# Improvement in Impact Strength of Modified Cardanol-Bonded Cellulose Thermoplastic Resin by Using Olefin Resins

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**ABSTRACT:** Impact strength of a modified cardanol-bonded cellulose thermoplastic resin was greatly improved by using a small amount of olefin resins. As we showed, this thermoplastic resin (3-pentadecylphenoxy acetic acid (PAA)-bonded cellulose diacetate (CDA): PAA-bonded CDA) exhibited high practical properties such as bending strength, heat resistance, and water resistance. However, its impact strength was insufficient for use in durable products. We improved the impact strength of PAA-bonded CDA by adding hydrophobic olefin resins, such as polyethylene or polypropylene, while maintaining good bending strength and breaking strain. Furthermore, the application of olefin resins also increased water resistance and fluidity. © 2013 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39829.

## INTRODUCTION

Bioplastics originating from plant sources have been studied with keen interest as promising materials for preventing the continuing drain on petroleum resources and for their anchoring effect on carbon dioxide emissions. Efforts to reduce the environmental load of products by replacing petroleum-based plastics with bioplastics have been attempted in various industrial fields. At present, mass-produced bioplastics such as polylactic acid (PLA)[1–4] use starches which are generally produced from edible plants as the main source. The possibility of future food shortages has emphasized the importance of using nonedible plant sources to produce bioplastics; therefore, we have been developing advanced bioplastics to be used in durable products by mainly using cellulose and cardanol for two readily procurable nonedible plant resources. Cellulose, which is widely present in grasses, agricultural crops, trees, and aquatic plants, is the most abundant renewable polymer in the world.[5,6] Furthermore, we recently focused on cardanol, a long alkyl chains combined with cellulose, made from a nonedible plant source that can be stably supplied. It is a phenol derivative with a long unsaturated hydrocarbon chain and is extracted from discarded cashew nutshells.

We have already synthesized cardanol-bonded cellulose thermoplastic resins.[7–9] As shown in Figure 1, bonding a modified-cardanol derivative (PAA) with cellulose diacetate (CDA) resulted in a bioplastic (PAA-bonded CDA) having good thermoplasticity, high strength, and high heat and water resistance, which were superior to those of conventional cellulose resins such as CDA with plasticizers including triethyl citrate (TEC). However, the impact strength of PAA-bonded CDA was insufficient for use in durable products.

Typically, the impact strength of thermoplastics has been mainly improved through two mechanisms: crazing or shearing deformations. Crazing deformation is done by adding small deformable particles that can be immiscible with thermoplastics and form microscopic cracks around the particles.[10] Shearing deformation is done by adding organic components that are miscible with thermoplastics; therefore, molecular chains of thermoplastics are deformed in the direction of maximum shear stress, consuming impact energy.[11]

Based on these mechanisms, the impact strength of conventional cellulose resins, such as cellulose acetate (CA) or CA butyrate, were improved by adding external plasticizers (di-*n*-hexyl phthalate, diethyl sebacate, etc.),[12–15] or by combining the resins with branched and flexible structures as internal plasticizers (2-ethylhexanoyl, etc.).[16] However, these plasticizers degraded other characteristics, such as bending strength and heat resistance, of cardanol-bonded cellulose thermoplastic resins.[7,8] Furthermore, the impact strength of cellulose resin (CA propionate) was improved by adding another type of resin (acrylonitrile-butadiene-styrene: ABS).[17] As far as we know, however, there have been no reports on improving the impact strength of cardanol-bonded cellulose thermoplastic resins by using other types of resins.
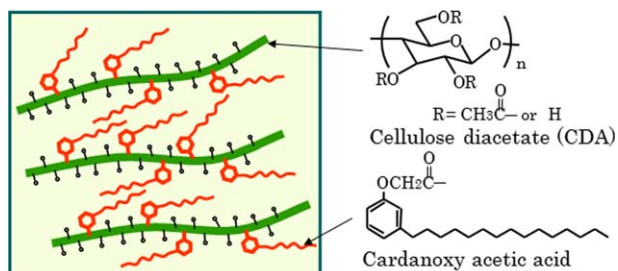
**Figure 1.** Hypothesized structure of PAA-bonded CDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

With the objective of simultaneously achieving impact strength and flexural properties (flexural strength and breaking strain), we attempted to improve the impact strength of PAA-bonded CDA by systematically adding relatively flexible resins. First, we investigated the addition of general petroleum plastics [ABS, acrylonitrile-styrene (AS), polyamide 6 (PA6)]. Second, we studied the application of olefin resins [polyethylene (PE), polypropylene (PP)], which are expected to show high affinities to hydrophobic cardanol side chains. Finally, to investigate the effect of the interfacial state between PAA-bonded CDA and olefin resins, we verified the effect of adding several types of PP with different concentrations of maleic anhydride. The following is a summary of the results.

