Development of Cardanol-Bonded Cellulose Thermoplastics: High Productivity Achieved by Using Isocyanate-Modified Cardanol

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ABSTRACT: A highly efficient process of synthesizing a cardanol-bonded cellulose thermoplastic has been developed by using isocyanate-modified cardanol. As recently shown by us, the thermoplastic consisting of cellulose diacetate (CDA) and cardanol extracted from cashew nutshells performed high practical properties such as bending strength, heat resistance and water resistance. However, its synthesis process by esterification using acid chlorides of cardanol in a solvent as a common procedure, required high energy consumption by using a large amount of poor solvent to isolate the resulting product from the solvent. Using an isocyanate-modified cardanol, 3-penta-decylcyclohexyl (6-isocyanatohexyl) carbamate (PICC) greatly improved the productivity of the modified cardanol-bonded CDA (PICC-bonded CDA). After bonding PICC to CDA in a solvent, the remaining PICC coagulated and was easily removed by filtration, which resulted in remarkably simplifying the separation process of the product. The resulting PICC-bonded CDA showed insufficient thermoplasticity due to its high interaction between PICC parts. Additional bonding propionyl group improved the thermoplasticity while maintaining good thermal and mechanical properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1578–1587, 2013

INTRODUCTION

Increasing environmental awareness has accelerated research and development on bioplastics from renewable resources.[1–4] However, while current leading bioplastics primarily use feed grains as renewable plant resources, the possibility of future food shortages has emphasized the importance of using nonedible plant resources to produce bioplastics. Cellulose, which is widely present in grasses, agricultural crops, trees, and aquatic plants, is the most abundant renewable polymer in the world.[5,6] It is therefore important to broaden the present range of its applications.

Cellulose is a polysaccharide consisting of D-glucose units linked together by β1-4 glycosidic bonds into linear chains. Esterification is commonly used to produce thermoplastics from cellulose, mainly by using various acids such as acetic acid, propionic acid, and nitric acid.[7] Because of these cellulose derivatives' narrow windows between the melting and degradation temperatures, large amounts of external plasticizers such as diethyl phthalate, polyethylene glycol, and triethyl citrate (TEC) must be generally added.[8] However, adding the external plasticizers can reduce the maximum strength and heat resistance of cellulose ester composites.

To overcome this problem, numbers of researches have attempted thermoplasticization of cellulose by bonding long alkyl chain in various solvents that can dissolve cellulose and its derivatives. This has included esterification by carboxylic acids and their derivatives such as carboxylic anhydrides and carboxylic acid chlorides,[9,10] etherification by using alkyl halides with alkalis,[11] and graft polymerization from the hydroxyl groups on the glucose units.[12–15] However, as far as we know, no thermoplastic cellulose with long alkyl side chains has been manufactured due to its complicated process of synthesis, especially the process of separating final products by the precipitation using a large amount of poor solvent.

As a long alkyl chains combined with cellulose, we recently focused on cardanol, made of an inedible plant resource that could be stably supplied. It is a phenol derivative with a long unsaturated hydrocarbon chain and is extracted from discarded cashew nutshells. We have studied it for application to novel cardanol-bonded cellulose thermoplastics.[16,17] As can be seen from Figure 1, bonding cardanol derivatives, pentadecylphenoxy acetic acid (PAA), with cellulose diacetate (CDA) resulted in a bioplastic with good thermoplasticity, high strength, and high heat and water resistance, which were superior to those of

Additional Supporting Information may be found in the online version of this article.

conventional cellulose resins such as CDA with plasticizers. We demonstrated the possibility that the thermoplastic cellulose was used for durable products such as electric devices. However, the synthesis process was esterification by using carboxylic acid chloride of PAA (PAC). Although being a common procedure in esterification, this process was not practical due to the generation of equivalent moles of hydrochloride as byproduct, and the required large amounts of solvents to isolate the resulting pentadecylphenoxy acetate of CDA (PA-bonded CDA). It is therefore necessary to improve the productivity by developing a more practical and efficient process of synthesis.

Three conditions are necessary to develop an efficient process of synthesis: it needs to (1) have high degree of reactivity, (2) inhibit side reactions as much as possible, and (3) easily isolate final products. We focused on diisocyanate compounds as modifiers of cardanol. Diisocyanate compounds, which easily generate carbamate bonds to hydroxyl groups without any elimination of byproducts, are promising candidates to meet conditions (1) and (2).

Diisocyanate compounds are very important raw materials for polyurethanes such as foams and elastomers in practice. Diphenylmethane diisocyanate (MDI), tolylene diisocyanate (TDI), and hexamethylene diisocyanate (HDI) are manufactured in large quantities. As the study about chemical modification of cellulose by diisocyanate compounds, there have been some previous reports concerning cross-linked polyurethane,[18] and the surface treatment of cellulose acetate membranes.[19,20] There have been no reports, however, on cellulose thermoplastic resin.

The efficient process of synthesis is finally required to satisfy condition (3). If remaining raw materials coagulate in solution after reaction, we can simplify its separation and obtain the final products easily only by evaporating solvents. From among representative diisocyanate compounds, we selected HDI as a modifier for cardanol in this study because HDI-modified cardanol has possibility for coagulation with strong interactions resulted from its linear structure, and investigated whether using HDI-modified cardanol simplified the process of separating modified cardanol-bonded cellulose thermoplastics.

In this study, we reported an efficient process of synthesis for cardanol-bonded CDA by using HDI as a modifier for cardanol. It was revealed that HDI-modified cardanol, 3-pentadecylcyclohexyl (6-isocyanatohexyl) carbamate (PICC), shows high reactivity for residual hydroxyl groups on CDA, and the remaining PICC coagulates and is simply filtered after PICC bonds to CDA. We estimated the resulting PICC-bonded CDA, comparing with PA-bonded CDA. We also cleared that PICC-bonded CDAs thermoplasticity was decreased due to the strong interaction between the PICC parts and was improved by additional bonding of propionyl groups.

