Cellulose Acetate Thermoplastics with High Modulus, Dimensional Stability and Anti-migration Properties by Using CA-g-PLA as Macromolecular Plasticizer

Ru-Meng Xu\textsuperscript{a,b,t}, Tian-Tian Yang\textsuperscript{a,b}, Elfira Vidović\textsuperscript{c}, Ruo-Nan Jia\textsuperscript{a}, Jin-Ming Zhang\textsuperscript{*a}, Qin-Yong Mi\textsuperscript{a} and Jun Zhang\textsuperscript{a,b*}

\textsuperscript{a} CAS Key Laboratory of Engineering Plastics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, China
\textsuperscript{b} University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{c} Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb 10000, Croatia

Abstract Cellulose diacetate (CDA) can be melt-processed to produce numerous and widely-used plastic products. However, due to the high glass transition temperature \(T_g\) of CDA, the addition of up to 30 wt\% of micromolecular plasticizers is indispensable, which significantly reduces the dimensional stability and raises safety concerns from the migration of plasticizers. In this work, a series of CDA-graft-poly(lactic acid) (CDA-g-PLA) copolymers were synthesized by ring-opening polymerization of lactide onto the hydroxyl groups of CDA. The resultant CDA-g-PLA copolymers possess adjustable degrees of substitution (DS\textsubscript{PLA}) and side chain length (DP\textsubscript{PLA}) by controlling the reaction time and feed ratio. The \(T_g\), thermal flow temperatures (\(T_f\)) and glass transition temperature (\(T_g\)) of CDA-g-PLA strongly depend on DP\textsubscript{PLA} such as the \(T_g\) decrease linearly with the increase of DP\textsubscript{PLA}. The CDA-g-PLA copolymers with the DP\textsubscript{PLA} of 3–9 can be directly processed to transparent plastics by melt processing without any external plasticizers, because of their low \(T_g\) of 170–215 °C. More impressively, the CDA-g-PLA can act as the macromolecular plasticizer. The obtained CDA/CDA-g-PLA has higher storage modulus, flexural modulus and Young’s modulus than the commercial CDA plasticized with triethyl citrate. In addition, the CDA/CDA-g-PLA exhibits high dimensional stability and anti-migration property. During a long-term treatment at 80 °C and 60% humidity, the CDA/CDA-g-PLA has higher storage modulus, flexural modulus and Young’s modulus than the commercial CDA plasticized with triethyl citrate. More interestingly, CDA possesses thermoplastic character with the addition of external plasticizers. Via a thermoplastic processing, CDA can be shaped into various sheets, plates, strips and other plastic forms to fabricate eyeglass frames, toys, tool handles, and so on. In addition, CDA-based materials have high rigidity, moderate impact strength, excellent transparency, special absorption ability and good selective permeability. Hence, they have been extensively used in many fields.

Keywords Cellulose diacetate; Thermoplastic processing; Macromolecular plasticizer; Poly(lactic acid)

INTRODUCTION

Eco-friendly, renewable, and recyclable materials have received an increasing attention, due to the escalating environmental pollution.\cite{1,2} Cellulose diacetate (CDA) obtained by the acetylation of the biopolymer cellulose is one kind of the commercial and important polymer materials. CDA with an average degree of substitution (DS) of acetyl groups of 2.2–2.7 per glucose unit is industrially produced by a heterogenous acetylation of cellulose followed by a hydrolysis process. Since CDA exhibits excellent solubility and formability, \textit{via} a solution processing strategy, it can be readily processed into fibers, films and coatings, which have been used as fabrics, cigarette filters, separation films, printing ink, paint, etc.\cite{3,4} More interestingly, CDA possesses thermoplastic character with the addition of external plasticizers. \textit{Via} a thermoplastic processing, CDA can be shaped into various sheets, plates, strips and other plastic forms to fabricate eyeglass frames, toys, tool handles, and so on.\cite{5,6} In addition, CDA-based materials have high rigidity, moderate impact strength, excellent transparency, special absorption ability and good selective permeability. Hence, they have been extensively used in many fields.\cite{7,8}