## EXPERIMENTAL

### Materials

CDA (LM-80, degree of substitution (DS) of acetic acid: 2.1, viscosity: 200 mPa·s/6 weight (wt) % in acetone) was supplied by Daicel Corporation (Japan). Hydrogenated cardanol (3-pentadecyphenol), in which the unsaturated bonds in the alkyl side chain were changed to saturated ones, was purchased from ACROS Organics and used as received. The change ratio was more than 99 wt %, as measured by ACROS Organics. Chloroacetic acid, chloroform, acetone, 1,4-dioxane, methanol, hexane, diethyl ether, triethyl amine, sodium hydroxide, hydrochloric acid, oxalyl chloride, and $N,N$-dimethylformamide were the analytical reagents and used as received from Kanto Chemical (Japan) without further purification. ABS resin (GA-701) was supplied by Nippon A&L (Japan). AS resin (SAVREX) was supplied by Techono Polymer (Japan). PA6 (Amilan CM1007) was supplied by Toray Industries (Japan). Three types of PE, which were manufactured by Japan Polyethylene Corporation (Japan), were used as impact modifiers, high-density PE (HDPE; product name: HJ490; density: 0.96 g/cm³; melting point (m.p.): 133°C; melt flow rate (MFR): 20 g/10 min), low-density PE (LDPE; product name: UJ370; density: 0.92 g/cm³; m.p.: 120°C; MFR: 16 g/10 min), and Branched-PE (product name: KS560T; density: 0.90 g/cm³; m.p.: 90°C; MFR: 16.5 g/10 min). Furthermore, three types of PP, which were manufactured by SunAllomer (Japan), were used as another impact modifier, high-flow-type PP (HFlow-PP; product name: PM900A; density: 0.90 g/cm³; MFR: 30 g/10 min), low-flow-type PP (LFlow-PP; product name: PM600A; density: 0.90 g/cm³; MFR: 7.5 g/10

min), and middle-flow-type PP (MFlow-PP; product name: PM801A; density: 0.90 g/cm³; MFR: 13 g/10 min) Furthermore, PP with different concentrations of maleic anhydride (MAH-PP) supplied by Sanyo Chemical Industries were tested. MAH7-PP (product name: Umex 110TS; acid value: 7; softening point: 149°C) and MAH52-PP (product name: Umex 1010; acid value: 52; softening point: 148°C) were applied for investigating the effect of the interfacial state between cardanol-bonded cellulose thermoplastic and olefin resins. Incidentally, the above acid values indicate the weights of potassium hydroxide (KOH), which were needed for neutralizing the acid ingredients in 1 g of MAH-PP; therefore, MAH-PP with higher acid values show higher polarities.

### Synthesis of PAA-Bonded CDA

The synthesis process of PAA-bonded CDA is shown in Figure 2. The method of preparing PAA chloride is the same at that used by Iji et al.[8] The charge-in quantities of each material for obtaining PAA chloride were 1.5 times those presented in their study. PAA-bonded CDA was synthesized using the same method as that used by Iji et al. The charge-in quantities of each material to obtain PAA-bonded CDA were 25 times those presented in their study. The final product (PAA-bonded CDA) resulted using a ¹H-NMR spectrometer. The DS of PAA was calculated using the ratio between the area corresponding to the proton resonance of the methyl protons of the acetate group ($\delta 1.80$–$2.20$) and the corresponding resonance for the methyl protons of CDA ($\delta 0.86$). As a result, the DS of PAA was 0.53 (the ratio of bonded PAA content calculated using the ¹H-NMR spectrometer as mentioned above was 42 wt %). The molecular weight of PAA-bonded CDA was estimated using gel permeation chromatography (GPC: Shimadzu LC-VP system with Shimpack GPC-8025C and GPC-80MC column, Shimadzu Corporation, Japan) calibrated using polystyrene standards (solvent:
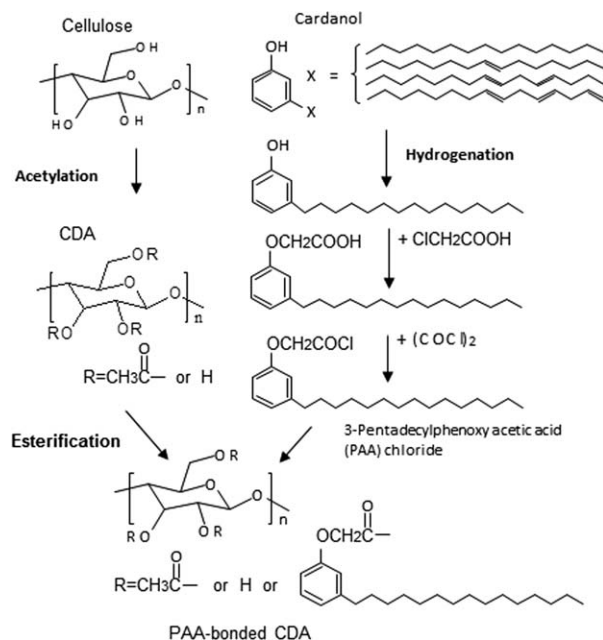