EXPERIMENTAL

Measurements

Nuclear magnetic resonance (NMR) spectra were obtained with a JEOL EX 400 MHz NMR spectrometer at ambient temperature. The infrared spectra were recorded on a Jasco FTIR-4100 spectrophotometer. The weight average molecular weight and the purity measured by GPC on a Shimadzu 10A-VP system; all the measurements were carried out at 40°C using polystyrene gel columns (Shimadzu Simpack GPC-80MC × 2, and GPC-8025C), and chloroform was used as an eluent at a flow rate of 1.0 mL min^{-1}. The purities of PICC-bonded cellulose derivatives were calculated from the peak ratios of main polymers with high molecular weights and impurities with low molecular weights on GPC charts. Differential scanning calorimetric (DSC) analyses were performed using a Seiko DSC6200/EXSTAR6000 apparatus. The samples were first heated from ambient temperature (25°C) to +230°C at a scanning rate of 10°C min^{-1} (first heating scan) and then immediately quenched to –100°C at a rate of 100°C min^{-1}. The second heating scans were run from –100 to +250°C at a scanning rate of 10°C min^{-1} to record stable thermograms. The data for the glass transition temperature (T_g) were obtained from the second run and corresponded to the midpoint of discontinuity in the heat flow. X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) patterns were recorded using a Shimadzu XRD-6100 and a Rigaku Kratky camera with a Ni-filtered Cu Kα radiation (wavelength 0.15148 nm). Polarized microphotographs were taken using a Keyence VHX-2000 digital microscope with cross polarizers equipped with a Mettler hot stage model FP82 and a temperature controller model FP90, where a small amount of a sample was placed between a slide glass and a coverslip.

All samples were more purified by reprecipitation by using relatively small amount of poor solvent before mechanical and other properties were measured to accurately measure the properties of PICC-bonded cellulose derivatives. The 10.0 g of resulted polymer was dissolved in chloroform (100 mL, 148 g). After the solution poured into hexane (200 mL, 131 g), precipitate was filtered and dried to obtain the purified sample.

Mechanical properties were characterized by bending measurements according to the ASTM D790 standard by using an INSTRON5567 testing system. The samples after the synthesis process were obtained as flakes. These flakes were fed to an injection molding machine. Bar-type specimens (2.4 × 80 × 12.4 mm^3) were molded using a Thermo Fisher Scientific HAAKE Minijet II injection molding machine operating at 210°C. The water resistance was evaluated by calculating the water absorption ratios of the molded samples by weighing them before and after they had been soaked for 24 h in distilled water at RT. The melt flow rate (MFR), which is the weight of a melted sample passing through a capillary in 10 min, was estimated by using a Shimadzu CFT-500D capillary rheometer at 180, 200, or 215°C with a 500 kgf cm^{-2} load; the capillary was 10mm long and 2mm in diameter. Each sample was kept for 5 h in an oven preheated to 105°C before the measurements were done to remove humidity.

DS Calculation

The DS values of the bonded PICC group (DS$_{PICC}$) were calculated from ^{1}H NMR spectra as follows. The representative ^{1}H NMR spectrum of PICC-bonded CDA was shown in the Supporting Information (Figure S1).
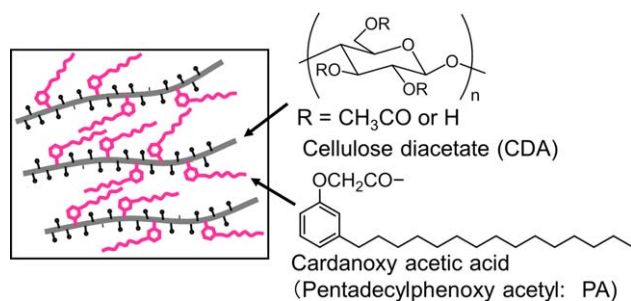
Figure 1. Molecular structure and schematic representation of PA-bonded CDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$DS_{PICC} = \frac{7 \times I_{\delta 0.85}}{(3 \times I_{\delta 3.3-5.4} - I_{\delta 0.85})} \quad (1)$$

where

$I_{\delta 0.85}$: integrals of the triplet peak at $\delta 0.85$ assigned to the protons of terminal methyl group in PICC

$I_{\delta 3.3-5.4}$: integrals of the multiple peaks from $\delta 3.3$ to $\delta 5.4$ including the protons of anhydroglucose unit (AGU) and the O-methine proton of cyclohexyl group in PICC

Materials

Two kinds of CDA (degree of substitution of acetyl groups (DS_{Ac}): 2.4 and 2.1) were supplied by Daicel (Japan). Cellulose acetate propionate (CAP, DS_{Ac}: 0.18, DS of propionyl groups (DS_{Pr}): 2.49) was supplied by Eastman Chemical Company (USA). Hydrogenated cardanol (3-pentadecylphenol), in which

the unsaturated bonds in the alkyl side chain were changed to saturated ones was purchased from ACROS Organics (USA), and used as received. HDI, propionic anhydride, acetonitrile, pyridine, methanol, and hexane were the analytical reagents and were used as supplied by Kanto Chemical (Japan) without further purification. The 2-butanone and 1,4-dioxane used as the reaction solvent, also supplied by Kanto Chemical, was dried with a molecular sieve (4A) for 24 h. Dibutyltin dilaurate and N,N-dimethylaminopyridine (DMAP) purchased from Aldrich Chemical Company (USA) were applied as catalysts.
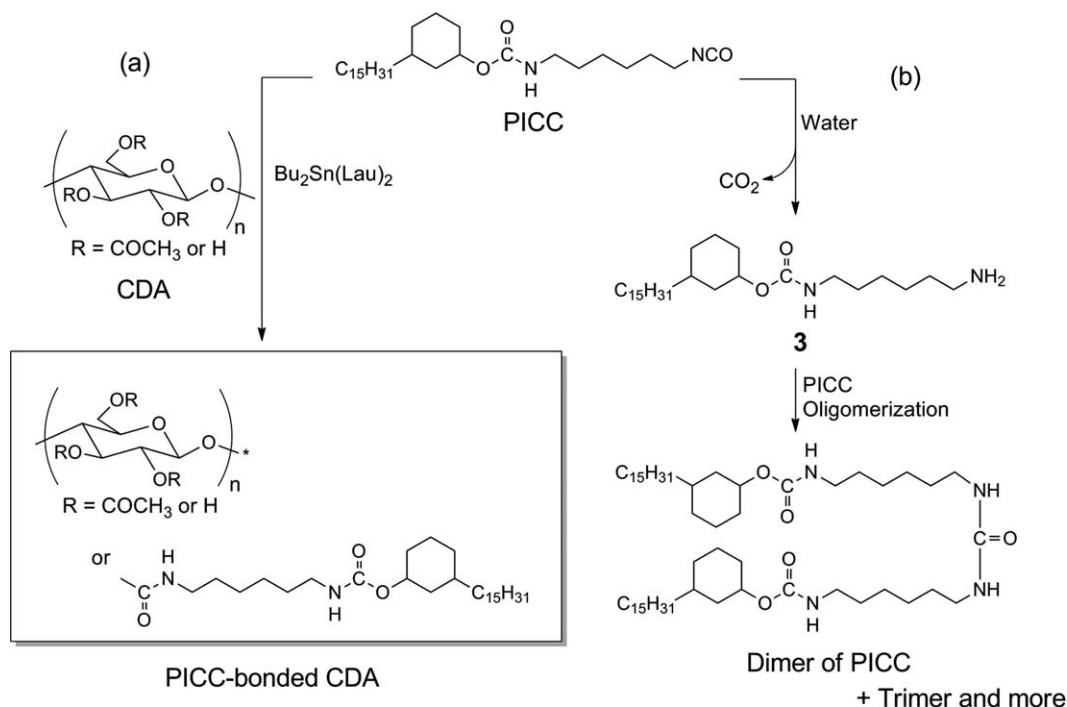
Synthesis

