

## Improvement in Impact Strength of Modified Cardanol-Bonded Cellulose Thermoplastic Resin by Adding Modified Silicones

Makoto Soyama, Yukihiro Kiuchi, Masatoshi Iji, Shukichi Tanaka, Kiyohiko Toyama

Smart Energy Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

Correspondence to: M. Soyama (E-mail: m-soyama@cj.jp.nec.com)

**ABSTRACT:** The impact strength of cellulose diacetate (CDA) bonded with a modified cardanol (3-pentadecylphenoxy acetic acid: PAA) was greatly improved up to 9 kJ/m<sup>2</sup> by adding a relatively small amount of modified silicones while suppressing a decrease in bending strength. In our recent research, this thermoplastic resin (PAA-bonded CDA) exhibited high rigidity, glass transition temperature, and water resistance. However, its impact strength was insufficient for use in durable products. Therefore, silicones modified with polyether, amino, and epoxy groups were investigated as possible ways to improve the impact strength. The results show that adding polyether-modified silicone (polyether silicone) with moderate polarity relative to PAA-bonded CDA resulted in shearing deformation greatly enhances its impact strength while maintaining other properties, including glass transition temperature ( $T_g$ ), water resistance, and thermoplasticity. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40366.

**KEYWORDS:** biopolymers & renewable polymers; composites; cellulose and other wood products

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### INTRODUCTION

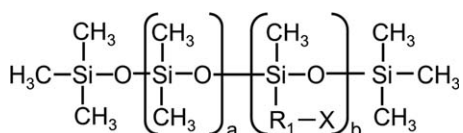
Bioplastics producing from plant sources have been studied with keen interest as environmentally friendly material that contributes to conserve petroleum and to fix carbon dioxide that causes global warming.<sup>1–3</sup> Currently, mass-produced bioplastics, such as polylactic acid (PLA)<sup>4,5</sup> and polyhydroxyalkanoate (PHA), are used as durable materials for automobiles and electronics, as well as consumer products such as textiles and tableware.<sup>6–11</sup> These bioplastics mainly use starch, which is produced from edible plants. Fears of future food shortages, however, are driving efforts to use inedible plant sources.

Cellulose, which is present in grasses, agricultural crops, trees, and aquatic plants, is the most abundant renewable raw inedible material on Earth. Since cellulose has strong hydrogen bonds between molecules, it is difficult to thermally plasticize and mold. To solve these problems, a number of researchers have attempted heat plasticization by synthesizing cellulose derivatives such as cellulose acetate (CA) and cellulose acetate propionate (CAP), and by adding large amounts of plasticizers. CA and CAP are including short-chain fatty acids such as acetic and propionic acids bonded to hydroxyl groups of cellulose. However, CA and CAP are able to absorb large amounts of water, and this has so far limited their use in durable products. Furthermore, adding a large amount of plasticizers reduces rigidity and glass transition temperature of these cellulose derivatives. As a way of avoiding these problems, an advanced cellu-

lose diacetate (CDA) resin bonding cardanol, which is a principal organic ingredient in cashew nut shells, has been produced. Cardanol is a uniquely structured phenol derivative with a linear alkyl side chain, and it is hydrophobic and flexible. Esterification of the modified cardanol (3-pentadecylphenoxy acetic acid: PAA) and CDA results in a thermoplastic PAA-bonded CDA resin, which has excellent properties such as rigidity, glass transition temperature, and water resistance.<sup>12,13</sup> However, this PAA-bonded CDA has insufficient impact strength for use in durable products.

High-impact-strength polymers withstand impacts through shearing and crazing deformations. Some plasticizers and silicones increase the mobility of polymers to shear deformations, which absorb the energy of an impact.<sup>14–24</sup> Crazing deformations mainly occur in thermoplastics including rubber particles such as acrylonitrile butadiene styrene (ABS) and lead to an observable whitened area on the fracture surface. This is a typical response to rubber toughening, where crazes are initiated at the surfaces of the rubber particles and absorb the energy of an impact.<sup>25</sup>

Using external plasticizers, such as diethyl sebacate, dihexyl phthalate, and ethyl hexanoate, improve the impact strength of cellulose derivatives,<sup>26</sup> but these plasticizers decrease rigidity and glass transition temperature. Furthermore, these plasticizers are usually used in large amounts, and as a result, they might migrate to the surfaces of polymers when they are used under high temperatures.<sup>27,28</sup>



**Figure 1.** Structures of tested silicones. Dimethyl silicone (D-Si):  $b = 0$  Polyether silicone (PE-Si):  $R_1 = (\text{CH}_2)_3$ ,  $X = \text{O}-(\text{C}_2\text{H}_4\text{O})_c - (\text{C}_3\text{H}_6\text{O})_d - \text{R}_2$ ,  $R_2 = \text{H}, -\text{CH}_3, -\text{C}_4\text{H}_9, -\text{COCH}_3$ . Epoxy silicone (E-Si):  $X = \text{O}-\text{CH}_2\text{CH}(\text{O})\text{CH}_2$ . Amino silicone (A-Si):  $X = \text{NH}-\text{CH}_2-\text{NH}_2$ .