In CDA, there are abundant polar groups, including hydroxyl and acetyl groups, which form strong intermolecular interactions. As a result, the polymer chain of CDA is difficult to move, resulting in a high glass transition temperature \(T_g\).
of 190 °C. In addition, CDA does not display crystallization behavior and usually exists in an amorphous form. Therefore, in the absence of external plasticizers, CDA cannot be melt-processed and degrades at a high temperature. It is of significant importance to plasticize CDA and reduce the $T_g$ in order to achieve a thermoplastic processing of CDA. Two strategies, including physical blending (external plasticizing) and chemical modification (internal plasticizing), have been developed to plasticize CDA. The external micromolecular plasticizer is industrially used in the thermoplastic processing of CDA. Generally, 30 wt% of micromolecular plasticizer is added during the thermoplastic processing of CDA. The common plasticizers are phthalates (dimethyl phthalate, diethyl phthalate, dioctyl terephthalate, etc.), epoxides (epoxidized soybean oil, etc.), glycerol esters (glycerol diacetate, glycerol triacetate, etc.) and citrates (triethyl citrate, acetyl triethyl citrate, etc.). Recently, ionic liquids, such as 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate, were used as new and efficient plasticizers for CDA in lab-scale studies. However, since most of the micromolecular plasticizers tend to migrate out and to be released into the environment during the preparation and usage, the corresponding products have gradually deteriorative properties and short service life. Moreover, the migrating chemicals even cause serious hazards to the human health and environment. To overcome these disadvantages of the micromolecular plasticizers, some polymers with low $T_g$ have been employed to plasticize CDA, such as poly(ethylene glycol) (PEG), modified starch, polycaprolactone (PCL) and poly(lactic acid) (PLA). The plasticizing effect of PEG200 is comparable to that of citrate plasticizers, resulting in the excellent fracture toughness in the final product. Unfortunately, due to the low molecular weight, PEG200 is prone to migrate. In addition, the high molecular-weight PEG1500, modified starch, PCL and PLA have poor compatibility with CDA.

Chemically introducing the substituents containing long-chain groups can effectively reduce $T_g$ of cellulose derivative to achieve a thermoplastic processing. Tederschi et al. modified CDA with oleate groups in a mixture of trifluoroacetic acid and trifluoroacetic acid anhydride. The obtained cellulose acetate oleate mixed esters have low $T_g$, high oxygen barrier properties and mechanical behaviors closer to ductile materials. Lij et al. reported the bonding of CDA with cardanol group containing a terminal long alkyl chain. The synthesized cardanol-bonded CDA has low $T_g$, which is as low as 140 °C by adjusting the degrees of substitution (DS) of cardanol. Boulven et al. found that the substituent with the most effective plasticization effect consists of a linear aliphatic segment as the spacer and a bulky and rigid moiety (particularly aromatic moiety) as the terminai. In addition, to graft flexible side chains as internal plasticizers is also an effective method for achieving a thermoplastic processing of CDA. Poly(3-hydroxy butyrate) (PHB), poly(valerolactone) (PVL), PCL, PLA, and PEG have been introduced into CDA. However, in order to achieve sufficient plasticization effect, it generally needs a high content of grafted side chains, which will cause a considerable change in the properties of CDA-based materials.

In this work, we synthesized a series of CDA-graft-poly(lactic acid) (CDA-g-PLA) copolymers with controllable structures. Subsequently, the effect of CDA-g-PLA structures on their thermal properties and compatibility was systematically researched. The resultant CDA-g-PLA copolymers were directly processed to transparent plastics by thermoplastic processing without any external plasticizers. Moreover, they acted as a macromolecular plasticizer for CDA to improve mechanical strength, stability and anti-migration property.

**EXPERIMENTAL**

**Materials**

CDA was supplied by Sichuan Pushi Acetati Co., Ltd. The DS of acetyl groups in CDA was 2.44 as determined by $^1$H-NMR. L-lactide (LA) was purchased from J&K Scientific Ltd. 4-Dimethylaminopyridine (DMAP) with a purity of 99.5% was provided by Haili Chemical Industry Co., Ltd. All other chemicals used were of analytical grade, and were purchased from Sinopharm Chemical Reagent Co., Ltd.

**Synthesis of CDA-g-PLA**

A typical polymerization procedure was used as illustrated in Fig. 1(a). Firstly, dried CDA powder (4.0 g) was dissolved in N/N-dimethylformamide (DMF) to obtain a 5 wt% CDA/DMF solution. Subsequently, 0.915 g of DMAP and a certain amount of L-lactide were added. The reaction was carried out under nitrogen atmosphere at 80 °C for different time. The resultant homogenous solution was added dropwise into the methanol/water mixture (V/V, 1/1) to terminate the reaction. The precipitate was filtered, washed thrice with methanol, and dried. Then, the precipitate was dissolved in DMF and precipitated with water/toluene mixture (V/V, 1/1) to remove the homopolymer of L-lactide. Finally, the product was filtered and dried under vacuum at 60 °C for 24 h.