The synthesis of 3-pentadecylcyclohexanol, **1** is described in the Supporting Information.

3-Pentadecylcyclohexyl (6-Isocyanatohexyl) Carbamate (PICC)
PICC was synthesized as shown in Scheme 1(a). The 3-pentadecylcyclohexanol, **1**, (31.0 g, 0.10 mol) and hexamethylene diisocyanate (168.2 g, 1.00 mol) were mixed and stirred at 80°C for 3 h under a dry nitrogen atmosphere. The reacted mixture was poured into 500 mL of acetonitrile, generating a white solid precipitate. After cooling the solution including the precipitate at –24°C overnight to improve the yield, the precipitate was filtered and dried to provide the required product (yield 82%). The purity of the product that was obtained was 90% measured by gel permeation chromatography (GPC) on average; the main component of the impurities (7%) was bis(3-pentadecylcyclohexyl) hexane-1,6-diyldicarbamate, **2**. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, ppm): 0.9 (t, J = 6.8 Hz, ω-CH$_3$), 1.2–1.8 (m; alkyl), 2.0 (t, J = 13.2 Hz, α-CH$_2$), 3.2 (m, CH_2NHCOO), 3.3 (t, J = 6.4 Hz, CH$_2$NCO), 4.6 (br, CHOCO); IR
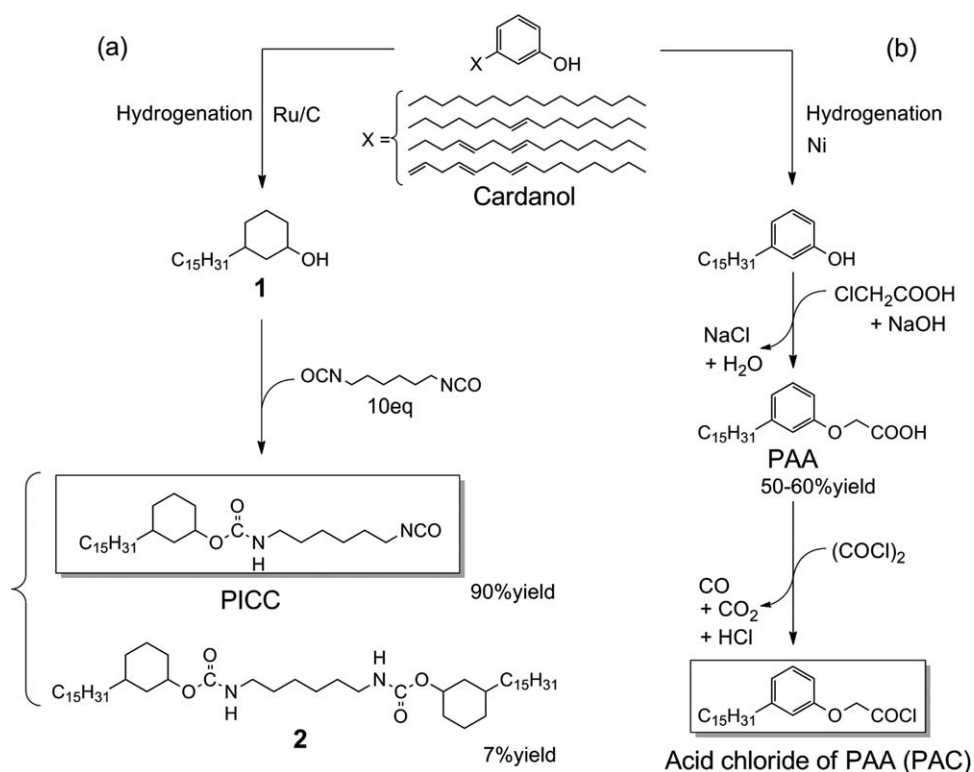
Scheme 1. Modifying process of cardanol to PICC (a) and acid chloride of PAA (b).

Scheme 2. Reaction of PICC: (a) bonding to CDA, (b) oligomerization with water.

(KBr, cm^{-1}):3339 (N–H), 2918, 2849 (alkyl), 2271 + 1465 (NCO), 1686 + 1536 + 1255 (urethane).

The synthesis process only consisted of two steps from cardanol with few byproducts. It was therefore easier to synthesize PICC than the acid chloride derivative of PAA (PAC) that required three steps from cardanol and that generated many byproducts [Scheme 1(b)].

PICC-Bonded Cellulose Diacetate (PICC-Bonded CDA)
The synthesis process is illustrated in Scheme 2(a). CDA (DS_{Ac}: 2.4, 20.0 g, 76.0 mmol) was dissolved in dehydrated 2-butanone (300 mL) at 70°C under a dry nitrogen atmosphere. After it was cooled to room temperature (RT), dibutyltin dilaurate (40 mg) was added followed by the dropwise addition of PICC (purity 90%, 20.0 g, 38.0 mmol), which was predissolved into 100 mL of dehydrated 2-butanone. After the solution was refluxed for 14 h, water (0.68 mL, 38.0 mmol) was added and refluxed for 1 h. A white solid precipitated when the solution had cooled to RT. After the precipitate was separated by filtration, the remaining solvent was evaporated to obtain the target PICC-bonded CDA (weight yield 76%; the denominator for the calculation of the weight yield is total quantity of raw materials including CDA, PICC, catalyst and water). The purity of the product that was obtained was 95% measured by GPC on average. The DS of PICC (DS_{PICC}) was 0.58 calculated by ^{1}H NMR spectrum. GPC: M_n = 108,000; ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, ppm): 0.9 (t, J = 6.8 Hz, ω-CH$_3$), 1.1–1.8 (m, alkyl), 1.9–2.2 (m, acetyl), 3.1 (br, C*H$_2$NHCOO), 3.3–5.4 (m, AGU and OC*H); IR (KBr, cm^{-1}):3404 (N–H + O–H), 2925, 2854 (alkyl), 1752 + 1527 + 1239 (urethane), 1051 (glycoside).