It is easy to adjust of the polarity of highly flexible silicones, such as polydimethylsiloxane derivatives, by adding polar functional groups to their structures. Because of this, silicones modified with these groups have been used in polymers such as epoxy resin and polyester resin to improve their impact strength by adequately controlling their dispersions in the polymers.<sup>29,30</sup> However, there have been few studies on improving the impact strength of cellulose derivatives by adding silicones. It has been assumed that typical silicones with low polarity have trouble dispersing in cellulose derivatives with high polarity. However, the polarity of PAA-bonded CDA is lower than that of cellulose derivatives such as CA and CAP because PAA-bonded CDA contains cardanol with low polarity. Therefore, we tried to enhance the impact strength of PAA-bonded CDA by using modified silicones that had various polarities by including polar groups (polyether, amino, and epoxy groups) with various concentrations and viscosities. Furthermore, the dispersed particle diameter of polyether silicone in PAA-bonded CDA, effects on impact strength of the composites was investigated.

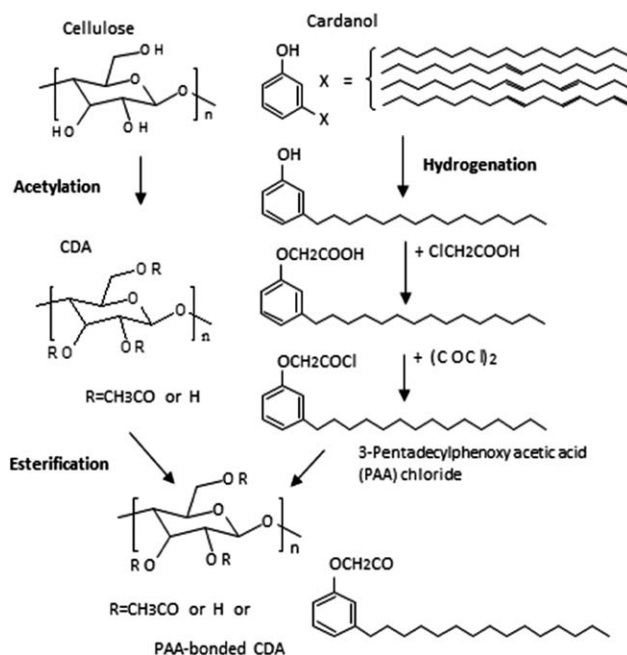
## EXPERIMENTAL

### Materials

CDA [LM-80; degree of substitution (DS\*) of acetic acid: 2.1; viscosity: 200 mPa·s/ 6 wt % in acetone] was supplied by Daicel Chemical Industries (Japan) (\*DS: ratio of replacing three

**Table I.** Properties of Tested Silicones

Silicone name	Viscosity [25°C] (mm <sup>2</sup> /s)	Hydrophile-lipophile balance (HLB)	Functional equivalent (g/mol)	Functional group
D-Si	200	-	-	none
PE-Si5	900	5	-	Polyether
PE-Si6	110	6	-	Polyether
PE-Si7a	1200	7	-	Polyether
PE-Si7b	1300	7	-	Polyether
PE-Si8	3500	8	-	Polyether
PE-Si10	920	10	-	Polyether
PE-Si13	390	13	-	Polyether
PE-Si14	1000	14	-	Polyether
A-Si-H	70	-	350	Amino
A-Si-M	1300	-	600	Amino
A-Si-L	1500	-	3800	Amino
E-Si-H	1500	-	350	Epoxy
E-Si-L	17000	-	3500	Epoxy



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

hydroxide groups in one glucose unit in cellulose with acetic acids). Hydrogenated cardanol (m-n-pentadecyl phenol), in which the unsaturated bonds in the alkyl side chain were changed to saturated ones by adding hydrogen, was supplied by Acros Organics Co. The change ratio was more than 99 wt %, as measured by Acros Organics. 1, 4-dioxane and methanol were supplied by Kanto Chemical Co. (Japan) and used as the reaction and isolation solvent reagents without further purification. Triethyl amine also was supplied by Kanto Chemical Co. as catalysts.