**Figure 2.** Preparation process of PAA-bonded CDA.

**Table I.** Characteristics of PAA-Bonded CDA with Polymers

| Sample content | Izod impact strength (kJ/m$^2$) | Bending test | | | Water absorption (%) | Melt flow rate (g/10 min) |
| --- | --- | --- | --- | --- | --- | --- |
| | | Strength (MPa) | Modulus (GPa) | Breaking strain (%) | | |
| Cellulose diacetate (CDA)[a] | – | – | – | – | 17.0 | – |
| PAA-bonded CDA (DS of PAA: 0.53, 42 wt %) | 3.8 | 72 | 2.3 | 8.2 | 0.85 | 1.50 |
| PAA-bonded CDA + **ABS 5 wt %** | 3.4 | 59 | 1.9 | 9.2 | 0.80 | 15.2 |
| PAA-bonded CDA + **AS 5 wt %** | 3.7 | 61 | 2.0 | 9.1 | 0.76 | 16.1 |
| PAA-bonded CDA + **PA6 5 wt %** | 9.6 | 52 | 1.9 | 4.0 | 0.88 | 11.0 |
| PAA-bonded CDA + **Branched-PE 5 wt %** | 7.7 | 53 | 2.3 | >10 | 0.69 | 15.6 |
| PAA-bonded CDA + **MFlow-PP 5 wt %** | 7.3 | 55 | 2.3 | >10 | 0.65 | 16.4 |

[a] DS of acetic acid: 2.1.

chloroform). The number-average molecular weight ($M_n$) of PAA-bonded CDA was about 120,000.

**Preparation of Test Specimens**

The above PAA-bonded CDA was dried at $105 \pm 5°C$ for 7 h before using. This dried material was preblended with other resins. The blends were kneaded in a twin extruder (product name: HAAKE MiniLab Rheomex extruder: Model CTW5, Thermo Fisher Scientific, (Germany)) at $200 \pm 5°C$. The kneaded materials were then pelletized into a square, about 2 mm on each side. Test specimens (80 (length) by 12.4 (width) by 2.4 (thickness) mm) were prepared from the pellets by using an injection-molding machine (HAAKE MiniJet II, Thermo Fisher Scientific). The temperature of the molten pellets was $210 \pm 5°C$ and that of the mold was $110 \pm 5°C$. The injection pressure was 70–120 MPa, and that of the value of pressure keeping was 40 MPa for 5 s.

**Measurements**

Bending tests on the specimens with 2.4-mm thickness were done in accordance with ISO 178 by using an Instron 5567 universal testing machine manufactured by Instron (United states; cross-head speed: 1.2 mm/min; span: 50 mm). Izod impact tests on 2.4-mm-thick notched specimens were conducted in accordance with ISO 180 by using the Universal Impact Tester C1, manufactured by Toyo Seiki Seisakusho (Japan; pendulum: 2.75 J; upswing angle: 150°). Fracture surfaces were observed using a scanning electron microscope (SEM; product name: VE-7800; manufactured by KEYENCE (Japan)). Water absorption was calculated by measuring the finite difference of weights before and after dipping specimens in distilled water at room temperature for 24 h. Fluidity (MFR (g/10 min)) was estimated using a capillary rheometer (product name: CFT-500D; capillary size: 10 (length) by 2 (diameter) mm; cylinder temperature: 200°C; load: 5 or 500 kgf; preheat: 120 s). The molecular weight of PAA-bonded CDA in terms of polystyrene was measured using gel permeation chromatography (liquid chromatograph; product name: LC-10ADvp; manufactured by SHIMADZU CORPORATION (Japan)) with columns for chloroform (product name: GPC-80MC, GPC-80M, GPC-8025C; manufactured by SHIMADZU CORPORATION (Japan)).

**RESULTS AND DISCUSSION**

**Addition of General Petroleum Plastics**

We first measured the impact strength and flexural properties of compounds consisting of PAA-bonded CDA with 5 weight (wt) % of general petroleum plastics such as ABS, AS, and PA6. As shown in Table I, the compounds obtained by adding these plastics could not simultaneously exhibit high impact strength and good flexural properties. Additionally, these plastics exhibited low dispersibilities in PAA-bonded CDA; therefore, these compounds were opaque. When adding PA6, the outside appearance of this compound was marblelike, and continuous layers of PA6 were clearly observed. The impact strength of the compound with PA6 was improved, while those of the compounds with ABS or AS decreased.

A fracture surface of the PAA-bonded CDA with PA6 was more rugged and had a larger specific surface area than those of the compounds with ABS or AS. We believe that the increase in impact strength by adding PA6 was due to the forming of continuous layers of PA6. These continuous layers were formed by almost completely phase separation between PAA-bonded CDA and PA6. The dispersed direction of these layers, which show excellent impact strength (PA6 alone does not break in the izod impact test), coincided approximately with the vertical direction of applied impact force. These layers would prevent the progress of destruction cracks; therefore, a large amount of energy during the impact test was spent to form this fracture surface. In contrast, fracture surfaces of the PAA-bonded CDA with ABS or AS were less rugged and flatter than that of the PAA-bonded CDA with PA6. ABS and AS showed better dispersion in PAA-bonded CDA than that of PA6 and could not form the continuous layers. From these results, the addition of ABS or AS would not be able to improve impact strength.