Other PICC-bonded CDA, that had different amounts of bonding of PICC and/or acetyl groups, was prepared by using the same procedure as that described above. The various amounts of bonding of PICC and acetyl groups were adjusted by changing the amount of PICC that was fed, and the acetyl content of CDA.

PICC-Bonded Cellulose Acetate Propionate (PICC-Bonded CAP)
This derivative was prepared by adopting the same procedure as that for PICC-bonded CDA using CAP (DS_{Ac}: 0.18, DS_{Pr}: 2.49) instead of CDA. Weight yield 72%, the purity 95%, and the DS_{PICC} 0.33. GPC: M_n = 48,600; ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, ppm): 0.9 (t, J = 6.8 Hz, CH$_3$), 1.1 (m, CH$_2$ of propionyl on C2 and C3), 1.2 (m, CH$_2$ of propionyl on C6), 1.1–1.8 (m, alkyl), 1.9–2.2 (m, acetyl), 2.2 (m, CH$_3$ of propionyl on C2 and C3), 2.4(br, CH$_2$ of propionyl on C6), 3.1 (br, C*H$_2$NHCOO), 3.3–5.4 (m, glucose).

To change the amount of bonding in the propionyl group, we incorporated the propionyl group to PICC-bonded CDA by using propionyl anhydride[21] because only one kind of commercial CAP was available.

RESULTS AND DISCUSSION

Efficient Synthesis of PICC-Bonded CDA
We investigated bonding HDI-modified cardanol (PICC) to CDA to develop an efficient process of synthesizing modified cardanol-bonded cellulose thermoplastics. Thermoplastic cellulose carbamates were produced by bonding PICC, which has one isocyanate group in its molecule, to CDA. Moreover, its process of separation of resulting products was simplified by coagulation and easy separation of the remaining PICC. We reported the reaction of PICC with CDA, the separation of remaining PICC by its coagulation after the reaction, and the comparison of productivity between "isocyanate process" using PICC and "acid chloride process" using acid chloride of PAA (PAC).
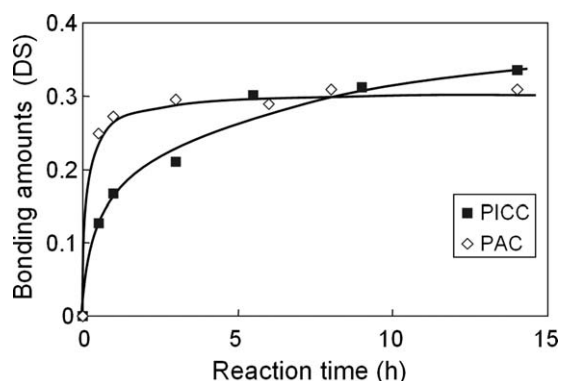
Figure 2. Bonded amounts of PICC and PAC on reaction with CDA (DS_{Ac} = 2.4) at 80°C. PICC: solvent is 2-butanone. PAC: solvent is 1,4-dioxane.

Reaction of PICC with CDA

PICC-bonded CDA was obtained by coupling the residual hydroxyl groups of CDA with PICC in the presence of dibutyl-tin dilaurate as a catalyst, as shown in Scheme 2(a). The reaction progressed homogeneously in a solution. When CDA with DS_{Ac} :2.4 and CAP were used as starting materials, we selected 2-butanone as a solvent because it was relatively easy to filter out PICC oligomers in the solvent. On the other hand, when CDA with DS_{Ac} :2.1 was used as a starting material, 1,4-dioxane was chosen as a solvent because 2-butanone was not sufficient to dissolve it. The ^{1}H NMR spectrum of PICC-bonded CDA (Supporting Information Figure S1) provided a clear indication that PICC had been incorporated. Further evidence was furnished by the presence of peaks that were characteristic of C=O stretching (1752 cm^{-1}) and N—H bending (1527 cm^{-1}) of the carbamate, in the IR spectra of the resulting polymers (Supporting Information Figure S2).

The amount of bonding of PICC to CDA (DS_{Ac}, 2.4) was compared with that of the acid chloride of PAA (PAC), which is acid chloride and is known to be one of the most efficient reagents for este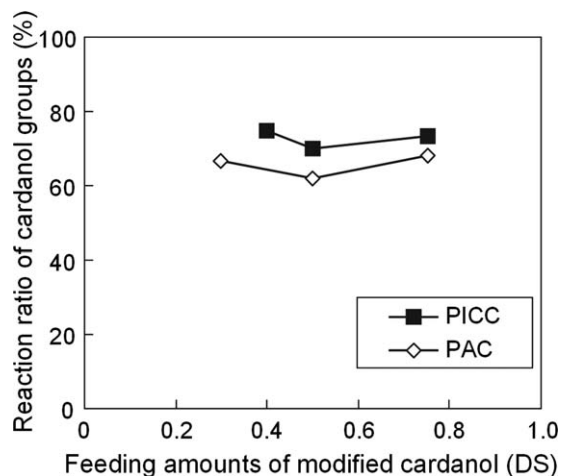rification. As seen in Figure 2, although the early reaction rate of PICC was slower than that of PAC, the amount of bonding of PICC increased with increasing of the reaction time. Comparing the amounts of bonding of the cardanol derivatives for the amounts of their feeding showed that the reaction ratios of PICC and PAC were almost at the same level (Figure 3). We clarified from these results that PICC has sufficient reactivity that is as high as that of PAC.

