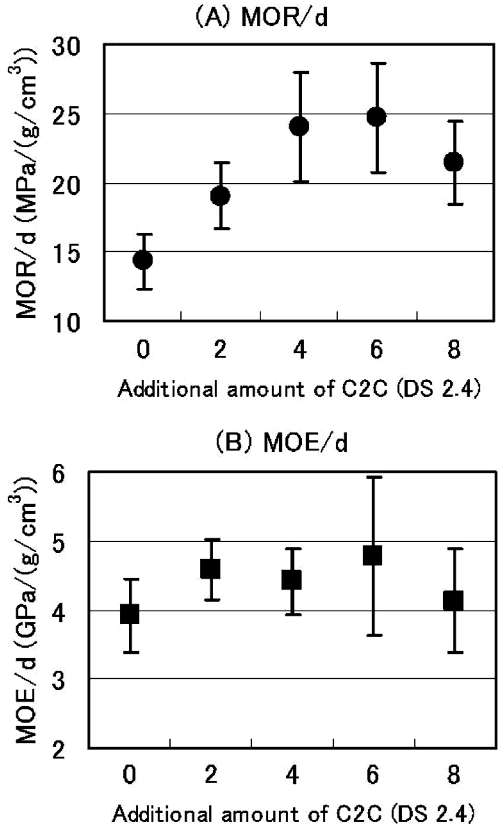


FIGURE 4 Effect of DS of C2C on mechanical properties of WPLC. (A) MOR/d, (B) MOE/d C300G/PL002/C2C (DS 1.5, 2.4, 2.8), 80/20/2; density of WPC, None d = 1.22, DS0 d = 1.18, DS1.5 d = 1.22, DS2.4 d = 1.19, DS2.8 d = 1.22 g/cm^3. Solid circle: MOR/d, Solid square: MOE/d.

of the composite. The addition of C2C (DS 2.4) slightly improved WA, TS, and LE of WPLCs [1].

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. The effects of the carbon chain length on MOR/d and MOE/d of WPLC are shown in Figure 5. 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

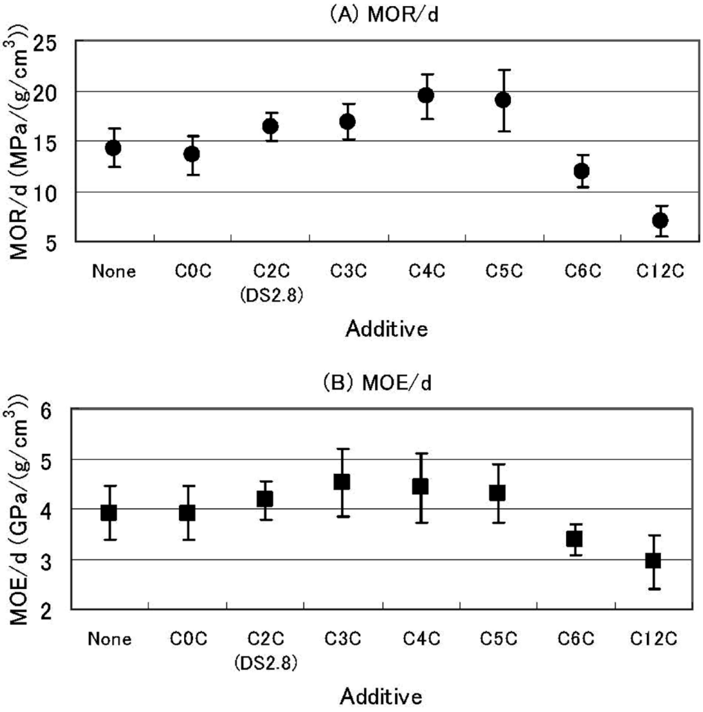
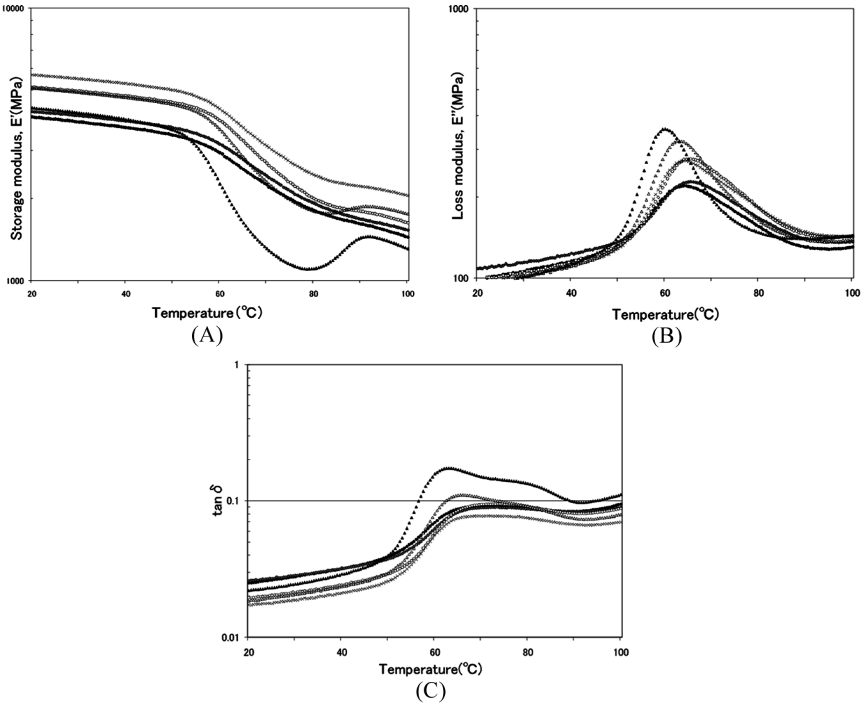