**Preparation of CDA/CDA-g-PLA Blend Films**

CDA (1.0 g) and CDA-g-PLA (1.0 g) were simultaneously dissolved in DMF to get a CDA/CDA-g-PLA/DMF solution. Then, the CDA/CDA-g-PLA blend films were obtained by the solvent evaporation and drying at 80 °C for 12 h.

**Melt Processing of CA-g-PLA Copolymers and CDA/CDA-g-PLA Blends**

The dumbbell samples were prepared by injection molding with a Haake Mini jet apparatus. The injection temperature was in a range of 200–220 °C, the mold temperature was controlled at 60 °C, and the pressure was 80 MPa. The disk samples and films were prepared by hot pressing at 180–200 °C. CDA/CDA-g-PLA fibers were fabricated by a melt spinning process using a Haake-SWO 556-0031 melt flow speed indicator. About 5.0 g of CDA/CDA-g-PLA was put into the barrel of the equipment, heated at a rate of 40 °C/min up to 180–220 °C, kept at this temperature for 2 min, and then extruded through a capillary under a constant load of 1.2 kg. The extruded fiber was taken up at a speed of 10 m/min at room temperature.

**Characterization**

$^1$H-NMR spectra were acquired on a Bruker AV-400 NMR spectrometer with 16 scans at room temperature in DMSO-$d_6$. A few drops of trifluoroacetic acid-$d_4$ were added to shift the signals of the active hydrogens downfield. FTIR spectra were recorded with a Nicolet 6700 FTIR spectrometer (Thermo Fisher, USA) from 650 cm$^{-1}$ to 4000 cm$^{-1}$.
with 16 scans.

UV-Vis transmittance spectra were recorded using a UV-Vis spectrophotometer (Lambda 35, Perkin-Elmer, USA) from 200 nm to 900 nm.

Differential scanning calorimetry (DSC) was conducted on a Q2000 differential scanning calorimeter (TA Instruments, USA) under a nitrogen atmosphere. To provide the same thermal history before the measurements, each sample was heated to 240 °C at a scanning rate of 20 °C/min and maintained at 240 °C for 5 min. Then, the samples were cooled to 20 °C, kept for 5 min. Then, the samples were heated from 20 °C to 240 °C at a rate of 20 °C/min again. All the reported Tg,s were calculated from a second heating cycle.

Thermal flowing behaviors were observed by an Olympus BX5.1 optical microscope equipped with a Linkam THMS 600 hot-stage device. A small piece of the sample was sandwiched between two cover glasses and heated from 20 °C to 260 °C at a rate of 10 °C/min. The whole process was monitored by recording the photos at the desired temperature intervals. The temperature, at which the cellulose ester was completely transparent and flowed, is regarded as the thermal flowing temperature (Tf).

Thermogravimetric analysis (TGA) was carried on Perkin-Eimer Pyris 1 thermogravimetric analyzer in nitrogen atmosphere. Each sample was heated from 50 °C to 750 °C at a rate of 20 °C/min.

Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA Q800. The specimen was a rectangular strip with dimensions of 17 mm × 12 mm × 1 mm, which was obtained by injection molding process. The measurements were performed in the single cantilever mode at a constant frequency of 1 Hz over a temperature range from −50 °C to 250 °C and a heating rate of 3 °C/min in nitrogen atmosphere.

The cross-sectional morphologies of CDA/CDA-PLA blends were observed with a scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan) at an accelerating voltage of 10 kV. The samples were coated with platinum before observation.

Tensile test and bending test were performed on a universal testing machine (Instron 3365, Instron, USA) with a tensile speed of 5 mm/min or a bending speed of 2 mm/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of CDA-g-PLA

The hydroxyl groups can effectively trigger the ring-opening polymerization of L-lactide.[39–41] Thus, a series of CDA-g-PLA copolymers were synthesized by using the hydroxyl groups in CDA as the initiator and the DMAP as the catalyst. CDA-g-PLA copolymers with adjustable structures were obtained via controlling the reaction conditions, such as the reaction time and the molar ratio of L-lactide (LA) to anhydroglucose unit (AGU) (Fig. 1a). 1H-NMR spectra (Fig. 1b) and FTIR spectra (Fig. 1c) confirm that CDA-g-PLA copolymers with different structures are fabricated. As shown in Fig. 1(b), the signal at 5.0–5.2 ppm belongs to the internal methine protons of PLA side chain. The signal at 4.2 ppm is attributed to the terminal methine protons of PLA side chain. The signal at 1.4–1.5 ppm belongs to the internal methyl protons of PLA side chain. The signals at 1.3 ppm is attributed to the terminal methyl protons of PLA side chain. The signals at 2.8–5.5 ppm are assigned to the protons of CDA backbone. The signals at 1.7–2.2 ppm are ascribed to the methyl protons of acetyl groups. The DSPLA (defined as the DS of PLA chain), DPPLA (defined as the degree of