On the other hand, the addition of PA6 drastically decreased the breaking strain. As is evident from low dispersibilities of PA6 in PAA-bonded CDA, interfacial coherency between PAA-bonded CDA and PA6 was too weak. This too weak interfacial coherency between PAA-bonded CDA and PA6

resulted in low breaking strain. The weak coherency was derived from the large difference in the intermolecular force between PAA-bonded CDA and PA6 with higher polarity than those of ABS or AS. Destruction began at a smaller strain than that of PAA-bonded CDA alone because stresses were concentrated on the weak interfaces between PAA-bonded CDA and PA6. During the bending test of the compound with PA6, we heard the beginnings of fracture around 4% of strain.

### Addition of Olefin Resins

As previously mentioned, the addition of three types of general petroleum resins (ABS, AS, or PA6) could not simultaneously exhibit high impact strength and flexural properties. We believe that the reason for these results was derived from insufficient dispersibilities of the three resins in PAA-bonded CDA.

Based on the above results and considering a proper structure of PAA-bonded CDA, which is different from conventional cellulose resins such as CDA, we aimed at adding resins that can disperse in PAA-bonded CDA. The center
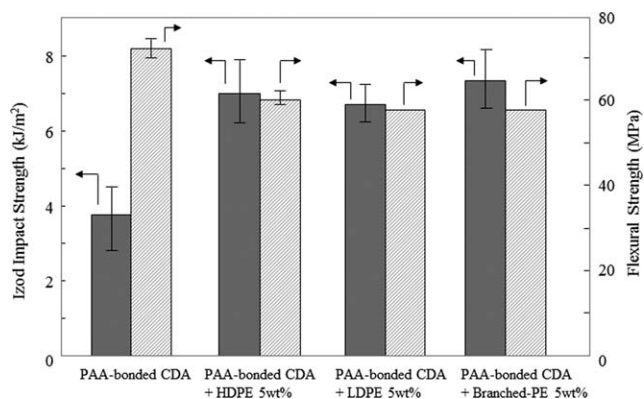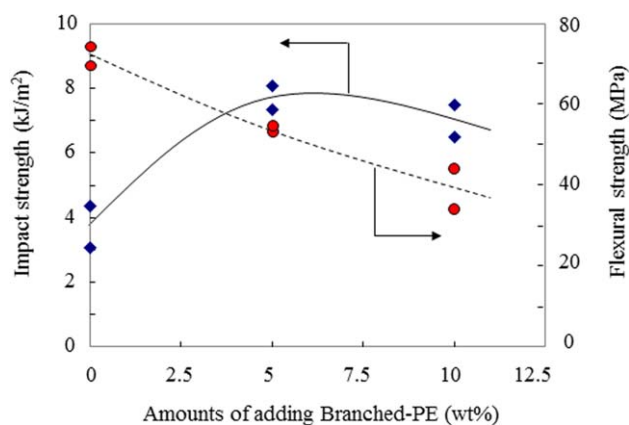