Separation of Remaining PICC After the Reaction

The separation process of the resulting product was remarkably simplified by using coagulation of PICC oligomerized with an equivalent mole of water. The side reaction between PICC and water is shown in Scheme 2(b). We found that after the bonding reaction of PICC with CDA, the remaining PICC coagulates and precipitates with its oligomerization after adding an equivalent mole of water (Figure 4), and therefore a highly pure final product (95% purity) can be provided only by simple filtration of remaining PICC and evaporation of the solvent. The oligomerization of PICC was confirmed by IR, DSC, and GPC measurements. The disappearance of peaks that corresponded to NCO groups (2271 cm^{-1}) and the appearance of peaks that corresponded to urea groups (1628 and 1568 cm^{-1}) in the IR spectra of the precipitates (Figure 5) indicated that PICC oligomerized with water. This PICC oligomer had a melting point at 118°C that was 72°C higher than that of PICC itself (Figure 6), and was a mixture that consisted of 90.6% of dimmers and 8.0% of trimmers and more (Supporting Information Figure S4).

The solution of PICC-bonded CDA after the bonding reaction included the impurity, **2** [Scheme 1(a)] and remaining PICC. This impurity was separated by filtration together with PICC oligomer because the molecular structure of **2** is similar to PICC dimmer.

On the other hand, the oligomers of cardanol modified with TDI with an aromatic structure instead of HDI with a linear alkyl structure did not coagulate. Therefore, the PICC oligomers, mainly its dimmers including the linear HDI parts are likely to be highly crystallized, which mainly causes the coagulation of PICC.
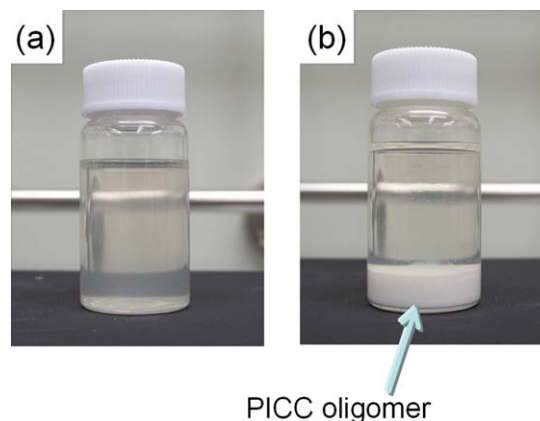

Figure 3. Reaction ratio (= bonding amount/feeding amount) of modified cardanols for CDA (DS_{Ac} = 2.4) at 80°C. Reaction times are 14 h, respectively.

PICC oligomer

Figure 4. Observation of separating PICC-bonded CDA: (a) reaction solution including PICC-bonded CDA and remaining PICC at 60°C before adding water, and (b) coagulation of remaining PICC by adding an equivalent mole of water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
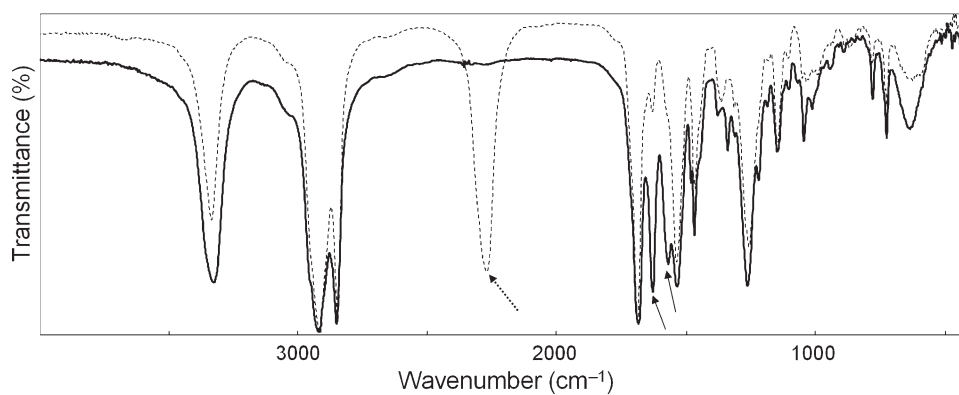
Figure 5. IR spectra of PICC (dotted line) and PICC oligomer (solid line).

The oligomerization of PICC involved a two step reaction [Scheme 2(b)]: the decarboxylation of PICC and water in the solution resulting in the generation of amino PICC (**3**), and the condensation of **3** and PICC; the latter reaction was a rate-determining step because the reaction of isocyanate groups with amino groups is known to be much faster than that with water. This side reaction was greatly affected by water. Therefore, efficiently promoting the bonding reaction [Scheme 2(a)] needed to control the amount of water in the solution under 0.1 wt % (2.9 mol %) for the amount of feeding of PICC at the start of the reaction because the selectivity of PICC for the bonding reaction decreased from 73% to about 54% where over 0.1 wt % of water existed in the solution. Moreover, we found that the oligomerization of PICC is promoted effectively by adding 3.4 wt % (equivalent mole) of water for the amount of feeding of PICC after the bonding reaction. The importance of adding water after the bonding reaction was confirmed because the purity of the final product without water being added was 87 wt %, which was lower than the purity (95 wt %) in the case of adding water.

Comparison of Productivity Between "Isocyanate Process" and "Acid Chloride Process"

We compared productivity between "isocyanate process" using PICC and "acid chloride process" using acid chloride of PAA (PAC).

The PICC-bonded CDA synthesis described here named "isocyanate process" is not only a homogeneous reaction process that maintains high reactivity and uniformity, but also a procedure that simplifies the process of separation. The productivity of cardanol-bonded cellulose thermoplastics should be remarkably improved by this process. The required amounts of each feedstock to produce final products, which have 2.4 of DS_{AC} and 0.30–0.35 of DS of cardanol groups, are listed in Table I. In the case of PA-bonded CDA synthesis named "acid chloride process," large amount of poor solvent is usually required. For example, using <76 times of a poor solvent as large as the final product decreased the yield to <40 wt %. On the other hand, the required amount of solvent in the synthesis of PICC-bonded CDA, "isocyanate process" is greatly reduced because no solvents, especially for isolation, are needed, while maintaining the yields and purities of the final products. This reduction brings the large saving of the solvent recovery energy,

resulting in decrease of the impact on the environment in the production. Additionally, we believe that cardanol-bonded cellulose thermoplastic is manufactured at a higher cost performance than in the "acid chloride process." As was explained in the experimental section, it is possible to apply the isocyanate process to CAP with residual hydroxyl groups as well as CDA. Figure 7 outlines the isocyanate process. Consequently, the isocyanate process was demonstrated to obtain a highly pure final product only by simple filtration and easy separation of byproducts from the reaction solution, while maintaining the yield as high as the acid chloride process (Figure 8).