Modified silicones (dimethyl silicones modified with polyether, amino, and epoxy groups) and a dimethyl silicone were prepared with the structure outlined in Figure 1 and the properties listed in Table I. Dimethyl silicones (polydimethylsiloxane : D-Si), dimethyl silicones modified with polyether group (PE-Si 5, 6, 7a, 7b, 8, 13, 14) and dimethyl silicone modified with amino group (A-Si-M) were produced by TORAY Dow Corning Silicone Co. Dimethyl silicones modified with polyether group (PE-Si 10), dimethyl silicones modified with epoxy group (E-Si-H, L), and dimethyl silicones modified with amino group (A-Si-H, A-Si-L) were produced by Shin-Etsu Chemical Co. The hydrophile-lipophile balance (HLB), which shows the polarity of a polyether silicone, was calculated by using eq. (1). The epoxy and amino equivalents were measured in accordance with the ISO 3001 and ISO 3771 standard test method.

$$\text{HLB} = 20 \times M_h / M \quad (1)$$

$M_h$  is the sum of molecular mass of the hydrophilic portion of the molecule and  $M$  is the molecular mass of the whole molecule (polyether silicone).

The plasticizer: triethyl citrate TEC for CDA was supplied by Pfizer. PLA (TE-4000) was supplied by Unitika (Japan). PA11: poly11-aminoundecanoic acid (RilsanBMFO) was supplied by

**Table II.** Properties of PAA-bonded CDA Composites with Silicones

Sample	Compatibility of compound <sup>a</sup>	Impact strength (kJ/m <sup>2</sup> )	Standard deviations of the impact strength	Bending Strength (MPa)
PAA-bonded CDA	-	3.2	0.89	62
PAA-bonded CDA composite				
with 5wt% of D-Si	Bleed	IM <sup>b</sup>	-	IM <sup>b</sup>
with 5wt% of PE-Si5	Bleed	IM <sup>b</sup>	-	IM <sup>b</sup>
with 5wt% of PE-Si6	Poor	5.4	0.73	49
with 5wt% of PE-Si7a	Moderate	9.1	1.30	47
with 5wt% of PE-Si7b	Moderate	7.7	0.40	47
with 5wt% of PE-Si8	Moderate	7.8	0.97	47
with 5wt% of PE-Si 10	Good	5.9	0.73	49
with 5wt% of PE-Si 13	Good	5.9	0.83	47
with 5wt% of PE-Si 14	Poor	IM <sup>b</sup>	-	IM <sup>b</sup>
with 5wt% of A-Si-H	Moderate	5.6	0.46	55
with 5wt% of A-Si-M	Poor	6.5	0.50	53
with 5wt% of A-Si-L	Bleed	IM <sup>b</sup>	-	IM <sup>b</sup>
with 5wt% of E-Si-H	Bleed	IM <sup>b</sup>	-	IM <sup>b</sup>
with 5wt% of E-Si-L	Bleed	IM <sup>b</sup>	-	IM <sup>b</sup>

<sup>a</sup> Good: <0.1  $\mu\text{m}$ , Moderate: 0.1–0.5  $\mu\text{m}$ , Poor: >0.5  $\mu\text{m}$ , Bleed: Silicone migration.

<sup>b</sup> IM: Impossible to measure.

Arkema Japan (Japan). ABS resin (GA-701) was supplied by Nippon A&L Co. (Japan).

#### Preparation of PAA-bonded CDA

PAA-bonded CDA was prepared using the same method as described in the article by Iji et al. (Figure 2).<sup>12</sup> That is, CDA (LM-80) (10.0 g) was dissolved in dehydrated 1, 4-dioxane (200 mL) by stirring at 100°C under a dry nitrogen atmosphere. After cooling to room temperature, 5.0 mL (0.036 mol) of triethyl amine was added as an acid scavenger. Then, a solution of chloride cardanoxy acetic acid (9.4 g, 0.025 mol) in dehydrated 1, 4-dioxane (100 mL) was slowly added dropwise, and the mixture was refluxed for 5 h under a nitrogen atmosphere for their bonding reaction. The reaction solution was poured into 1.5 L of methanol while it was being vigorously stirred to isolate a solid. The solid was filtered by suction filtration and washed three times with 0.3 L of methanol. The resultant product was dried overnight at room temperature and dried under a vacuum for 5 h at 105°C to obtain the target PAA-bonded CDA (yield about 96%). The final product (PAA-bonded CDA) was determined by using the <sup>1</sup>H-NMR spectrometer. The DS of the PAA was calculated by 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 0.47. The molecular weight of the PAA-bonded CDA was estimated by using a gel permeation chromatography (GPC: Shimadzu LC-VP system with a Shim-pack GPC-8025C and GPC-80MC column, Shimadzu Co., Japan), calibrated by using polystyrene standards (solvent: chloroform). The average molecular weight ( $M_n$ ) of the PAA-bonded CDA was about 120,000.