**Figure 3.** Impact strength and flexural strength of PAA-bonded CDA with PE.

structure of PAA-bonded CDA is hydrophilic resembling CDA, while the periphery structure of PAA-bonded CDA is extremely hydrophobic by adding alkyl long chains of the modified cardanols. Therefore, the total polarity of PAA-bonded CDA is hydrophobic (Figure 1). As shown in Table I,
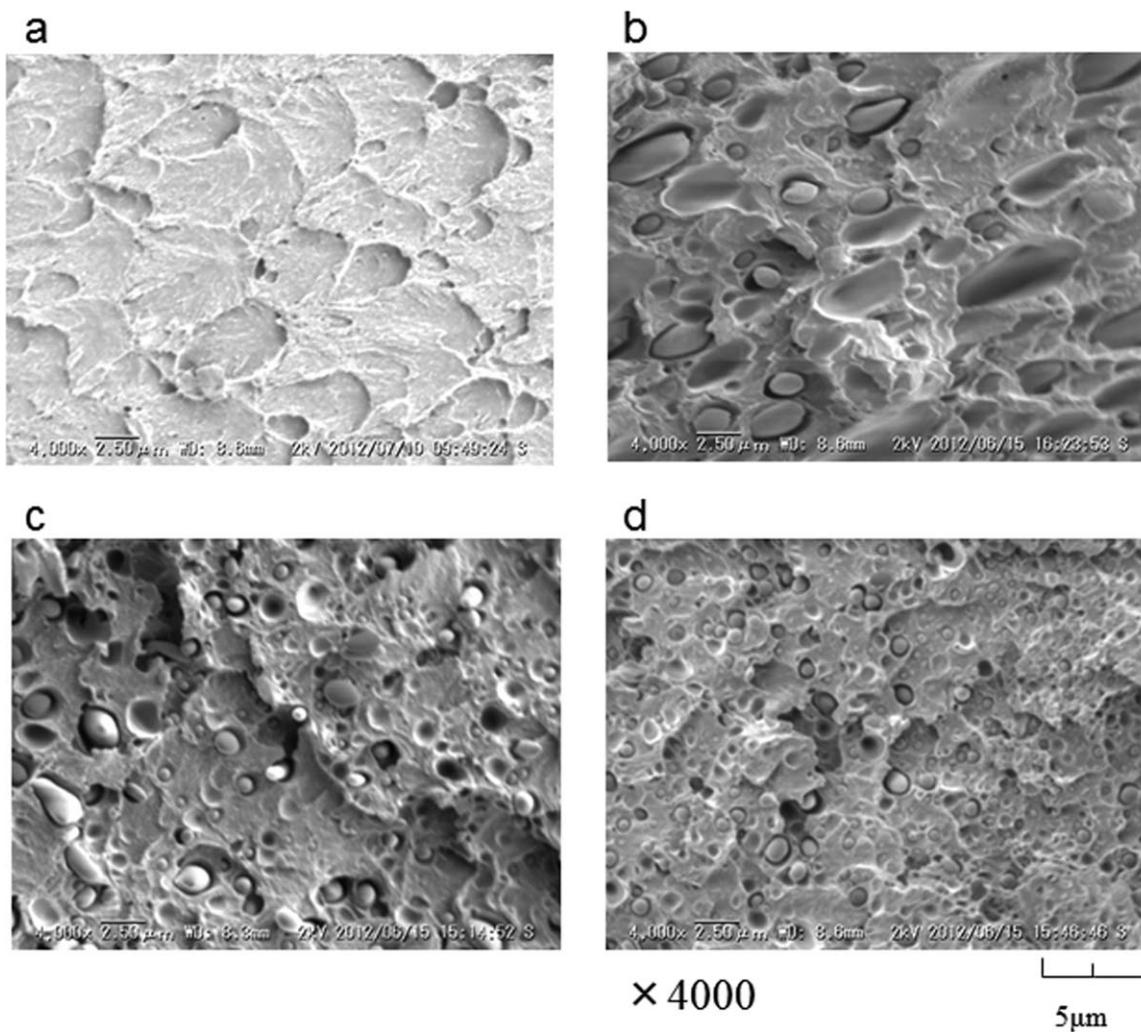


**Figure 4.** SEM images (4000 magnifications) of fracture surfaces of PAA-bonded CDA with PE after impact tests: (a) PAA-bonded CDA. (b) PAA-bonded CDA + HDPE 5 wt %. (c) PAA-bonded CDA + LDPE 5 wt %. (d) PAA-bonded CDA + Branched-PE 5 wt %.
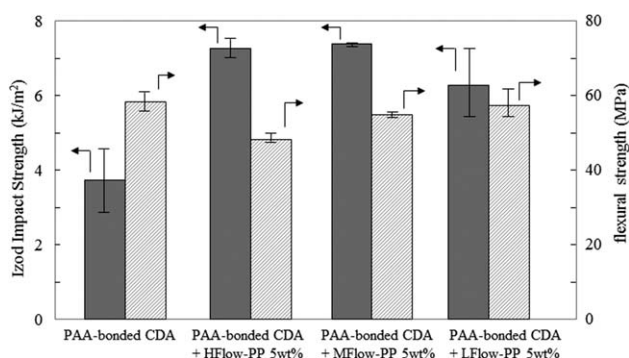
**Figure 5.** Impact strength and flexural strength of PAA-bonded CDA with Branched-PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the hydrophobicity of PAA-bonded CDA is obvious from its low water absorption (0.85 wt %), which is 1/20th of that of CDA (17.0 wt %).

For improving impact strength, therefore, we investigated the addition of hydrophobic olefin resins, which is expected to show high affinities to hydrophobic cardanol side chains. Several types of PE and PP were used as olefin resins. Table I lists the best results of adding representative olefin resins (Branched-PE, MFlow-PP), which showed high effectiveness in improving impact strength. In the near future, PE and PP will be able to be produced from plant sources; therefore, these resins have potential for use in the manufacture of bio-plastics. The detail results and discussions were described as follows.

**Addition of Several Types of PE**

The impact strength of compounds consisting of PAA-bonded CDA and 5 wt % of PE (HDPE, LDPE, Branched-PE) was drastically increased (Figure 3, >7 kJ/m$^2$). We observed the outside appearances of these compounds. The appearance of the compound with HDPE was opaque, and those of the compounds with LDPE and Branched-PE were translucent. Dispersibilities of LDPE and Branched-PE in PAA-bonded CDA were the most favorable.