Mechanical and Other Properties of PICC-Bonded CDA

The mechanical, thermal, and hydrophobic properties of PICC-bonded CDA were measured by the bending strength and modulus, melt flow rate (MFR), and water absorption ratios. The mechanical and hydrophobic properties of PICC-bonded CDA compared favorably with those of PA-bonded CDA. However, thermoplasticity was decreased by the increased interaction among molecules. The results are summarized in Table II.

The water absorption ratios of PICC-bonded cellulose derivatives were all <2.0%, indicating high hydrophobicity. In the series of samples having almost no hydroxyl group, the water absorption ratio decreased with the increased DS of PICC, and then the hydrophobicity of cellulose derivatives was expected to be related to the weight ratio of the additional components (PA, PICC, and propionyl group) in the cellulose derivatives.
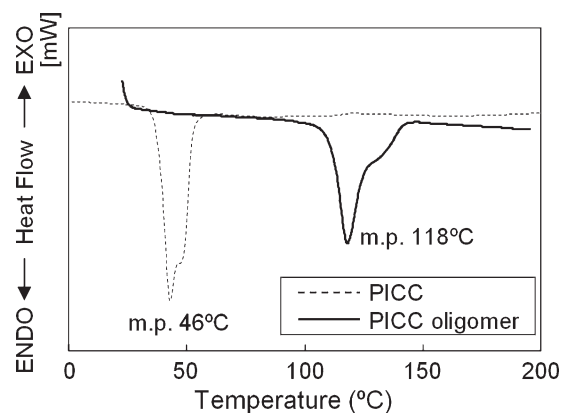

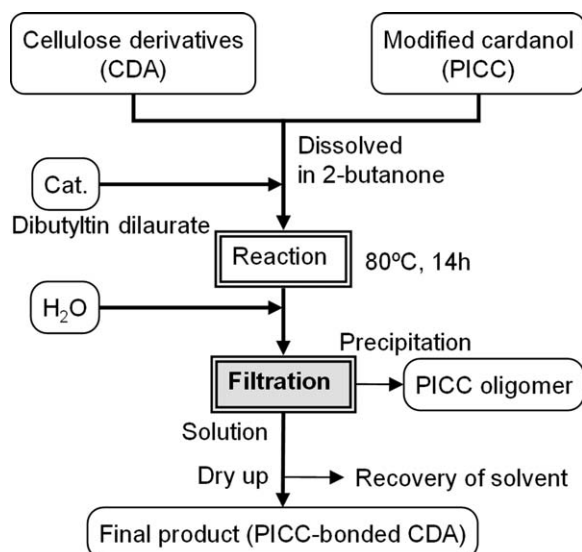**Figure 6.** DSC thermograms of PICC and PICC oligomer.

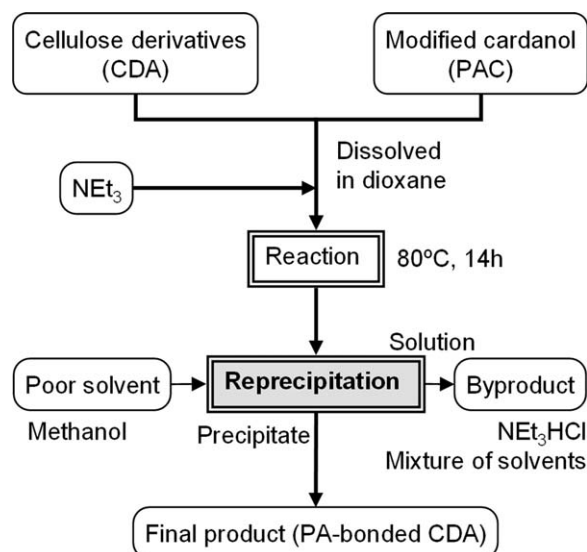**Figure 7.** Process of synthesizing PICC-bonded CDA.

Figure 8. Process of synthesizing PA-bonded CDA.

The water absorption ratios almost fit the same curve regardless of the content of additional components (Figure 9) as a result of having plotted the samples with complete conversion of hydroxyl group (Total DS is over 2.9). This suggests that the hydrophobic effect by the weight of PA, PICC, and propionyl group is approximately equal when there is no influence by hydroxyl groups.

Although the bending strength and heat resistance of PICC-bonded CDA was similar to those of PA-bonded CDA at the same DS of the cardanol group, the thermoplasticity of PICC-bonded CDA was much lower than that of PA-bonded CDA (Ref. 1 and No. 1 in Table II). In addition, decreasing the DS of PICC and substituting acetyl groups to decrease the interaction between PICC side chains led to further decreases in thermoplasticity (Nos. 1–3). The thermoplasticity was too low to mold sample No. 3 with the lowest DS of PICC (DS_{PICC}, 0.17). These results indicate that while the effect of PICC as an internal plasticizer is smaller than that of PA, it is larger than that of acetyl groups because of the effect of long alkyl chains in PICC.

Interaction Between PICC Side Chains in PICC-Bonded CDA
Thermoplasticity of PICC-bonded CDA was much lower than that of PA-bonded CDA including ester groups. We analyzed the structure of this resin with DSC, XRD, SAXS, and the observations by polarized optical microscopes to clarify the reason for the decreased thermoplasticity.

DSC thermograms of PICC-bonded CDA and PA-bonded CDA are shown in Figure 10. The PA-bonded CDA had a glass transition temperature (T_g) at 138°C. However, an endothermic peak was observed at 175°C in the PICC-bonded CDA and reduced and vanished with decreasing DS_{PICC} [Figure 10(b1–3)]. In the XRD pattern for PICC-bonded CDA with DS_{PICC} 0.57 (Supporting Information Figure S3) at room temperature, there was not any diffraction peaks at $2\theta > 5°$ without amorphous halo. However, as shown in Figure 11, the SAXS pattern for PICC-bonded CDA showed single diffraction peak at $2\theta = 2.06°$ ($d = 4.29$ nm). According to the previous researches,[22,23] this peak must originate from the periodicity of a columnar hexagonal packing of cellulose backbone chain. Moreover, when observed with cross polarizers, PICC-bonded CDA showed

Table I. Required Amounts of Each Feedstock to Produce Final Products

		PICC-bonded CDA isocyanate process	PA-bonded CDA acid chloride process
Final product[a]		10.0 g	10.0 g
Whole weight yield		76 wt %	65 wt %
Purity		95 wt %	99 wt %
Raw material	CDA (DS 2.4)	6.7 g	7.4 g
	PICC or PAC (Feed DS 0.5eq)	PICC 6.7 g (purity 90%)	PAC 5.4 g (purity 99%)
	Others	0.23 g (Cat. + water)	2.3 g (Et₃N)
Solvent	for reaction	107 g (2-butanone)	152 g (dioxane)
	for isolation	≈0 g	Min. 760 g (Methanol)

[a] DS0.30–0.35 of cardanol groups.