FIGURE 5 Effect of acyl carbon chain length on mechanical properties of WPLC. (A) MOR/d, (B) MOE/d C300G/PL002/cellulose esters (C0C (raw cellulose), C2C (DS 2.8), C3C, C4C, C5C, C6C, or C12C), 80/20/2; density of WPC, None d = 1.18, C0C d = 1.18, C2C(DS2.8) d = 1.20, C3C d = 1.22, C4C d = 1.19, C5C d = 1.20, C6C d = 1.16, C12C d = 1.23 g/cm^3. Solid circle: MOR/d, Solid square: MOE/d.

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 addition of C3C, C4C, or C5C improved WA [1] parallel with the strength above.

In these results, the miscibility of the additive with the polymer matrix was noted. Nishio et al. reported the miscibility of plastic polymer such as poly(ε-caprolactone) (PCL), poly(N-vinyl pyrrolidone) (PVP), polyvinyl acetate (PVAc), and several cellulose esters [13–16]. In particular, they studied the miscibility of PCL and several cellulose esters in terms of the alkyl-chain length and the DS through thermal analysis by differential scanning calorimetry [13]. They reported that a pair, C4C/PCL, showed the highest miscibility. They also reported that more DS of C4C increased miscibility, and C5C also had good miscibility with PCL [14]. 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. Since both PLA and PCL are polyester, 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 Henshel-type mixer (Super mixer) under melt conditions, which is contrary to the film prepared by casting homogeneous solutions of cellulose esters and PCL of Nishio's works [13–16]. The results of dynamic viscoelasticity measured in a tensile mode are summarized in Figure 6. Figure 6A shows storage modulus, E′. E′ of WPLC containing C5C or C6C decreased rapidly at about 60°C, and showed the lowest value at about 80°C, then increased up to about 90°C. C4C showed a little similar tendency. Long acyl carbon chains of carboxylic acid would induce these changes. Mathew et al. [17] and Yoshioka [18] suggested that this type of change in E′ of PLA is ascribed to crystallization of PLA. Then, present results indicate increase in the part of crystallization at the stage of dynamic viscoelasticity test in response to the slow-down of crystallization rate of PLA in WPLC by the addition of C4C, C5C, or C6C. Although there are reports that crystallization of PLA increases the MOR of composite, decrease in MOR of composite is also reported in other cases. Park et al. suggested that quasi-static fracture strength of PLA decreases with increase of crystallinity [19]. On the other hand, the impact fracture toughness was improved with crystallinity. Therefore, when crystallization induces the increase of defects in the composite that behave as the points of stress concentration, crystallization of composite would decrease the mechanical properties of