**Figure 6.** Impact strength and flexural strength of PAA-bonded CDA with PP.
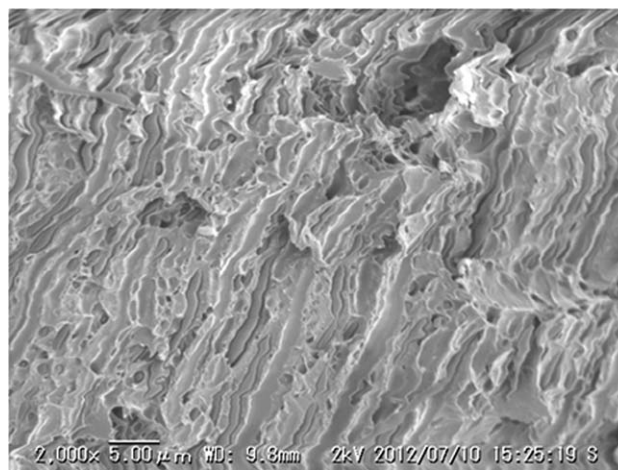


× 2000 ⊢—⊣ 5μm

**Figure 7.** SEM image (2000 magnifications) of fracture surface of PAA-bonded CDA with MFlow-PP after impact test.

When we observed fracture surfaces after the impact tests (Figure 4), the dispersing of PE particles could be observed for all three types of PE added to PAA-bonded CDA. Furthermore, many exfoliated interfaces between PAA-bonded CDA and PE particles were observed. From these images, Branched-PE showed the most uniform dispersibility in PAA-bonded CDA. The average diameters of the dispersed Branched-PE were under 2.5 μm.

Next, we estimated the impact and flexural strength by changing the amount of Branched-PE, which showed the most uniform dispersibility among the three types of PE (Figure 5). When the amount of Branched-PE was over 5 wt %, the impact strength tended to slightly decrease. Furthermore, by increasing the amount of Branched-PE, flexural strength also tended to decrease.

We discuss two effects for increasing impact strength by adding PE. The first is PE's deformation consuming the impact energy as heat, which is well known for adding elastomer and rubber particles in resins. The second is from moderate weak interfaces between PAA-bonded CDA and PE; therefore, the shearing deformation of PAA-bonded CDA prominently increased. This was obviously from the relatively high breaking strain (8%) of PAA-bonded CDA, and traces of shearing deformation on the surface of PAA-bonded CDA alone fractured by impact test [Figure 4(a)] were observed. Finally, we considered that the moderate adhering strength between PAA-bonded CDA and low modulus PE particles mainly resulted in the increase in shearing deformation of the matrix resin (PAA-bonded CDA).

In contrast, with increases in the amounts of Branched-PE and the other PE resins, the bending strength of the compounds with these PE resins decreased. We considered that these decreases were derived from the increases in the shearing deformations of PAA-bonded CDA by including deformable PE resins.
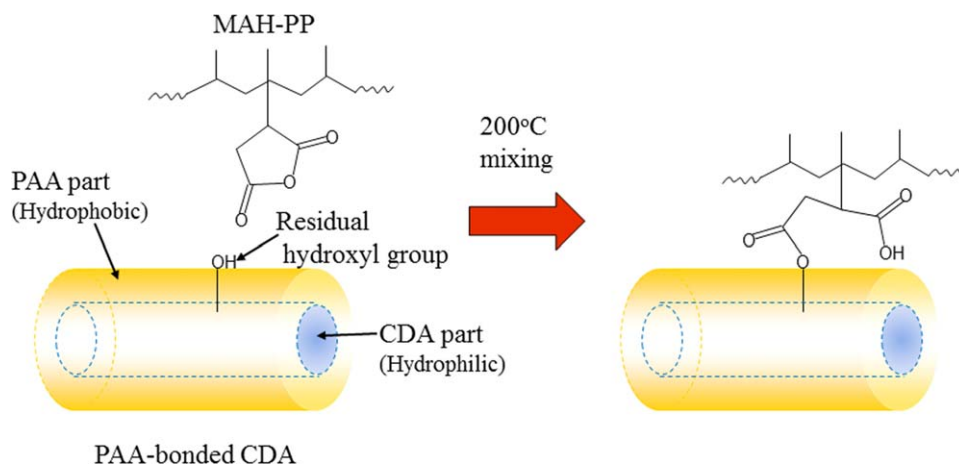
**Figure 8.** Reaction scheme of MAH-PP with residual hydroxyl group in PAA-bonded CDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Addition of Several Types of PP

We measured the impact strength of compounds consisting of the PAA-bonded CDA with several types of PP (HFlow-PP, LFlow-PP, and MFlow-PP). All these PP improved the impact strength of the compounds (Figure 6, >6 kJ/m$^2$). Furthermore, the outside appearances of these compounds with PP were transparent, and the dispersibilities were observed to be good.

By observing the fracture surfaces of compounds after the impact tests, dispersed liner PP domains can be seen on all three PP cases. Figure 7 shows the typical fracture surfaces of the compounds observed using SEM. From Figure 7, the same as with the compounds with PE, exfoliated-like interfaces between PAA-bonded CDA and the liner PP were clearly observed at many points of the fractured surfaces.

From these results, we consider two effects for increasing the impact strength by adding PP. The first is deformations of PP using the impact energy as heat. The Second is from moderate weak interfaces between PAA-bonded CDA and PP; therefore, the shearing deformation of PAA-bonded CDA prominently increased. From the dispersing morphology of PP, which is liner in PAA-bonded CDA, we considered that the liner PP behaved as rubber-like reinforced fibers.