Table II. Characteristics of Cardanol-Bonded Cellulose Derivatives

No.	DS Ac	DS Pr	DS PICC	Ratio of hydrophobic elements (PA, PICC and Pr) (wt %)	T_g (°C)	Endothermic peak in DSC (°C)	Water absorption (wt %)	Bending test[a] Strength (MPa)	Bending test[a] Modulus (GPa)	MFR (g/10 min) at 200°C
Ref1	2.4	0	0.52 (DS_{PA})	41(PA)	138	n.a.	1.2	(57)	(1.5)	738
1	2.4	0	0.57	51 (PICC)	155	175	0.9	(55)	(1.2)	122
2	2.65	0	0.35	38 (PICC)	146	170	1.6	(90)	(2.0)	35
3	2.86	0	0.17	22 (PICC)	163	n.a.	n.a.[b]	n.a.[b]	n.a.[b]	26 (215°C)
4	2.4	0.33	0.28	39 (7 (Pr) + 32 (PICC))	138	153	1.5	90	2.5	662
5	2.1	0.54	0.30	41 (7 (Pr) + 34 (PICC))	127	147	1.3	86	2.3	1105
6	0.18	2.49	0.33	64 (30 (Pr) + 34 (PICC))	90	111	0.8	60	1.6	1280 (180°C)
Ref2	0.18	2.81	0	49 (Pr)	133	n.a.	n.a.	n.a.	n.a.	785 (220°C)

[a] Ref1 and Sample no.1 and 2 were formed by press-molding, and other samples except Sample 3 were formed by injection-molding.
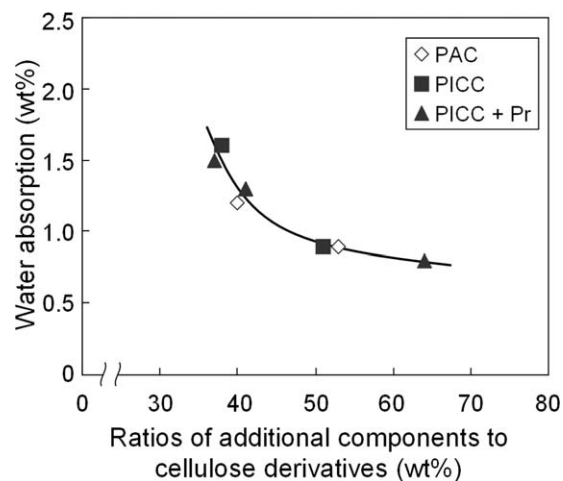[b] Sample 3 was not able to be formed.

Figure 9. Water resistance of modified cardanol-bonded cellulose derivatives.

birefringence or anisotropic phase up to 150°C, and then this birefringence mostly disappeared together with melting around 200°C, indicating the occurrence of a transition from anisotropic phase to isotropic one [Figure 12(a)]. Consequently, PICC-bonded CDA has thermotropic liquid crystalline behavior due to the high interaction between PICC side chains in the wide temperature range from –10°C to 175°C. In line with this consideration, an endothermic peak at 175°C in the DSC thermograms of PICC-bonded CDA [Figure 10(b1)] is likely to originate from anisotropic/isotropic phase transition point. Moreover, another endothermic peak at − 10°C is able to be assigned to an order-disorder transition of PICC side chains.

On the other hand, the reference PA-bonded CDA, which has the ester bond part replacing the HDI part of PICC-bonded CDA, hardly showed such a birefringence in the polarized
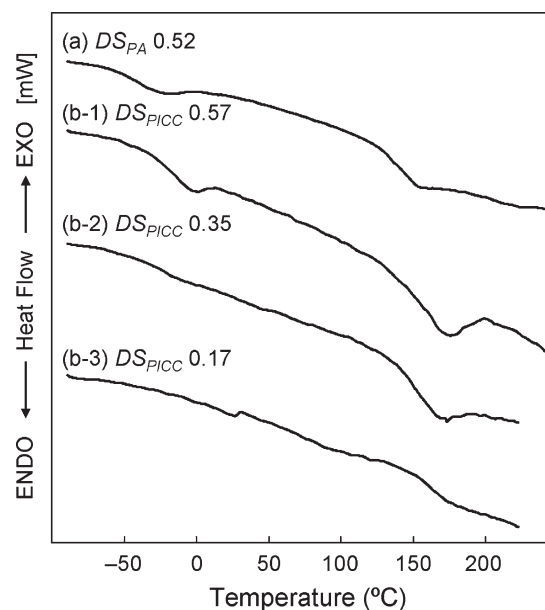

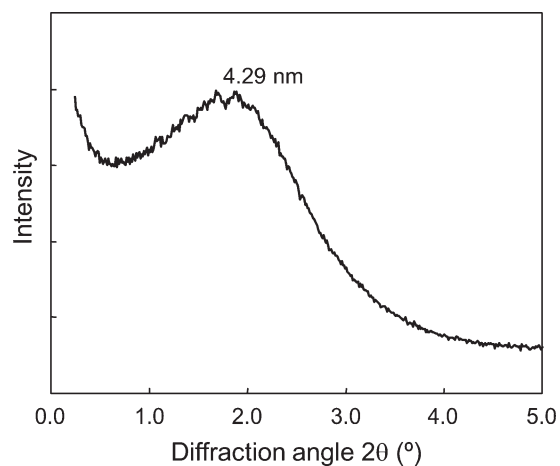**Figure 10.** DSC thermograms of PA-bonded CDA(a) and PICC-bonded CDA (b).