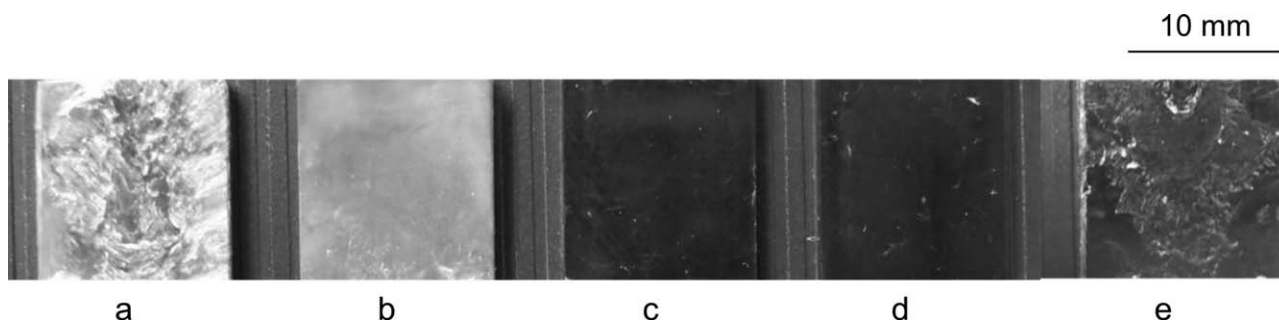
#### Preparation of Test Specimens

Sample composites were prepared by mechanically kneading PAA-bonded CDA and 1–5 wt % of modified silicones using an extruder (Haake MiniLab, Thermo Electron Co., Germany) at 200  $\pm$  5°C. Each sample was kept for 5 h in a 105°C preheated oven before injection-molding to remove humidity. For the mechanical tests, PAA-bonded CDA and its derivatives with additional components, such as modified silicones, were molded into test pieces by using an injection-molding machine (Haake Mini Jet II, Thermo Fisher Scientific Co., Germany). The temperature of the molten pellets was 200–210°C and that of the mold was 110  $\pm$  5°C. The injection pressure was 70–120 MPa, and the pressure was subsequently kept at 40 MPa for 5 s.

#### Measurements

The mechanical characteristics of the molded samples were measured in bending tests conducted in accordance with the ASTM D790 on a universal testing machine (Instron 5567, Instron Co., cross-head speed: 0.85 mm/min; span: 32 mm) at room temperature. The test pieces of the molded samples in the bending test were 2.4-mm thick, 80-mm long, and 12.4-mm wide. An Izod-impact test was conducted in accordance with the JIS K7110 by using an impact testing instrument (Universal Impact Tester C1, Toyo Seiki Seisaku-sho, Ltd., Japan; pendulum: 2.75 J; upswing angle: 150°). The test pieces with notches were 2.4-mm thick, 80-mm long, and 12.4-mm wide. The impact resistance was calculated in accordance with the JIS K7110 standard test method.

To measure the glass transition temperature ( $T_g$ ) of the resulting resin samples, differential scanning calorimetric (DSC) analysis of the samples was conducted using a differential scanning calorimeter (DSC 6200/EXSTAR6000; Seiko Instrument Inc., Japan).



**Figure 3.** Appearance of PAA-bonded CDA composites with polyether silicones. (a) PAA-bonded CDA composite with 5 wt % of PE-Si5:HLB = 5 (b) with 5 wt % of PE-Si6:HLB = 6 (c) with 5 wt % of PE-Si7:HLB = 7 (d) with 5 wt % of PE-Si13:HLB = 13 (e) With 5 wt % of PE-Si14:HLB = 14.

The same thermal history as before the measurement was performed by heating each sample from  $-100$  to  $230^{\circ}\text{C}$  at a scanning rate of  $10^{\circ}\text{C}$  per minute, then keeping it at  $230^{\circ}\text{C}$  for 3 min, and finally quenching it to room temperature.

Water resistance was evaluated by calculating the water absorption ratios of the molded samples of the bending test by measuring them before and after soaking them for 24 h in distilled water at room temperature.

The melt flow rate (MFR), which is the weight of a melted sample passing through the capillary (size:  $10\text{ mm} \times 2\text{ mm}\phi$ ) in 10 minutes, was estimated by using a capillary rheometer (CFT-500D; Shimadzu Co., Japan) at  $200^{\circ}\text{C}$  with a  $500\text{-kgf/cm}^2$  load. Each sample was kept for 5 h in a  $105^{\circ}\text{C}$  preheated oven before the MFR test to remove humidity.

The appearance of the molded samples was observed with a digital microscope (KEYENCE, VHX-500F). The fracture surfaces of the molded samples after the impact test were observed with a scanning electron microscope (KEYENCE, VE-7800).