### Effect of Interfaces Between PAA-Bonded CDA and Olefin Resins

As mentioned above, compounds that consisted of PAA-bonded CDA and olefin resins, such as PE or PP, showed higher impact strength than that of PAA-bonded CDA alone. At the many points of fracture surfaces of the compounds, exfoliated interfaces between PAA-bonded CDA and olefin resins could be observed using SEM. To investigate the effect of the interfacial adhesiveness between PAA-bonded CDA and olefin resins, we estimated the impact strength and observed the fracture surfaces of compounds consisting of PAA-bonded CDA and PP with different concentrations of maleic anhydride (MAH-PP), which can react with the residual hydroxyl groups (OH) of PAA-bonded CDA. Therefore, interfacial adhesiveness between PAA-bonded CDA and MAH-PP can be regulated (Figure 8). In a previous study, to improve impact strength of an alloy of PA6 and AS, as a compatibilizer, a copolymer of styrene and maleic
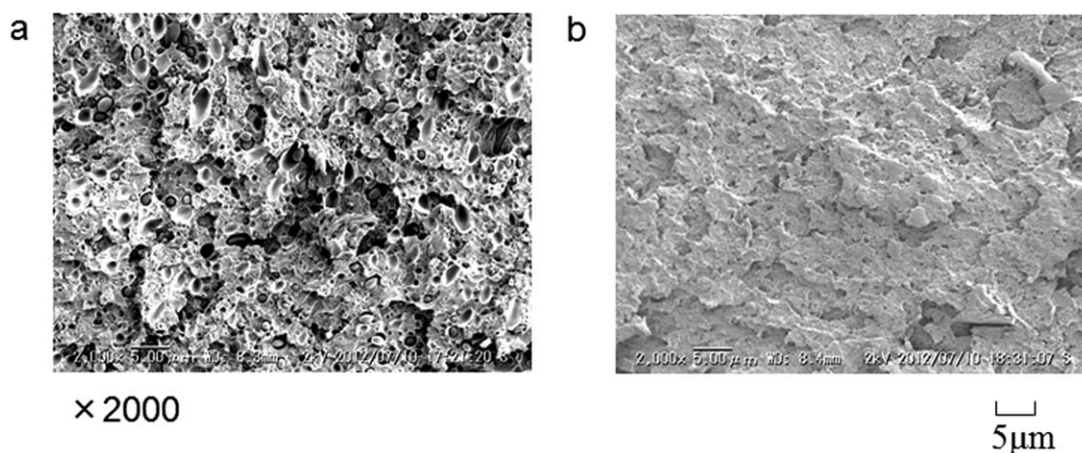


**Figure 9.** SEM images (2000 magnifications) of fracture surfaces of PAA-bonded CDA with MAH-PP after impact tests: (a) PAA-bonded CDA + MAH7-PP 5 wt %. (b) PAA-bonded CDA + MAH52-PP 5 wt %.
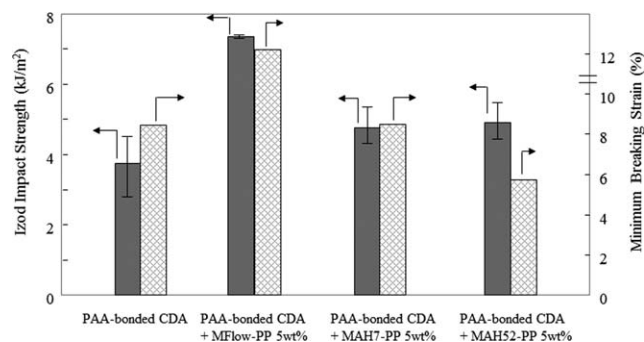
**Figure 10.** Impact strength and flexural strain of PAA-bonded CDA with MAH-PP.

anhydride was added to PA6 and AS for reinforcing the interfacial adhesiveness between PA6 and AS.[18] However, there were no examples for investigating the effect of interfacial adhesiveness between cardanol-bonded cellulose resin and additive resins.

As shown in Figure 9, with an increase in polarities (acid values) of MAH-PP (MAH7-PP; acid value: 7, MAH52-PP; acid value: 52), the points of the exfoliated interfaces between PAA-bonded CDA and MAH-PP disappeared. Consequently, as

shown in Figure 10, the impact strength and breaking strains of the PAA-bonded CDA with MAH-PP decreased.

We discuss the reason for the disappearance of the exfoliated interfaces as the polarities of MAH-PP increased. The disappearance was derived from an increase in interfacial adhesiveness due to partially reaction of the residual OH with MAH-PP; therefore, the dispersibilities of MAH-PP increased. As a result, it was difficult to observe shearing deformation in the PAA-bonded CDA with MAH-PP. Additionally, finer particle sizes of MAH-PP than that of PP alone decreased the effect for using impact energy by deformation, mainly resulting in that the impact strength of the PAA-bonded CDA with MAH-PP decreased.