https://doi.org/10.1007/s10118-020-2470-2
polymerization (DP) of PLA chain), MSPLA (molar substitution, defined as the PLA number per AGU), and WPLA (defined as the weight content of PLA chain) were calculated according to the 1H-NMR spectra. The results are shown in Table 1. Compared with FTIR spectrum of PLA, FTIR spectra of CDA-g-PLA copolymers show the characteristic C—O—C band at 1030 cm⁻¹ (Fig. 1c), indicating that the products are not a homopolymer of LA and the grafting reaction occurs on the hydroxyl groups of CDA. Compared with FTIR spectrum of PLA, the bending vibration band of CH₂ at 1430 cm⁻¹ in FTIR spectra of CDA-g-PLA gives a blue shift as the increase of MSPLA, meanwhile the rocking vibration bands of CH₃ at 868 and 756 cm⁻¹ appear, confirming the formation of PLA side chain.²⁹⁻⁴² Moreover, in FTIR spectra of CDA-g-PLA copolymers, there is a stretching vibration band of C=O at 1740 cm⁻¹, a stretching vibration band of CH₃ at 1370 cm⁻¹, and an asymmetric stretching vibration band of C—O—C at 1210 cm⁻¹, which are the characteristic bands of CDA. These results prove that PLA chains are successfully grafted on the CDA chains.

Reaction conditions, including LA/AGU molar ratio and reaction time, significantly affect the chemical structure of CDA-g-PLA copolymers (Table 1 and Fig. S1 in the electronic supplementary information, ESI). For instance, under the reaction time of 6 h, DPPLA and MSPLA exhibit an approximately linear growth as the increase of LA/AGU molar ratio. The DSSLGA increases rapidly at first, then the increase rate of DSSLGA becomes slow when the LA/AGU molar ratio is higher than 8/1. Under the LA/AGU molar ratio of 20/1, the DPPLA increases linearly with the prolongation of reaction time. The DSSLGA and MSPLA increase rapidly at first, then remain unchanged or increase slowly when the reaction time exceeds 10 h. Therefore, CDA-g-PLA copolymers with different DSPLA, DPPLA, and MSPLA have been synthesized by controlling the LA/AGU molar ratio and reaction time.

Thermal Properties of CDA-g-PLA

The CDA-g-PLA copolymers with different DPRLA exhibit the diverse initial degradation temperatures (Tₙ) (Table 1 and Fig. S2 in ESI). The TGA curves of CDA-g-PLA copolymers with the short PLA side chains (DPRLA < 5) are similar to that of CDA. The Tₙ of these CDA-g-PLA copolymers are above 350 °C. The CDA-g-PLA copolymers with the long PLA side chains (DPRLA > 5) have slightly low Tₙ, which are higher than 330 °C. Therefore, all CDA-g-PLA copolymers have high thermal stability.

The Table 1 shows the chemical structure and thermal properties of CDA-g-PLA copolymers synthesized under various reaction conditions.