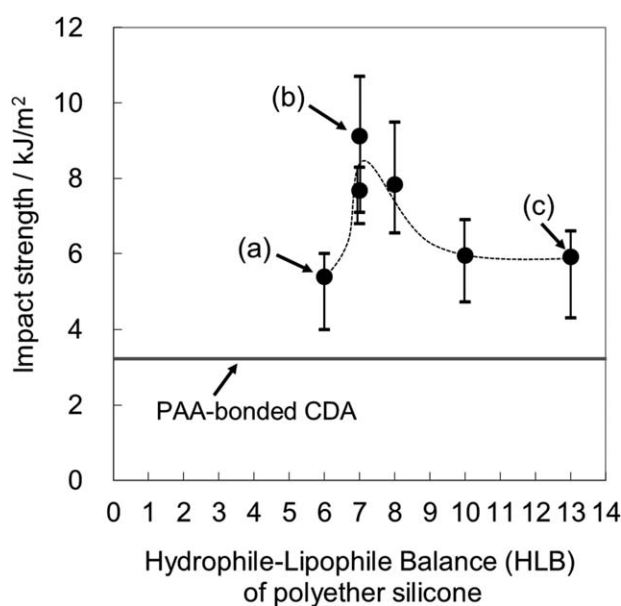
## RESULTS AND DISCUSSION

### Characteristics of PAA-bonded CDA after Adding Modified Silicones with Various Polar Groups

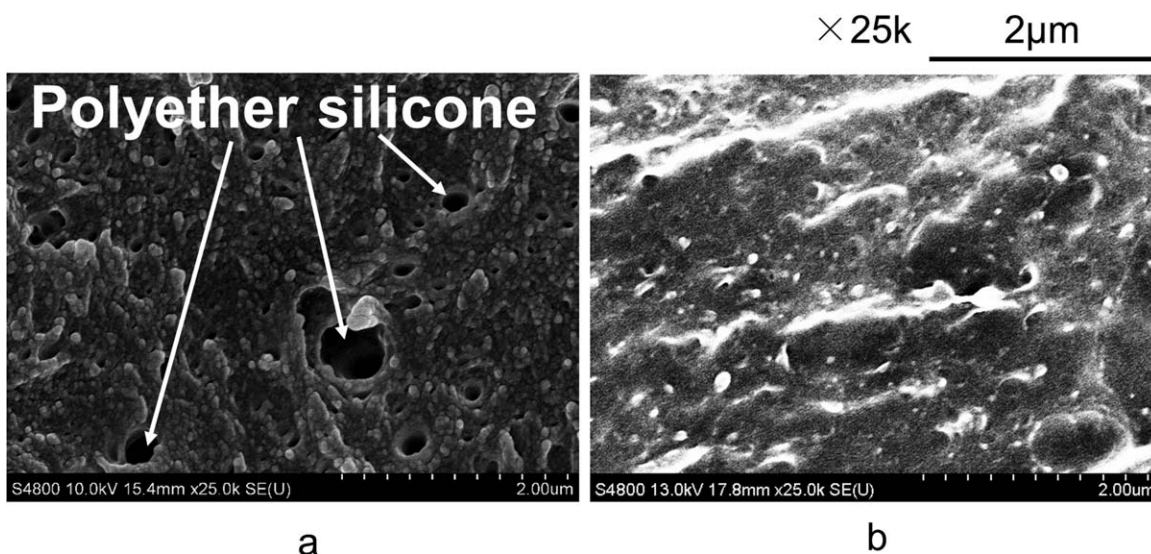
As the characteristics of PAA-bonded CDA composites with modified silicones, their mechanical properties (impact strength and maximum bending strength), and the dispersion of these silicones in the PAA-bonded CDA composites were investigated. A dimethyl silicone (polydimethylsiloxane: D-Si: 5 wt %) without a polar group migrated to the surface of the PAA-bonded CDA composite with D-Si (Table II). Since the dimethyl silicone was lower in polarity than the PAA-bonded CDA, the dimethyl silicone could not be uniformly dispersed in the PAA-bonded CDA composite. Modified silicones composed of dimethyl silicone and functional groups such as polyether, amino, and epoxy groups were used to enhance the dispersion of the silicones. As a result, adding dimethyl silicones with polyether group (polyether silicones: PE-Si) with relatively high polarity tended to disperse uniformly in the PAA-bonded CDA composite and greatly improved the impact strength of the PAA-bonded CDA. The silicones did not migrate to the surfaces of the PAA-bonded CDA composites with PE-Si during molding the composites. The dispersion of PE-Si in PAA-bonded CDA composite was affected by the polarity of PE-Si, which depended on the concentration of the polyether group in the PE-Si. That is,

PE-Si with relatively higher polarity became highly dispersed in the PAA-bonded CDA composite. In particular, adding PE-Si 7 (an HLB of 7) and PE-Si 8 (an HLB of 8) improved the impact strength of the PAA-bonded CDA the most (Table II).