(A)

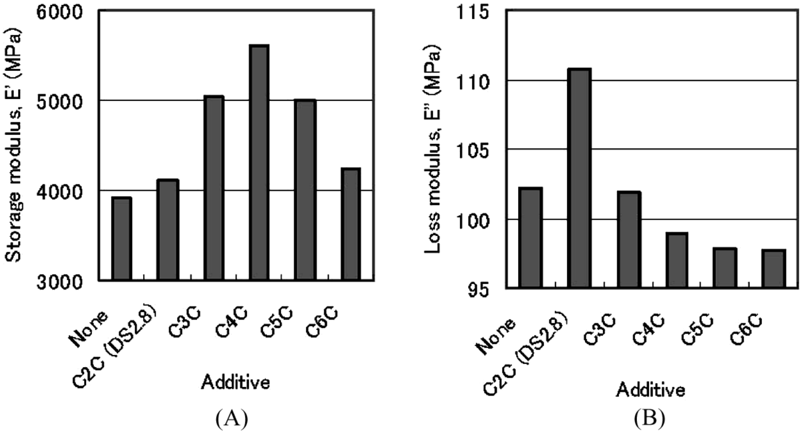
(B)

(C)

FIGURE 6 Effect of acyl carbon chain length of cellulose ester on dynamic viscoelsticity of composite. (A) Storage modulus E′, (B) loss modulus E″, (C) tan δ. C300G/PL002/cellulose esters (C2C (DS 2.8), C3C, C4C, C5C, or C6C), 80/20/2. Solid circle: None, Gray circle: C2C (DS2.8), Open circle: C3C, Cross: C4C, Open triangle: C5C, Solid triangle: C6C.

composite. In the present results, it is suggested that adding C4C, or C5C slow dawn the crystallization rate, and the composites have less weak points. Figure 6b 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 since it was broken in the early stage of the testing process. It is known that the glass transition temperature, Tg, is dependent on several factors such as molecular weight, cross-linking, plasticizer, and so on [20]. In this study, the amount of added cellulose ester was as low as 2%, and the molecular weight of cellulose esters are expected not to change significantly since they were prepared starting from the same cellulose as the raw material and 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 δ, 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 and C3C composites indicate an insufficient plasticizing effect because of the poor miscibility of esters in the matrix. In Figure 7, 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 will be accounted for as reflecting their plasticizing effects.

In conclusion, the addition of acyl esters of cellulose to wood/PLA composites as compatibilizers was studied, and 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 wt%. There was a significant effect of the carbon chain length of the acyl group to the mechanical property of WPLC, and the most effective additive for MOR, and MOE of WPC was C4C, or C5C, respectively. The viscoelastic



(A) (B)

FIGURE 7 Effect of acyl chain length on Storage modulus E′, Loss modulus E″, and tan δ at 25°C. (A) Storage modulus E′, (B) Loss modulus E″. C300G/PL002/cellulose esters (C2C (DS 2.8), C3C, C4C, C5C, or C6C), 80/20/2.

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.