| Sample  | LA/AGU (mol/mol) | Reaction time (h) | DMAP/OL (mol/mol) | DSSLGA (%) | DPPLA (%) | MSPLA (%) | WPLA (%) | Tₙ (°C) | Tᵣ (°C) | Tᵢ (°C) | Tₗ (°C) |
|---------|-----------------|------------------|-------------------|------------|-----------|-----------|---------|--------|--------|--------|--------|
| CDA     | 0               | 0                | 0.5               | 0.09       | 1.69      | 0.16      | 4.07    | 367    | 193    | 260    |
| CDA-g-PLA-1 | 1/1           | 6                | 0.5               | 0.18       | 1.96      | 0.35      | 8.64    | 371    | 178    | 235    |
| CDA-g-PLA-2 | 3/1           | 6                | 0.5               | 0.26       | 2.31      | 0.60      | 13.8    | 370    | 169    | 230    |
| CDA-g-PLA-3 | 5/1           | 6                | 0.5               | 0.31       | 3.14      | 0.98      | 20.8    | 360    | 150    | 215    |
| CDA-g-PLA-4 | 8/1           | 6                | 0.5               | 0.29       | 3.23      | 0.95      | 20.4    | 362    | 144    | 215    |
| CDA-g-PLA-5 | 10/1          | 6                | 0.5               | 0.33       | 4.45      | 1.48      | 28.6    | 353    | 132    | 195    |
| CDA-g-PLA-6 | 20/1          | 6                | 0.5               | 0.42       | 4.95      | 2.78      | 37.1    | 350    | 119    | 190    |
| CDA-g-PLA-7 | 30/1          | 6                | 0.5               | 0.42       | 5.24      | 2.22      | 37.5    | 349    | 118    | 190    |
| CDA-g-PLA-8 | 8/1           | 10               | 0.5               | 0.47       | 5.10      | 2.49      | 39.4    | 356    | 121    | 190    |
| CDA-g-PLA-9 | 20/1          | 10               | 0.5               | 0.52       | 8.87      | 4.39      | 54.2    | 338    | 78     | 170    |
| CDA-g-PLA-10 | 30/1          | 10               | 0.5               | 0.33       | 3.50      | 1.15      | 23.6    | 361    | 143    | 215    |
| CDA-g-PLA-11 | 2/1           | 24               | 0.5               | 0.53       | 2.64      | 0.67      | 15.3    | 367    | 164    | 225    |
| CDA-g-PLA-12 | 3/1           | 24               | 0.5               | 0.29       | 2.91      | 0.84      | 18.4    | 366    | 163    | 230    |
| CDA-g-PLA-13 | 5/1           | 24               | 0.5               | 0.49       | 7.23      | 3.25      | 46.8    | 349    | 86     | 180    |
| CDA-g-PLA-14 | 8/1           | 24               | 0.5               | 0.48       | 7.32      | 3.39      | 47.8    | 342    | 82     | 180    |
| CDA-g-PLA-15 | 20/1          | 24               | 0.5               | 0.53       | 6.81      | 3.16      | 46.1    | 345    | 86     | 190    |
| CDA-g-PLA-16 | 30/1          | 24               | 0.5               | 0.36       | 3.89      | 1.35      | 26.7    | 359    | 140    | 210    |
| CDA-g-PLA-17 | 30/1          | 4                | 0.5               | 0.47       | 5.10      | 1.69      | 4.07    | 367    | 193    | 260    |

https://doi.org/10.1007/s10118-020-2470-2
30 wt% have excellent compatibility with CDA. When the CDA-g-PLA-9 with a $W_{PLA}$ of 39.4 wt% is blended with CDA, the SEM image reveals that there is a phase separation. Although the CDA/CDA-g-PLA-9 film is still uniform and transparent, there are two $T_s$ in the DSC curve. When the $W_{PLA}$ of CDA-g-PLA is up to 54.2 wt%, such as CDA-g-PLA-10, the obtained CDA/CDA-g-PLA-10 film is opaque. Besides, an obvious phase separation phenomenon occurs, and there are two $T_s$ in the DSC curve. Therefore, the compatibility between CDA-g-PLA and CDA decreases as the increase of $W_{PLA}$.

**Thermoplastic Processing and Properties of CDA/CDA-g-PLA Blends**

Since CDA-g-PLA copolymers have low $T_s$, low $T_g$, and tunable compatibility with CDA, we used CDA-g-PLA copolymers as the macromolecular plasticizer to achieve a thermoplastic processing of CDA (Fig. 4 and Fig. S3). When CDA-g-PLA-6 with a good compatibility with CDA is used, the resultant CDA/CDA-g-PLA-6 blend can be hot pressed into transparent film at 180 °C, be injected into the disk and rectangular samples at 220 °C, and be spun into fiber by melt extrusion at 220 °C. The CDA-g-PLA-9 and CDA-g-PLA-10 with a poor compatibility with CDA can also act as the macromolecular plasticizer. As shown in Fig. 4 and Fig. S3 (in ESI), CDA/CDA-g-PLA-9 and CDA/CDA-g-PLA-10 can be processed into opaque plastics by hot pressing and injection molding. Therefore, the CDA-g-PLA can act as the macromolecular plasticizer to successfully realize the thermoplastic processing of CDA.