Adding amino silicones with middle and high concentrated amino group, that is, A-Si-M with an amino equivalent of  $600\text{ g/mol}$  and A-Si-H with an amino equivalent of  $350\text{ g/mol}$ , improved the impact strength of PAA-bonded CDA. However, the amino silicone with low concentration of amino groups, that is, A-Si-L with an amino equivalent of  $3800\text{ g/mol}$ , bled to the surface of the PAA-bonded CDA composite with A-Si-L. The reason is that the polarity of A-Si-L was not as high as that of PAA-bonded CDA. In comparison, epoxy silicones migrated to the surfaces of the PAA-bonded CDA composites with the epoxy silicones, regardless of the concentrations of epoxy group, that is, E-Si-H with an epoxy equivalent of  $350\text{ g/mol}$  and E-Si-L with an epoxy equivalent of  $3500\text{ g/mol}$ . This occurred because the epoxy group had low polarity compared with the polyether or amino group.



**Figure 4.** Effects of HLB of polyether silicone on impact strength of PAA-bonded CDA composites with polyether silicones. (a) PAA-bonded CDA composite with 5 wt % of PE-Si6:HLB = 6 (b) with 5 wt % of PE-Si 7a:HLB = 7 (c) with 5 wt % of PE-Si13:HLB = 13.



**Figure 5.** Scanning electron microscope image of PAA-bonded CDA composite with polyether silicones. (a) PAA-bonded CDA composite with 5 wt % of PE-Si 7a:HLB = 7 (b) with 5 wt % of PE-Si13:HLB = 13.

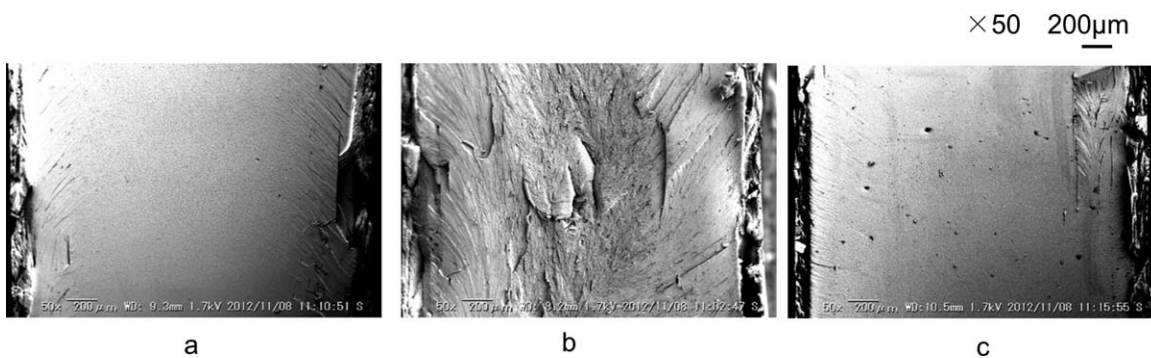
#### Effects of Amounts and Structure of Polyether Silicones on Impact Strength of PAA-bonded CDA

The polyether silicones that were optimized in terms of their amount, polarity, and viscosity enhanced the impact strength of the PAA-bonded CDA composites. Figures 3 and 4 show the mold surface and the impact strength of PAA-bonded CDA composites after adding the polyether silicones with different polarities (HLBs: from 5 to 14). These results indicate that adding the polyether silicones with HLBs from 6 to 13 (PE-Si6 to PE-Si 13) enhanced the impact strength of the PAA-bonded CDA and there was no silicone migration on the composites' surfaces. Adding PE-Si 7 and PE-Si 8 (polyether silicones with HLBs of 7 and 8) improved the impact strength of the PAA-bonded CDA the most, and its appearance was almost transparent.

It is known that crazing and shearing deformations enhance the impact strength of polymers. The impact strength of polymers, such as acrylonitrile-butadiene-styrene (ABS), has been enhanced by the inclusion of fine flexible domains made of elastomeric particles.<sup>31</sup> Crazing deformations tend to occur when elastomeric particles with moderate particle diameters (0.3–1.5  $\mu\text{m}$ ) are

dispersed in polymers. In comparison, smaller elastomeric particles (< 0.3  $\mu\text{m}$ ) are more likely to induce shearing deformation.