With an increase in the polarities of MAH-PP, the breaking strains of compounds consisting of PAA-bonded CDA and MAH-PP decreased. As shown in Figure 8, hydrophilic parts such as ester bonding and carboxyl groups were generated by reacting residual OH of the PAA-bonded CDA with MAH-PP. These hydrophilic parts resulted in the increase in intermolecular interaction, such as hydrogen bonding; therefore, local areas, which show high intermolecular forces, can be created. Hence, bending stress is probably concentrated at the local areas.
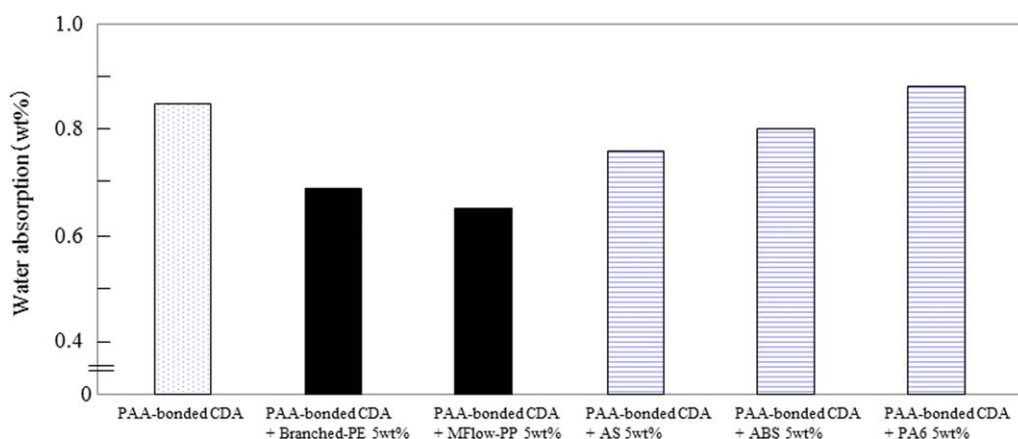


**Figure 11.** Water absorption of PAA-bonded CDA with polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
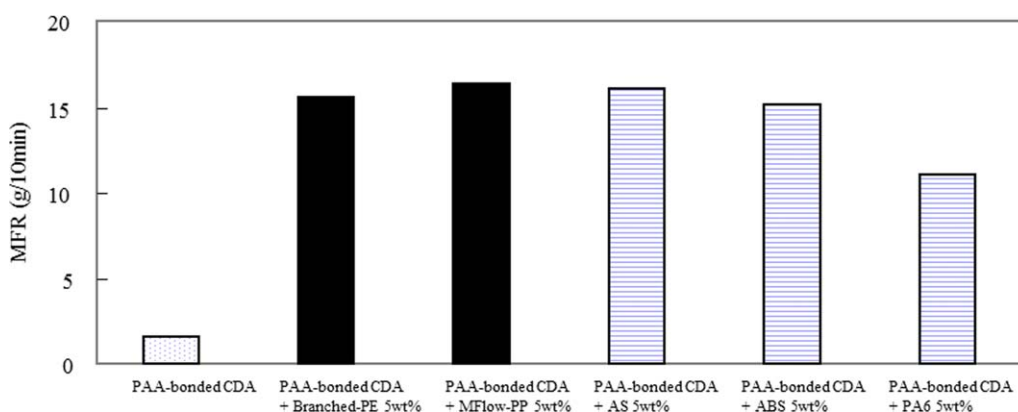


**Figure 12.** MFR of PAA-bonded CDA with polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Effects on Water Absorption and Fluidity by Adding Polymers

We measured the water absorption of the PAA-bonded CDA with 5 wt % of olefin resins. As shown in Figure 11, the addition of hydrophobic olefin resins showed the lowest water absorption and good water resistance. In contrast, only 5-wt % addition of PA6 with high polarity showed higher water absorption than that of PAA-bonded CDA alone.

As shown in Table I, compounds with all types of tested resins showed higher fluidity than that of PAA-bonded CDA alone. As shown in Figure 12, fluidities at low load (5 kgf) were about 10 times higher than that of PAA-bonded CDA alone. These higher fluidities resulted from the resins behaving as plasticizers at high temperatures (∼200°C) for measuring MFR.

### CONCLUSIONS

The impact strength of cardanol-bonded CDA (PAA-bonded CDA) was drastically increased by adding a small amount of olefin resins. In our past studies, PAA-bonded CDA indicated high practical properties such as bending strength, heat resistance, and water resistance. In contrast, its impact strength was not sufficient for use in durable products. In this study, improvement in the impact strength of PAA-bonded CDA was achieved by using hydrophobic olefin resins such as PE or PP, while satisfying good bending strength and breaking strain. Moreover, the addition of olefin resins improved water resistance and fluidity of the PAA-bonded CDA with olefin resins. We therefore conclude that the PAA-bonded CDA with olefin resins are thus promising cellulose-based bioplastics for use in various durable products requiring high impact strength and other practical properties.

### ACKNOWLEDGMENTS

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