Because the high molecular-weight CDA-g-PLA copolymers are used as the plasticizer, the obtained CDA/CDA-g-PLA exhibits extremely higher storage modulus than the CDA plasticized by 30 wt% triethyl citrate at room temperature, as shown in Fig. S5a (in ESI) and Table S1 (in ESI). More impressively, at a high temperature of 130 °C, the CDA/CDA-g-PLA-6 even has a high storage modulus, which is comparable to that of CDA/triethyl citrate at 25 °C. In addition, tensile and flexural tests show that CDA/CDA-g-PLA-6 has the higher flexural modulus and Young's modulus than CDA/triethyl citrate. Thus, the CDA-g-PLA copolymers as the plasticizer can remarkably improve the mechanical property and thermal stability of CDA-based thermoplastics, indicating that the CDA/CDA-g-PLA has a huge potential in lightweight and high-strength thermoplastics.
The common CDA/triethyl citrate plastics are easy to deform under high humidity and/or high temperature environment due to the water absorption and hence, showing poor dimensional stability in the real environment. Moreover, the micromolecular plasticizer in CDA/triethyl citrate plastics tend to leach out once the CDA/triethyl citrate plastics come into contact with water or other solvents. As shown in Fig. 5(c), CDA/triethyl citrate film gives a visible bend when it is exposed to a condition of 80 °C and 60% humidity for 1 h. When the CDA/triethyl citrate films are immersed in water and ethanol, their weight rapidly decreases, indicating that the micromolecular plasticizer leaches out (Fig. 5d). The high molecular-weight CDA-g-PLA copolymers as the plasticizer can effectively overcome these problems. As shown in Fig. 5(c), CDA/CDA-g-PLA-6 film can keep its initial shape without any deformation phenomenon after being placed at 80 °C and 60% humidity for 4 h. Moreover, the CDA/CDA-g-PLA-6 film is very stable in water and ethanol without any migration phenomenon (Fig. 5d). Thus, when the high molecular-weight CDA-g-PLA copolymers act as the plasticizer, the CDA/CDA-g-PLA exhibits high dimensional stability and anti-migration property, which provides an opportunity to construct lightweight, stable and safer biobased thermoplastics.
CONCLUSIONS

In this work, we synthesized a series of CDA-g-PLA copolymers by adjusting the reaction time and the molar ratio of LA/AGU. The resultant copolymers have significant differences in structure, thermal behavior, and compatibility with CDA. To be specific, the $T_g$s of CDA-g-PLA copolymers decrease linearly with the increase of $DP_{PLA}$, and the $T_f$s strongly depend on the PLA content. The CDA-g-PLA copolymers with the $DP_{PLA}$ of 3−9 can be directly processed to transparent plastics by thermoplastic processing without any external plasticizers, based on their low $T_f$s of 170−215 °C. Additionally, the prepared CDA-g-PLA was tested as macromolecular plasticizer for CDA. The compatibility between CDA-g-PLA and CDA decreases as the increase of PLA content. Then, the optimal CDA-g-PLA plasticizer was chosen to realize the thermoplastic processing of CDA. The obtained CDA/CDA-g-PLA can be readily processed into different shapes by traditional thermoplastic processing. The CDA/CDA-g-PLA plastics overcome the disadvantages of the CDA plastics containing a micromolecular plasticizer. They exhibit high modulus, excellent dimensional stability and anti-migration property. Therefore, the CDA thermoplastics plasticized with CDA-g-PLA can be used as safe, stable and lightweight biopolymer-based thermoplastics.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes effects of the reaction conditions on the structure of CDA-g-PLA copolymers, TGA curves, photomicrographs, and mechanical properties, is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2470-2.

ACKNOWLEDGMENTS

This work was financially supported by the National Key Research and Development Program of China (No. 2017YFA0403103), the Key Programs of the Chinese Academy of Sciences (No. ZDRW-CN-2018-2), and the Youth Innovation Promotion Association CAS (No. 2018040).

REFERENCES

1. Hillmyer, M. A. The promise of plastics from plants. *Science* 2017, 358, 868−870.
2. García, J. M.; Robertson, M. L. The future of plastics recycling. *Science* 2017, 358, 870−872.
3. Albertsson, A. C.; Hakkarainen, M. Designed to degrade. *Science* 2017, 358, 872−873.

https://doi.org/10.1007/s10118-020-2470-2
Xu, R. M. et al. / Chinese J. Polym. Sci. 2020, 38, 1141–1148

4 Keijer, T.; Bakker, V.; Sloatweg, J. C. Circular chemistry to enable a circular economy. New Chem. 2019, 11, 190–195.

5 Chen, X. S.; Chen, G. Q.; Tao, Y. H.; Wang, Y. Z.; Lv, X. B.; Zhang, L. Q.; Zhu, J.; Zhang, J.; Wang, X. H. Progress in eco-polymers. Acta Polymeric Sinica (in Chinese) 2019, 50, 1068–1082.