Therefore, we studied the dispersion of the polyether silicones (5 wt %) with HLBs from 6 to 13 (PE-Si 6 to PE-Si 13) in the PAA-bonded CDA composites. The polyether silicone with an HLB of 6 (PE-Si 6) was of micron-order size ( $>0.5 \mu\text{m}$ ) in the PAA-bonded CDA composite. The appearance of the PAA-bonded CDA composite with PE-Si 6 was translucent and it had a relatively low impact strength [Figures 3(b) and 4(a)]. The particles of polyether silicones with moderate concentration of polyether groups (PE-Si 7 with an HLB of 7 and PE-Si 8 with an HLB of 8) were also of submicron-order size (0.1–0.5  $\mu\text{m}$ ) as shown in Figure 5(a). These composites were almost transparent and had high impact strength [Figures 3(c) and 4(b)]. In addition, although the fracture cross sections of the PAA-bonded CDA before adding the silicones had a flat surface [Figure 6(a)], those of the PAA-bonded CDA composites with 5 wt % of PE-Si 7 [Figure 6(b)] and PE-Si 8 had corrugated surfaces due to shearing deformations. Moreover, whitened areas were observed in these fracture cross sections. It showed that when the test pieces were destroyed, stress concentrated on



**Figure 6.** Scanning electron microscope images of fracture surfaces. (a) PAA-bonded CDA (3  $\text{kJ}/\text{m}^2$ ) (b) PAA-bonded CDA composite with 5 wt % of PE-Si 7a:HLB = 7 (8  $\text{kJ}/\text{m}^2$ ) (c) with 5 wt % of PE-Si13:HLB = 13 (5  $\text{kJ}/\text{m}^2$ ).

the silicones with low elasticity and crazing deformations occurred. These results suggest that adding 5 wt % of PE-Si 7 and PE-Si 8 to PAA-bonded CDA resulted in both shearing and crazing deformations and increased the impact strength of the composites. The polyether silicones with the high concentrated polyether group (PE-Si 10 with an HLB of 10 and PE-Si 13 with an HLB of 13) were highly dispersed ( $<0.1 \mu\text{m}$ ) as shown in Figure 5(b). These composites were transparent. However, fracture cross sections did not have any whitened or flat surfaces [Figures 3(d) and 6(c)]. That is, crazing and shearing deformations rarely occurred in the fracture cross sections of these composites. The PAA-bonded CDA composites with PE-Si 10 and PE-Si 13 had relatively low impact strength [Figure 4(c)]. In comparison, the polyether silicone with an HLB of 5 (PE-Si 5), in which the concentration of the polyether group was low, bled to the surface of the PAA-bonded CDA composite [Figure 3(a)]. The polyether silicone with an HLB of 14 (PE-Si 14), in which the concentration of the polyether group was high, could not disperse uniformly in the PAA-bonded CDA composite [Figure 3(e)].

The effect of varying the amount of the most effective polyether silicone (PE-Si 7a : polyether silicones with an HLB of 7 and viscosity of  $1200 \text{ mm}^2/\text{s}$ ) on the impact strength, maximum bending strength, elastic modulus, elongation, thermoplasticity (in terms of MFR), and water resistance (in terms of water absorption ratio) were investigated. As shown in Table III and Figure 7, adding even 1 wt % of the polyether silicone (PE-Si 7a) improved the impact strength of PAA-bonded CDA. Additionally, reducing the amount of the polyether silicone suppressed the decrease in the bending strength and modulus of the PAA-bonded CDA composites. Although no whitened areas were observed in the fracture cross section of the composite with 1 wt % of PE-Si 7a, in which the silicone particles were  $0.1 \mu\text{m}$ , there were a large number of corrugations. These results indicate that adding 1 wt % of PE-Si 7a resulted in shearing deformation but no crazing deformation. The impact strength of the PAA-bonded CDA increased as the result of the shearing deformation.

The PAA-bonded CDA composites containing the polyether silicone were compared with reference current plastics, including a CDA composite with plasticizer (TEC), PLA: a mass-produced bioplastic derived from corn starch, Polyamide 11 (PA11): a bioplastic derived from castor beans used in durable products, and acrylonitrile-butadiene-styrene (ABS) resin: a petroleum-based plastic used in durable products.

Table III lists the impact strength, glass transition temperature ( $T_g$ ), water resistance (water absorption), maximum bending strength, and thermoplasticity (MFR) of the PAA-bonded CDA composites with 0–5 wt % of PE-Si 7a, the CDA composite with plasticizer (29 wt %), PLA, PA11, and ABS resin. Although the PAA-bonded CDA without PE-Si had a lower impact strength compared with PLA, the PAA-bonded CDA composites with 1–5 wt % of PE-Si 7a were higher in impact strength than PLA and were nearly equal in strength to PA11 and the CDA composite with plasticizer. The glass transition temperature ( $T_g$ ) of the PAA-bonded CDA composites with 1–5 wt % of PE-Si 7a was particularly higher than that of the CDA composite with