Procedure for Improving Weather Resistance of Wood/PP Composite

Weather resistance is a problem of present WPC to be improved. When WPC is kept outdoor, color change into gray proceeds in a relatively short period. Since addition of some functional materials by mixing in the compound is an easy process in the WPC preparation, addition of coloring pigments is used as an effective procedure for preventing color change. Here in this experiment, effects of colorless antiweathering additives and top-coating by clear lacquer were examined for increasing weather resistance of wood/PP composite. Composite was prepared by mixing three nitrogen containing commercial additives (X, hindered amino ester; Y, nitroxyl radical; Z, piperidine derivative) to the compound of wood/PP (W/PP/MAPP/additive, 85/15/2/1), and their effects on the bending strength, water absorption, and color change of molded samples prepared by compression and extrusion moldings were examined before and after weathering. The normal bending strength of compression mold exceeded the value of a control sample without an additive, but the results of extrusion molding tend to scatter, suggesting the importance of optimization of molding conditions. The additives tested did not decrease the bending strength so much, and best bending strength of 50 Mpa was obtained with additive A by extrusion molding. Water resistance after 24 h of soaking in water at room temperature did not show significant effect of addition as shown in Figure 8 for extruded composite containing A. However, there were some additives which induced poor water resistance of composite. To examine the effect of additives to weather resistance, extrusion molded composites with three additives above were kept outdoor without post-treatment, after additional application of a solution of weather retardant on the test pieces, or top-coating by clear acrylic paint, and the effects against weathering were studied. The results of color fading after 5 months exposure shown in Figure 9 indicate that addition of hindered amine showed better results than others, and surface coating by the agent improved the resistance in some extent. However, coating the sample with acrylic resin gave the best weather resistant result. It is notable that top coat by acrylic resin showed similar high resistance against color fading by weathering, even without an albinism inhibitor. Water absorption of the

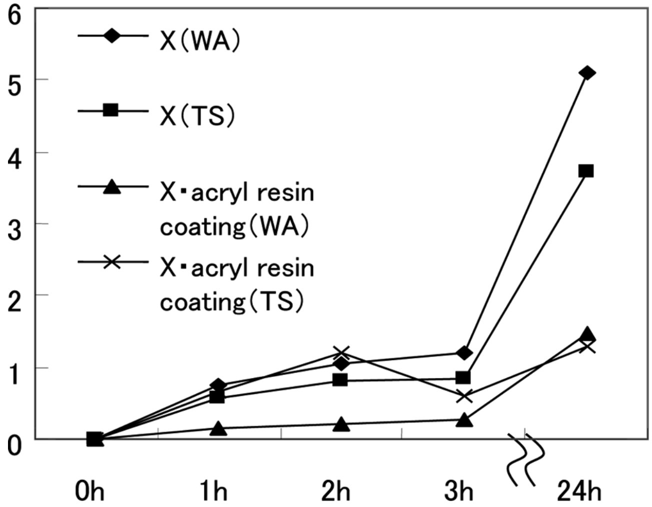


FIGURE 8 Water resistant test of extruded wood/PP/MAPP/additive for 24 hr in water at 25°C. Solid diamond: X, water absorption, Solid square: X, thickness swell (%), Solid triangle: X, acryl resin coating, water absorption (%), Cross: X, acryl resin coating, thickness swell (%).

top-coated mold showed similar excellent tendency as shown in Figure 8, suggesting that intrusion of water may play a crucial role in the color fading. Further study should be necessary for understanding the mechanism of color fading phenomenon in detail.

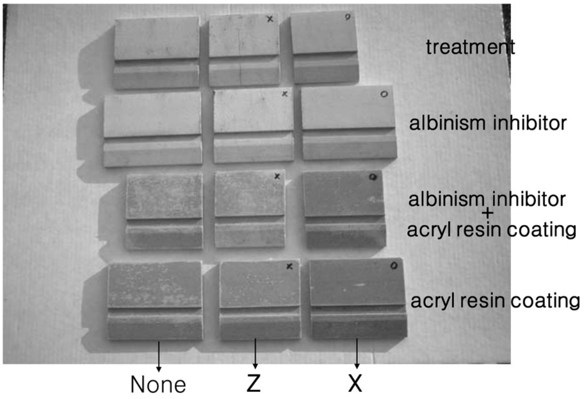


FIGURE 9 Weather resistance of extruded wood/PP/MAPP/additive after outdoor exposure for 5 months. X, hindered amino ester; Z, piperidine derivative.

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