6 Xia, Z. H.; Li, J. Y.; Zhang, J. M.; Zhang, X. C.; Zheng, X. J.; Zhang, J. Processing and valorization of cellulose, lignin and lignocellulose using ionic liquids. J. Biosour. Bioprod. 2020, 5, 79–98.

7 Law, R. C. Cellulose acetate in textile application. Macroly. Symp. 2004, 208, 255–265.

8 Rustemeyer, T. Plastic filter tow for cigarette filters. Macroly. Symp. 2004, 208, 267–291.

9 Shibata, T. Cellulose acetate in separation technology. Macroly. Symp. 2004, 208, 353–369.

10 Wsos, M. A.; Shahr, S.; Bohari, S. P. M.; Nayan, N. H. M.; Abd Razak, S. I. A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: a new perspective. Carbohyd. Res. 2020, 491, 107978.

11 Xie, G. Y.; Luo, H.; Ma, C. P.; Su, X. Q.; Wei, F. J.; Yang, J. K. Research progress of modified separation membrane based on cellulose acetate. Technol. Water Treat. 2020, 46, 19–24.

12 Sayed, A. J.; Deshmukh, N. A.; Pinjari, D. V. A critical review of manufacturing processes used in regenerated cellulose fibres: viscose, cellulose acetate, cuprammonium, UIC/DMAC, ionic liquids, and NMMO based lyocell. Cellulose 2019, 26, 2913–2940.

13 Edgar, K. J.; Buchanan, C. M.; Debenham, J. S.; Rundquist, B. D.; Seiler, M. C.; Tindall, D. Advances in cellulose ester performance and application. Prog. Polym. Sci. 2001, 26, 1605.

14 Corollo, P.; Grospietro, B. Plastic materials. Macroly. Symp. 2004, 208, 335–351.

15 Du, L. L.; Jiang, B. L.; Chen, X. L.; Wang, Y. Z.; Zou, L. M.; Liu, Y. L.; Gong, Y. Y. Wei; C. Yuan, W. Z. Clustering-triggered emission of cellulose and its derivatives. Chinese J. Polym. Sci. 2019, 37, 409–415.

16 Babar, A. A.; Miao, D. Y.; Ali, N.; Zhao, J.; Wang, X. F.; Yu, J. Y.; Ding, B. Breathable and colorable cellulose acetate-based nanofibrous membranes for directional moisture transport. ACS Appl. Mater. Interfaces 2018, 10, 22866–22875.

17 Xiao, Y. Q.; Zheng, M. M.; Liu, Z. S.; Shi, J.; Huang, F. H.; Luo, X. G. Constructing a continuous flow bioreactor based on a hierarchically porous cellulose monolith for ultrafast and nonstop enzymatic esterification/transesterification. ACS Sustain. Chem. Eng. 2019, 7, 2056–2063.

18 Lucena, M. C.; Alencar, A. V.; Mazzetto, S. E.; Soares, S. A. The effect of additives on thermal degradation of cellulose acetate. Polym. Degrad. Stab. 2003, 80, 149–155.

19 Schilling, B.; Bouchard, M.; Khanjian, H.; Leamer, T.; Phenix, A.; Rivenc, R. Application of chemical and thermal analysis methods for studying cellulose ester plastics. Acc. Chem. Res. 2010, 43, 888–896.

20 Quintana, R.; Persenaire, O.; Bonnauld, L.; Dubois, P. Recent advances in (reactive) melt processing of cellulose acetate and related biodegradable bio-compositions. Polym. Chem. 2012, 3, 591–595.

21 Muller, K.; Zollfrank, C.; Schmid, M. Natural polymers from biomass resources as feedstocks for thermoplastic materials. Macromol. Mater. Eng. 2019, 304, 1800760.

22 Rahman, M.; Brael, C. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges. Prog. Polym. Sci. 2004, 29, 1223–1248.

23 Bendaoud, A.; Chalamet, Y. Plasticizing effect of ionic liquid on cellulose acetate obtained by melt processing. Carbohyd. Polym. 2014, 108, 75–82.

24 Li, Z.; Liu, N.; Yao, Y.; Chen, S.; Wang, H.; Wang H. Thermal behavior of cellulose diacetate melt using ionic liquids as plasticizers. ACS Adv. 2015, 801–907.