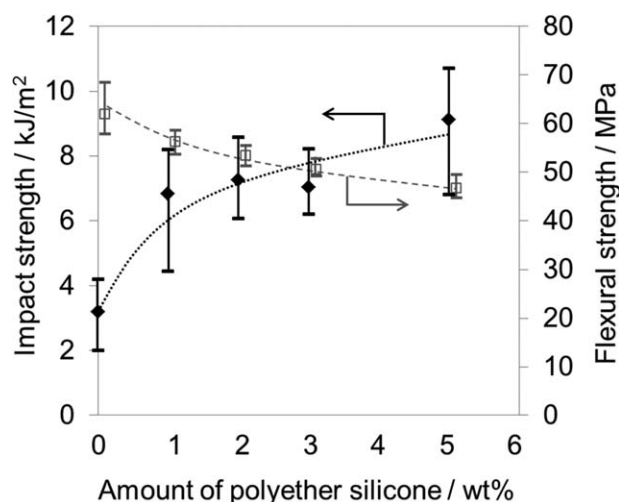
**Table III.** Characteristics of PAA-bonded CDA with Polyether Silicone: PE-Si 7a (HLB = 7,  $1200 \text{ mm}^2/\text{s}$ ) and References

Sample	Compatibility of Compound <sup>a</sup>	Impact strength ( $\text{kJ}/\text{m}^2$ )	Standard deviations of the impact strength	Tg ( $^{\circ}\text{C}$ )	Strength (MPa)	Bending test		Water absorption (%)	Melt flow rate ( $\text{g}/10 \text{ min}$ )
						Modulus (GPa)	Breaking Strain (%)		
Cellulose diacetate (CDA) <sup>b</sup>	-	-	-	227	-	-	-	17.0	-
PAA-bonded CDA	-	3.2	0.89	139	62	1.7	9.1	1.0	1011
PAA-bonded CDA composite with polyether silicone <sup>c</sup> 1wt%	Good	6.8	1.38	141	56	1.5	>10	1.0	1040
with polyether silicone <sup>c</sup> 2wt%	Good	7.3	0.95	140	54	1.5	>10	1.1	1073
with polyether silicone <sup>c</sup> 3wt%	Good	7.0	0.69	140	51	1.4	>10	1.1	1072
with polyether silicone <sup>c</sup> 5wt%	Moderate	9.1	1.30	138	47	1.4	>10	1.1	1094
CDA added with plasticizer (29wt%)	-	8.7	0.54	109	70	2.7	>10	5.9	960
Poly(lactic acid) (PLA)	-	4.4	0.48	60	93	4.4	2.3	0.4	1320
PA11	-	7.7	2.99	45	65	1.2	>10	0.3	1340
ABS resin	-	23.5	1.53	102	78	2.5	>10	0.5	1040

<sup>a</sup> Dispersion diameters of silicone; Good: $<0.1 \mu\text{m}$ , Moderated:  $0.1\text{--}0.5 \mu\text{m}$ .

<sup>b</sup> DS of acetic acid: 2.1.

<sup>c</sup> PE-Si7a:HLB= 7,  $1200 \text{ mm}^2/\text{s}$ .



**Figure 7.** Effects of amount of polyether silicone: PE-Si 7a (HLB = 7, 1200 mm<sup>2</sup>/s) on mechanical properties of PAA-bonded CDA composites with polyether silicones.

plasticizer and the other reference plastics. Their water resistance was superior to those of CDA and the CDA composite with plasticizer, as previously reported.<sup>12</sup> Moreover, the maximum bending strength of the PAA-bonded CDA composites with 1–2 wt % of PE-Si 7a was near that of PA11. Their thermoplasticity was comparable to those of the CDA composite with plasticizer and ABS resin.

## CONCLUSIONS

PAA-bonded CDA composites with sufficient impact strength and other good properties for durable products such as glass transition temperature ( $T_g$ ), water resistance and thermoplasticity were developed by adding polyether silicones while suppressing a decrease in bending strength. The polyether silicones with relatively high polarity became highly dispersed in the PAA-bonded CDA composites. The polyether silicones that were optimized in terms of their amount, polarity, and viscosity enhanced the impact strength of the PAA-bonded CDA composites. Compared with general plastics (the CDA composite with plasticizer, PLA, PA11, and ABS resin), the selected PAA-bonded CDA composites with the polyether silicones were higher in impact strength than PLA and were nearly equal in the impact strength to PA11 and the CDA composite with plasticizer. Their glass transition temperature was higher than that of the plastics. Furthermore, their other practical properties were comparable to or near those of the plastics. Therefore, PAA-bonded CDA composites with the polyether silicones are promising cellulose-based bioplastics for use in various durable products that require high impact strength and other practical properties.

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