Figure 11. SAXS pattern of PICC-bonded CDA (DS_{PICC}, 0.57).

microphotographs [Figure 12(b)], revealing the low interaction between PA side chains. This result suggests that the interaction between the HDI parts in PICC side chains is the important factor for the high interaction between PICC side chains. The interaction between HDI parts would been mainly derived from hydrogen bonding between the carbamate groups, which is supposed to be stronger than that of the ester groups in PA side chains due to the chemical structures. Furthermore, the interaction between HDI parts would be aided by the interaction between the linear six methylene groups in HDI parts, which is higher than that of one methylene groups in the ester bond parts of PA side chains.

As the results of structural analyses, we appeared that PICC-bonded CDA has strong interaction between PICC side chains,

resulting in thermotropic liquid crystalline behavior. The decreased thermoplasticity of PICC-bonded CDA was mainly due to this interaction.

Improvement of Thermoplasticity of PICC-Bonded CDA

Decreased intermolecular force is required to improve the thermoplasticity of PICC-bonded CDA. The incorporation of an industrially useful short aliphatic acyl group with lower polarity than the acetyl group is expected to be important. We therefore investigated the incorporation of propionyl group, and confirmed its effects (Figure 13).

The substitution of the propionyl group (DS_{Pr}, 0.33) for the acetyl group while maintaining the DS of PICC remarkably increased the melt flow rate (MFR) to about twenty times, improving the thermoplasticity of PICC-bonded cellulose derivatives. The bending strength and heat resistance barely decreased (Nos. 4 and 5 in Table II) at the same time. However, the extremely large propionyl group largely decreased them of PICC-bonded cellulose derivatives (No. 6). This was mainly attributed to the decreased intermolecular interaction of PICC-bonded cellulose derivatives by the propionyl group that had lower polarity than the acetyl group.

Additionally, most of the thermoplasticity was lost by replacing all PICC with the propionyl group (Ref. 2 in Table II). This means PICC was indispensable for thermoplasticity. PICC contributed to the thermoplasticization of PICC-bonded CDA, whereas the effect was smaller than PA due to the strong interaction as previously mentioned. The combination of PICC and the propionyl group as a short alkyl component remarkably improved the thermoplasticity. The other practical properties including bending strength, heat resistance (T_g), and water resistance, were maintained by the combination of PICC and the propionyl group, as shown in Table II.
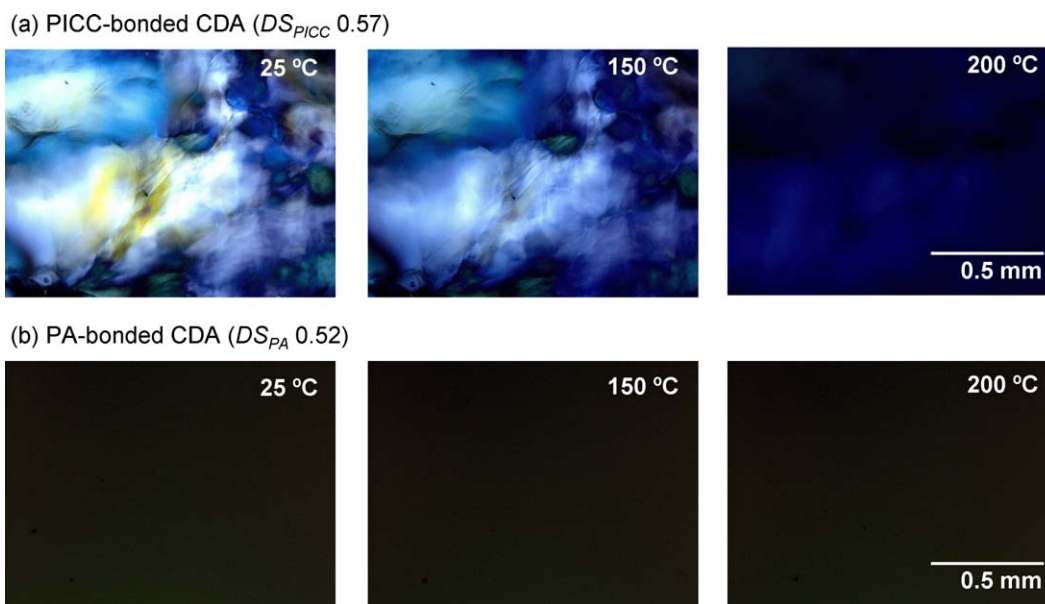

Figure 12. Optical microphotographs of (a) PICC-bonded CDA (DS_{PICC}, 0.57), and (b) PA-bonded CDA (DS_{PA}, 0.52) at various temperatures with cross polarizers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
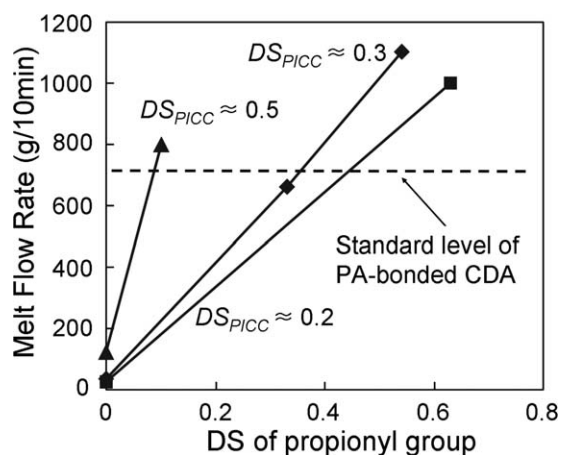
Figure 13. Improvement of thermoplasticity of PICC-bonded cellulose derivatives by substituting of propionyl group for acetyl group.

CONCLUSIONS

The efficient process of synthesizing cardanol-bonded cellulose thermoplastic using PICC and CDA was demonstrated. Especially, the easy separation of remaining PICC resulted from its coagulation with oligomerization that remarkably simplified the separation process of the resulting products after PICC was bonded to CDA in a solvent. PICC-bonded CDA obtained with this process had high strength, heat resistance and hydrophobicity, which compared favorably with those of PA-bonded CDA. However, the thermoplasticity decreased due to the strong interaction between PICC side chains. Partial substitution of propionyl groups for acetyl groups in CDA effectively decreased interactions, and then improved thermoplasticity while maintaining other characteristics. This process is expected to be an important method of improving the productivity of modified cardanol-bonded cellulose thermoplastics. We conclude that the PICC-bonded CDA is thus a promising cellulose-based bioplastic for use in various durable products such as electronic devises and automobiles, requiring high thermal resistance and other practical properties.

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