25 Montserrat, C. P.; Elena, H. F.; Silvia, L. Plastizers in drinking water and beverages. Curr. Anal. Chem. 2018, 14, 344–357.

26 Ma, Y. F.; Liao, S. L.; Li, Q. G.; Guan, Q.; Jia, P. Y.; Zhou, Y. H. Physical and chemical modifications of poly(vinyl chloride) materials to prevent plasticizer migration - still on the run. React. Funct. Polym. 2020, 147, 104458.

27 Tanaka, S.; Iwata, T.; Iji, M. Long/short chain mixed cellulose esters: effects of long acyl chain structures on mechanical and thermal properties. ACS Sustain. Chem. Eng. 2017, 5, 1485–1493.

28 Eischner, T.; Heinrich, T. Cellulose carbonates: a platform for promising biopolymer derivatives with multifunctional capabilities. Macromol. Biosci. 2015, 15, 735–746.

29 Teramoto, Y. Functional thermoplastic materials from derivatives of cellulose and related structural polysaccharides. Molecules 2015, 20, 5487–5527.

30 Chen, Z. Y.; Zhang, J.; Xiao, P.; Tian, W.; Zhang, J. Novel thermoplastic cellulose esters containing bulky moieties and soft segments. ACS Sustain. Chem. Eng. 2018, 6, 4931–4939.

31 Luan, Y. H.; Wu, J.; Zhan, M. S.; Zhang, J. M.; Zhang, J. He, J. S. “One pot" homogeneous synthesis of thermoplastic cellulose acetate-graft-PLLA copolymers from unmodified cellulose. Cellulose 2013, 20, 327–337.

32 Chen, J.; Zhang, J. M.; Feng, Y.; He, J. S.; Zhang, J. Effect of molecular structure on the gas permeability of cellulose aliphatic esters. Chinese J. Polym. Sci. 2014, 1, 8–18.

33 Tedeschi, G.; Guzman-Puyol, S.; Paul, U. C.; Barthelc, M. J.; Goldondl, L.; Caputob, G.; Ceseraccliu, L.; Athanassiou, A.; Heredia-Guerreros, J. A. Thermoplastic cellulose acetate oleate films with high barrier properties and ductile behaviour. Chem. Eng. J. 2018, 346, 840–849.

34 Iji, M.; Toyama, K.; Tanaka, S. Mechanical and other characteristics of cellulose ester bonded with modified cardanol from cashew nut shells and additional aliphatic and aromatic components. Cellulose 2013, 20, 559–569.

35 Toyama, K.; Soyama, M.; Tanaka, S.; Iji, M. Development of cardanol-bonded cellulose thermoplastics: high productivity achieved in two-step heterogeneous process. Cellulose 2015, 22, 1625–1639.

36 Bouwen, M.; Quintard, G.; Cottaz, A.; Joly, C.; Charlot, A.; Fleury, E. Homogeneous acylation of cellulose diacetate: towards bioplastics with tunable thermal and water transport properties. Carbohyd. Polym. 2019, 206, 674–684.

37 Teramoto, Y.; Ama, S.; Higeshiro, T.; Nishio, Y. Cellulose acetate-graft-hydroxyalkanoates: synthesis and dependence of the thermal properties on copolymer composition. Chem. Phys. 2004, 205, 1904–1915.

38 You, T. B.; Tan, B. Y.; Tang, Q. Preparation and characterization of cellulose diacetate- polyethylene glycol graft copolymer. Chinese J. Appl. Chem. 2006, 23, 346–348.

39 Shi, D. W.; Lai, X. L.; Jiang, Y. P.; Yan, C.; Liu, Z. Y.; Yang, W.; Yang, M. B. Synthesis of inorganic silica grafted three-arm PLLA and their behaviors for PLA matrix. Chinese J. Polym. Sci. 2019, 37, 216–226.

40 Yan, C. H.; Zhang, J. M.; Lv, Y. X.; Yu, J.; Wu, J.; Zhang, J.; He, J. S. Thermoplastic cellulose-graft-PLLA copolymers homogeneously synthesized in anionic liquid with 4-dimethylaminopyridine catalyst. Biomacromolecules 2009, 10, 2013–2018.

41 Ge, W. J.; Guo, Y. Z.; Zhong, H. Q.; Wang, X. H.; Sun, R. C. Synthesis, characterization, and micellar behaviors of hydroxyethyl cellulose-graft-poly(lactic acid)-poly(D,L-lactide-co-glycolide) hydrogels. J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 4536–4544.

https://doi.org/10.1007/s10118-020-2470-2