



Solvent effects on heterogeneous synthesis of cardanol-bonded cellulose thermoplastics



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ABSTRACT

Focusing on a one-pot heterogeneous process, we synthesized a promising mixed cellulose ester, cardanol-bonded cellulose thermoplastic, with bonding a short side chain (acetyl) and a long one (a derivative of cardanol). In the heterogeneous process, reaction solvents are important factors in the reactivity of long and short side chain moieties on cellulose. Investigating various kinds of solvents, we found that the solvents' affinity for cellulose was an important parameter for the reactivity of long side chain moiety, and the polarity of solvents affected the reaction ratio of long and short chain moieties. Especially, when the middle-basic type of the solvent such as *N,N*-dimethylformamide or *N*-methylpyrrolidone was used, the obtained thermoplastics had adequate degree of substitutions of long and short chain moieties, and sufficient mechanical properties (50 MPa of bending strength, and 1.4 GPa of bending modulus) to use in durable products such as electric devices in addition to general products.

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1. Introduction

Increasing environmental awareness has accelerated research and development on bioplastics from renewable resources [1–4]. However, while current leading bioplastics, such as polylactic acid (PLA), primarily use feed grains as renewable plant resources, the possibility of future food shortages has emphasized the importance of using non-edible plant resources to produce bioplastics. We have produced novel bioplastics for use in durable products by mainly using two readily procurable inedible plant resources: cellulose, very abundant renewable polymer in the world [5,6], and cardanol, a uniquely structured phenol derivative with a long unsaturated hydrocarbon chain, derived from cashew nutshells generated in large amounts as a byproduct [7].

Esterification is commonly used to produce thermoplastics from cellulose, primarily by using short chain acids such as acetic, propionic, and nitric acids. These classical cellulose esters are mainly used in films, fibers and filters, and are normally melt-processed with large amounts of external plasticizers that enlarge the processing window between the melting and degradation

temperatures. However, using these thermoplastics in durable products has been restricted because external plasticizers can be prone to extraction or volatilization, and reduce the flexural strength and heat resistance of cellulose ester composites.

Confronted by this problem, many researchers have attempted to thermoplasticize cellulose by bonding long acyl chains as internal plasticizers [8,9], and the effect of chain length and amount on several properties has been comprehensively investigated [10,11].

Cardanol, a principal organic ingredient (about 30 wt%) in cashew nutshells, is made of inedible plant resources that could be stably supplied. In processing cashew nuts, large quantities of shells are generated as an inedible byproduct. Cardanol is a very promising candidate as a long acyl chains combined with cellulose to produce bioplastics. We have studied it for applications to novel cardanol-bonded cellulose thermoplastics [12,13]. As can be seen from Fig. 1, the thermoplastic is a mixed cellulose ester with a 3-pentadecylphenoxy acetyl (PA) group derived from cardanol as a long side chain and acetyl (Ac) group as a short chain. Bonding this unique long chain resulted in a bioplastic with good thermoplasticity, high strength, and high heat and water resistance, which were superior to those of conventional cellulose resins such as cellulose diacetate (CDA) with plasticizers. We demonstrated the possibility that the thermoplastic cellulose could be used for durable products such as electronic devices [14–16]. However, this mixed cellulose ester was synthesized from CDA, which was

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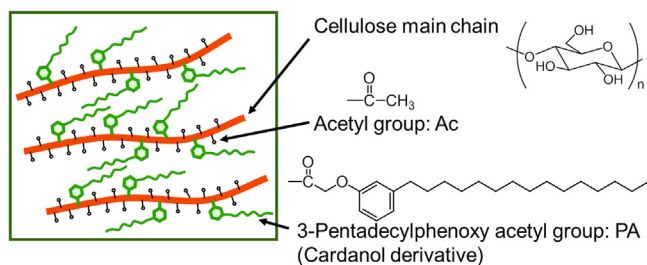


Fig. 1. Schematic of cardanol-bonded cellulose thermoplastic.

derived by acetylation of cellulose, and PA groups were bonded after CDA was dissolved in a reaction solvent. This homogeneous process was not practical due to the requirement for an onerous two-step procedure from cellulose (CDA synthesis and PA bonding).

We focused on a simple one-pot heterogeneous process to synthesize cardanol-bonded cellulose thermoplastics. Although there are some one-pot homogeneous process such as *N,N*-dimethylacetamide (DMAc) and lithium chloride (LiCl) system [17], the heterogeneous process does not require the complicated pretreatment method which is required in the homogeneous process to dissolve cellulose clearly. Moreover, the heterogeneous process does not require adding the special salts, which are expensive and difficult to recycle. Then, the heterogeneous process is more practical than the homogeneous process. Many attempts have been made to synthesize cellulose esters with long side chains in heterogeneous processes, as have been published in several reviews [18,19]. In the heterogeneous process, various practical solvents can be selected because it is not necessary to dissolve cellulose before the reaction. The reaction solvent in this process is an important factor in the reactivity of long and short side chain moieties on cellulose. However, there has been limited empirical knowledge and few systematic studies on solvent effects for the synthesis of cardanol-bonded cellulose thermoplastics.

In this paper, cardanol-bonded cellulose thermoplastics were synthesized in the one-pot heterogeneous process, and the solvent effects on the heterogeneous synthesis were studied systematically by using solvents with various structures and polarities. We also confirmed mechanical properties of the obtained thermoplastics to be usable for durable products. Moreover, a mechanism for the heterogeneous process was suggested by analyzing the bulk products and their chloroform-soluble fractions in detail.

2. Experimental

2.1. Materials

Cellulose powder (KC FLOCK, W50GK, DP: 1300, purity: 95–97%) made from wood pulp was supplied by Nippon Paper Industries Co., Ltd., Japan. The cellulose powder's diameter was 10–50 μm and length was 100–500 μm , as we measured by observation with a digital microscope (Keyence, VHX-2000). We synthesized 3-pentadecylphenoxy acetic acid (PAA), which is hydrogenated and carboxymethylated cardanol, as has previously been reported [20]. Acetic anhydride, *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), DMAc, pyridine (Py), 1,4-dioxane, tetrahydrofuran (THF), propylene carbonate (PC), dimethylsulfoxide (DMSO), triethylamine (TEA), benzonitrile, chloroform and methanol were used as supplied by Kanto Chemical Co., Inc., Japan without any further purification. Hexamethylphosphoric triamide (HMPA) purchased from Tokyo Chemical Industry Co., Ltd., Japan, 2-propanol purchased from Tokuyama Corp., Japan, and *N,N*-dimethylaminopyridine (DMAP) purchased from Sigma-Aldrich Co.

LLC., U.S.A. were also used as received without any further purification.

2.2. Preparing PA-Ac mixed anhydrides

Mixed anhydrides, which were used as esterification reagents in this study, were prepared as follows. PAA (40.2 g, 111 mmol, 3 eq per anhydroglucose unit (AGU)) and acetic anhydride (21.0 ml, 222 mmol, and 6 eq/AGU) were mixed at 100 $^{\circ}\text{C}$ for 1 h. As shown in Scheme 1, the liquid product consisted of three acid anhydrides and two acids: acetic anhydride (43.0 mol%), PA-Ac mixed anhydride (20.8 mol%), anhydride of PAA (2.0 mol%), acetic acid (24.2 mol%), and PAA (10.0 mol%). These molar ratios were calculated from proton nuclear magnetic resonance (^1H NMR) spectra.

2.3. Typical heterogeneous synthesis of cardanol-bonded cellulose thermoplastics (bulk products)

The design for the heterogeneous process is shown in Scheme 2. A heterogeneous product using DMF as a solvent was synthesized as follows. Cellulose powder with 6% adsorbed water (6.0 g by dry weight and 37 mmol/AGU) was stirred in de-ionized water (90 ml) overnight and the resulting dispersion liquid was filtered off by vacuum filtration. The swollen substrate was stirred twice in acetic acid (90 ml) overnight and isolated by vacuum filtration each time. DMF (150 ml) and 4-dimethylaminopyridine (DMAP) (3.0 g and 25 mmol) were added to the mixed anhydride; the pre-treated cellulose with about 8 g of the adsorbed acetic acid was then dispersed. The resulting dispersion liquid was stirred at 100 $^{\circ}\text{C}$ for up to 15 h under a dry nitrogen atmosphere. After it had been cooled down to 60 $^{\circ}\text{C}$, methanol (1.5 L) was added to precipitate the soluble fraction. Cellulose esters were separated by vacuum filtration, washed three times with 2-propanol (200 ml) at 60 $^{\circ}\text{C}$, and dried in a vacuum for 5 h at 105 $^{\circ}\text{C}$ to obtain 12.6 g of brown powder as a “bulk product”. Its degrees of substitution (DS) were calculated from Fourier transformed infrared (FTIR) spectra ($DS_{\text{PA}} = 0.57$, $DS_{\text{Ac}} = 1.8$). The method of DS calculation by FTIR was described in “DS calculation” section. The yield of the bulk product calculated from the DS was 78 wt%.

The method described above was used to prepare other products with different solvents. The solvents we examined in this study are plotted in Fig. S1 (shown in supplementary material), in terms of relative polarities and donor numbers (D_{N}). D_{N} is a quantitative measure of Lewis basicity. The solvents were grouped into several types, i.e., ether- (dioxane and THF), high polar- (DMSO and PC), high basic- (TEA), middle basic- (DMF, NMP, DMAc, Py and HMPA), and low basic-types (benzonitrile and chloroform). The same quantity of each solvent was used and reaction temperatures and times were kept constant (100 $^{\circ}\text{C}$, up to 15 h). When using THF, TEA and chloroform, the reaction temperatures were their boiling points (THF: 66 $^{\circ}\text{C}$, TEA: 90 $^{\circ}\text{C}$, Chloroform: 61 $^{\circ}\text{C}$).

2.4. Fractionation of bulk products

The bulk products obtained in several solvents (0.2 g) were placed into screw tubes with precise weighing, and chloroform (15 ml) was added to them. After they had been vigorously shaken for several minutes, the chloroform-insoluble fractions were filtered off, and dried in a vacuum for 3 h at 105 $^{\circ}\text{C}$. On the other hand, the chloroform-soluble fractions were obtained by the evaluation of chloroform.

2.5. Measurements

FTIR spectra were recorded on a Jasco FTIR-4100

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